I - STRUCTURE AND SCATTERING

As it is well known (8.64) the differential cross section for an elastic process is given by

$$\frac{d\sigma(\vec{p}_i \to \vec{p}_f)}{d\Omega_f} = (2\pi\hbar)^4 \left(\frac{k_i}{v_i}\right)^2 \left| T_{E_i}(\hat{p}_f, \hat{p}_i) \right|^2 \tag{1}$$

Notice that in the non-relativistic case $p_i \equiv \hbar k_i = M v_i$. Furthermore (8.106)

$$T_{E_i}(\hat{p}_f, \hat{p}_i) = \langle \vec{p}_f | T(E_p + i0) | \vec{p}_i \rangle \tag{2}$$

Where $T(z)$ is the solution of (8.105)

$$T(z) = V + V G_0(z) T(z) \tag{3}$$

$$G_0(z) = \frac{1}{z - H_0} \tag{4}$$

and (8.113)

$$\langle \vec{x} | G_0(z) | \vec{y} \rangle = - \frac{M}{2\pi\hbar^2} \frac{e^{ik|\vec{x}-\vec{y}|}}{|\vec{x}-\vec{y}|} \tag{5}$$

In the Born approximation (8.121)

$$T_B(z) = V \tag{6}$$

and

$$\left(\frac{d\sigma(\vec{p}_i \longrightarrow \vec{p}_f)}{d\Omega_f}\right)_B = (2\pi)^4 \hbar^2 M^2 \left| \langle \vec{p}_f | V | \vec{p}_i \rangle \right|^2 \tag{7}$$

If we introduce

$$U \equiv \frac{2M}{\hbar^2} V \qquad [U] = L^{-2} \tag{8}$$

we obtain

$$\left(\frac{d\sigma(\vec{p}_i \to \vec{p}_f)}{d\Omega_f}\right)_B = \frac{1}{4} (2\pi)^4 \hbar^6 \left| \langle \vec{p}_f | U | \vec{p}_i \rangle \right|^2 \tag{9}$$

In multiparticle systems, the scattering potential is the sum of terms arising from each of the individual atoms in the system:

$$U(\vec{x}) = \sum_\alpha U_\alpha(\vec{x} - \vec{x}_\alpha) \tag{10}$$

where x_α is the position of the atom arbitrary labeled α. Notice

$$\langle \vec{p}_f | U | \vec{p}_i \rangle = \int d^3x\, d^3y\, \langle \vec{p}_f | \vec{x} \rangle \langle \vec{x} | U | \vec{y} \rangle \langle \vec{y} | \vec{p}_i \rangle = \int d^3x\, \langle p_f | \vec{x} \rangle\, U(\vec{x})\, \langle \vec{x} | \vec{p}_i \rangle$$

$$= \frac{1}{(2\pi\hbar)^3} \int d^3x\, U(\vec{x})\, e^{-i(\vec{p}_f - \vec{p}_i)\cdot\vec{x}/\hbar} = \frac{1}{(2\pi\hbar)^3} \int d^3x\, U(\vec{x})\, e^{-i\vec{q}\cdot\vec{x}} \tag{1}$$

where

$$\vec{q} = \frac{1}{\hbar}(\vec{p}_f - \vec{p}_i) \tag{2}$$

and hence

$$\left(\frac{d\sigma(\vec{p}_i \longrightarrow \vec{p}_f)}{d\Omega_f}\right)_B = \frac{1}{16\pi^2} \left| \int d^3x\, U(\vec{x})\, e^{-i\vec{q}\cdot\vec{x}} \right|^2 \tag{3}$$

In the multiparticle case

$$\int d^3x\, U(x)\, e^{-i\vec{q}\cdot\vec{x}} = \sum_\alpha \int d^3x\, U_\alpha(\vec{x} - \vec{x}_\alpha)\, e^{-i\vec{q}\cdot\vec{x}} = \left| \vec{R}_\alpha \equiv \vec{x} - \vec{x}_\alpha \right|$$

$$= \sum_\alpha \int d^3R_\alpha\, U_\alpha(\vec{R}_\alpha)\, e^{-i\vec{q}\cdot\vec{R}_\alpha}\, e^{-i\vec{q}\cdot\vec{x}_\alpha} .$$

$$= (2\pi)^{3/2} \sum_\alpha U_\alpha(\vec{q})\, e^{-i\vec{q}\cdot\vec{x}_\alpha} \tag{4}$$

where $U_\alpha(\vec{q})$ is the Fourier transform of the atomic potential. Then

$$\left(\frac{d\sigma(\vec{p}_i \to \vec{p}_f)}{d\Omega_f}\right)_B = \frac{\pi}{2} \sum_\alpha \sum_{\alpha'} U_\alpha(\vec{q})\, U^*_{\alpha'}(\vec{q})\, e^{-i\vec{q}\cdot\vec{x}_\alpha}\, e^{+i\vec{q}\cdot\vec{x}_{\alpha'}} \tag{5}$$

If the atoms are identical $U_\alpha(\vec{q})$ is independent of the considered atom and we can write $U_\alpha(\vec{q}) \equiv U(\vec{q})$, $\forall \alpha$; then

$$\left(\frac{d\sigma(\vec{p}_i \longrightarrow \vec{p}_f)}{d\Omega_f}\right) = \frac{\pi}{2} |U(\vec{q})|^2 \sum_\alpha \sum_{\alpha'} e^{-i\vec{q}\cdot(\vec{x}_\alpha - \vec{x}_{\alpha'})} \tag{6}$$

If the position of the atoms are rigidly fixed, as they would be in a classical system at absolute zero, then (5) correctly gives the cross section in the Born approximation. In real materials, particles move about, probing large regions of phase space determined by the rules of statistical mechanics, and some ensemble average of (5) is required. If our detector accepts all particles scattered by a certain $\vec{q}$, then each scattering event takes a snapshot of the sample. Since data are taken over a period of time that is long compared to thermal equilibration times, the different snapshots correspond to a time average over many sample configurations. Assuming that time averaging and average over all allowed configurations (ensemble averages - denoted by angular brackets < >) are equivalent (i.e. that the system is ergodic) we can write

$$\langle (d\sigma(\vec{p}_i \to \vec{p}_f)/d\Omega_i)_B \rangle = \frac{\pi}{2} |U(\vec{q})|^2 \, I(\vec{q}) \tag{1}$$

$$I(\vec{q}) \equiv \langle \sum_{\alpha} \sum_{\alpha'} e^{-i\vec{q}\cdot(\vec{x}_\alpha - \vec{x}_{\alpha'})} \rangle \qquad (\underline{\text{structure function}})$$

The function $I(\vec{q})$ depends only on the position of the atoms in the scattering medium and not on the nature of the interaction between atoms and the scattering probe.

For a system of N atoms, the structure function, $I(\vec{q})$, contains the sum of N^2 complex numbers with phases determined by the position of all N particles. If the relative positions of the atoms are random (as for an ideal gas) then the only terms that do not average to zero are those with $\alpha = \alpha'$ for which $\sum_{\alpha} \sum_{\alpha'} \longrightarrow \sum_{\alpha}$. In this case, $I(\vec{q})$ increases linearly with N (rather than with N^2), i.e. $I(\vec{q})$ is extensive. An <u>intensive variable</u> is a thermodynamic variable that remains unchanged when the system is doubled (or tripled, etc) in size. Examples are pressure, temperature, and chemical potential. <u>Extensive variables</u>, such as free energies, entropy, number of particles and volume can be made intensive by dividing by the volume (to make energy density, etc). An intensive version of the structure function $I(\vec{q})$ is obtained by dividing $I(\vec{q})$ by N or V. The resulting function

$$S(\vec{q}) \equiv N^{-1} I(\vec{q}) \qquad , \qquad S(\vec{q}) \equiv V^{-1} I(\vec{q}) \tag{2}$$

is called the <u>structure factor</u>. The first definition is more commonly used for classical fluids, whereas the second is used more often for quantum fluids. They clearly differ from each other only by a factor of the particle density $n = N/V$. The first one is dimensionless, while the second has dimensions of L^{-3}.

The structure function clearly contains information about the average relative position of atoms. We introduce the <u>number density operator</u> specifying the number of particles per unit volume at position $\vec{x}$ in space defined as

$$n(\vec{x}) \equiv \sum_{\alpha} \delta(\vec{x} - \vec{x}_\alpha) \qquad \text{(number density operator)} \qquad (1)$$

In quantum systems, $\vec{x}_\alpha$, is the position operator for particle α; in classical systems, it is the dynamical variable specifying the position of particle α. The ensemble average of the number density operator, $\langle n(\vec{x})\rangle$, is the average density at $\vec{x}$

$$n(\vec{x}) = \langle n(\vec{x}) \rangle \qquad (2)$$

In the fluid state there is rotational and translational invariance and $n(\vec{x})$ is independent of the magnitude and direction of $\vec{x}$ and it coincides with the average density $n = N/V$. In solids rotational and translational invariance are broken and as a consequence $n(\vec{x})$ is only a periodic function of $\vec{x}$. Notice that the Fourier transform of (1) is

$$n(\vec{q}) = \frac{1}{(2\pi)^{3/2}} \int d^3x \; n(\vec{x}) \, e^{-i\vec{q}\cdot\vec{x}} = \frac{1}{(2\pi)^{3/2}} \sum_{\alpha} e^{-i\vec{q}\cdot\vec{x}_\alpha} \qquad (3)$$

and from (3.1)

$$I(\vec{q}) = (2\pi)^3 \langle n(\vec{q}) \, n(-\vec{q}) \rangle \qquad (4)$$

Correlation functions of the density are ensemble averages of products of the density operators at different points in space. The most important of these functions is the two-point density-density correlation function

$$C_{nn}(\vec{x}_1, \vec{x}_2) \equiv \langle n(\vec{x}_1) \, n(\vec{x}_2) \rangle = \Big\langle \sum_{\alpha} \sum_{\alpha'} \delta(\vec{x}_1 - \vec{x}_\alpha) \, \delta(\vec{x}_2 - \vec{x}_{\alpha'}) \Big\rangle \qquad (5)$$

We can introduce its Fourier transform

$$C_{nn}(\vec{q}_1, \vec{q}_2) = \frac{1}{(2\pi)^3} \int d^3x_1 \, d^3x_2 \; C_{nn}(\vec{x}_1, \vec{x}_2) \, e^{-i\vec{q}_1\cdot\vec{x}_1} \, e^{-i\vec{q}_2\cdot\vec{x}_2} \qquad (6)$$

$$= \langle n(\vec{q}_1) \, n(\vec{q}_2) \rangle \qquad (7)$$

as a consequence of (3). In particular

$$I(\vec{q}) = (2\pi)^3 \langle n(\vec{q})\, n(-\vec{q}) \rangle = (2\pi)^3\, C_{nn}(\vec{q}, -\vec{q}) \qquad (1)$$

Notice that if

$$C_{nn}(\vec{x}_1, \vec{x}_2) \equiv \frac{1}{(2\pi)^{3/2}}\, C_{nn}(\vec{x}_1 - \vec{x}_2) \qquad (2)$$

We obtain

$$C_{nn}(\vec{q}_1, \vec{q}_2) = \frac{1}{(2\pi)^{9/2}} \int d^3x_1\, d^3x_2\, C_{nn}(\vec{x}_1 - \vec{x}_2)\, e^{-i\vec{q}_1\cdot\vec{x}_1}\, e^{-i\vec{q}_2\cdot\vec{x}_2}$$

$$= \frac{1}{(2\pi)^{9/2}} \int d^3x\, d^3x_2\, C_{nn}(\vec{x})\, e^{-i\vec{q}_1\cdot\vec{x}}\, e^{-i(\vec{q}_1+\vec{q}_2)\cdot\vec{x}_2}$$

$$= \frac{1}{(2\pi)^{3/2}} \int d^3x\, C_{nn}(\vec{x})\, e^{-i\vec{q}_1\cdot\vec{x}}\, \delta(\vec{q}_1 + \vec{q}_2)$$

and hence, when (2) is valid,

$$C_{nn}(\vec{q}_1, \vec{q}_2) = \delta(\vec{q}_1 + \vec{q}_2)\, C_{nn}(\vec{q}_1) \qquad (3)$$

$$C_{nn}(\vec{q}) = \frac{1}{(2\pi)^{3/2}} \int d^3x\, C_{nn}(\vec{x})\, e^{-i\vec{q}\cdot\vec{x}}$$

Equation (2) is true for homogeneous fluids but not in periodic solids.

There are several more functions related to the density - density correlation function that are conventionally used. In the limit of large separations $|\vec{x}_1 - \vec{x}_2| \longrightarrow \infty$, since

$$C_{nn}(\vec{x}_1, \vec{x}_2) \underset{|\vec{x}_1-\vec{x}_2|\to\infty}{\sim} \langle n(\vec{x}_1)\rangle \langle n(\vec{x}_2)\rangle \qquad (4)$$

it is useful to introduce the <u>Ursell function</u>, that we define as

$$S_{nn}(\vec{x}_1, \vec{x}_2) = C_{nn}(\vec{x}_1, \vec{x}_2) - \langle n(\vec{x}_1)\rangle\langle n(\vec{x}_2)\rangle =$$

$$= \langle n(\vec{x}_1)\, n(\vec{x}_2)\rangle - \langle n(\vec{x}_1)\rangle\langle n(\vec{x}_2)\rangle =$$

$$= \langle [n(\vec{x}_1) - \langle n(\vec{x}_1)\rangle][n(\vec{x}_2) - \langle n(\vec{x}_2)\rangle] \rangle \equiv$$

$$\equiv \langle \delta n(\vec{x}_1)\, \delta n(\vec{x}_2) \rangle \qquad (5)$$

which decays to zero for distances $|\vec{x}_1 - \vec{x}_2|$ larger than some characteristic length, usually of the order of interparticle separations except near phase transitions. The last form of $S_{nn}(\vec{x}_1, \vec{x}_2)$ shows that this function is a measure of the spatial correlations of the local density fluctuations $\delta n(\vec{x})$. Furthermore $S_{nn}(\vec{x}_1, \vec{x}_1)$ is a measure of fluctuations $\delta n(\vec{x}_1)$ of the local density from the average density. As before we can introduce its Fourier transform

$$S_{nn}(\vec{q}_1, \vec{q}_2) = \frac{1}{(2\pi)^3} \int d^3x_1\, d^3x_2\, S_{nn}(\vec{x}_1, \vec{x}_2)\, e^{-i\vec{q}_1 \cdot \vec{x}_1}\, e^{-i\vec{q}_2 \cdot \vec{x}_2} \qquad (1)$$

$$= C_{nn}(\vec{q}_1, \vec{q}_2) - \langle n(\vec{q}_1)\rangle \langle n(\vec{q}_2)\rangle \qquad (2)$$

$$= \langle n(\vec{q}_1)\, n(\vec{q}_2)\rangle - \langle n(\vec{q}_1)\rangle \langle n(\vec{q}_2)\rangle \qquad (3)$$

As before if

$$S_{nn}(\vec{x}_1, \vec{x}_2) \neq \frac{1}{(2\pi)^{3/2}} S_{nn}(\vec{x}_1 - \vec{x}_2) \qquad (4)$$

then

$$S_{nn}(\vec{q}_1, \vec{q}_2) = \delta(\vec{q}_1 + \vec{q}_2)\, S_{nn}(q_1) \qquad (5)$$

$$S_{nn}(\vec{q}) = \frac{1}{(2\pi)^{3/2}} \int d^3x\, S_{nn}(\vec{x})\, e^{-i\vec{q} \cdot \vec{x}}$$

From all that

$$I(\vec{q}) \equiv (2\pi)^3\, C_{nn}(\vec{q}, -\vec{q})$$

$$= (2\pi)^3 \left\{ S_{nn}(\vec{q}, -\vec{q}) + \langle n(\vec{q})\rangle \langle n(-\vec{q})\rangle \right\} \qquad (6)$$

One of the most convenient functions for visualizing how structure and correlations are related to the interparticle forces and the scattering is the <u>pair distribution function</u>, $g(\vec{x}_1, \vec{x}_2)$, defined via

$$\langle n(\vec{x}_1)\rangle\, g(\vec{x}_1, \vec{x}_2)\, \langle n(\vec{x}_2)\rangle \equiv \Big\langle \sum_{\alpha \neq \alpha'} \delta(\vec{x}_1 - \vec{x}_\alpha)\, \delta(\vec{x}_2 - \vec{x}_{\alpha'}) \Big\rangle =$$

$$= \Big\langle \sum_{\alpha, \alpha'} \delta(\vec{x}_1 - \vec{x}_\alpha)\, \delta(\vec{x}_2 - \vec{x}_{\alpha'}) \Big\rangle - \Big\langle \sum_{\alpha} \delta(\vec{x}_1 - \vec{x}_\alpha)\, \delta(\vec{x}_2 - \vec{x}_\alpha) \Big\rangle$$

$$= \langle n(\vec{x}_1)\, n(\vec{x}_2)\rangle - \langle n(\vec{x}_1)\rangle\, \delta(\vec{x}_1 - \vec{x}_2) \qquad (7)$$

Note that given a particle in $\vec{x}_1$, $g(\vec{x}_1, \vec{x}_2)$ is the probability of finding a different particle at $\vec{x}_2$ (actually in a volume d^3x about $\vec{x}_2$ and normalized by the density) The pair distribution function is particularly useful when the system is homogeneous and translationally invariant. In that case $g(\vec{x}_1, \vec{x}_2) \longrightarrow g(\vec{x}_1 - \vec{x}_2)$. If $\vec{x} = \vec{x}_1 - \vec{x}_2$ and we take into account that $\langle n(\vec{x}_1)\rangle = \langle n\rangle$, equation (6.7) can be written as

$$\langle n\rangle^2 g(\vec{x}) = \Big\langle \sum_{\alpha\neq\alpha'} \delta(\vec{x}_1 - \vec{x}_\alpha)\, \delta(\vec{x}_1 - \vec{x}_{\alpha'} - \vec{x}) \Big\rangle =$$

$$= \frac{1}{V} \int d^3x_1 \, \Big\langle \sum_{\alpha\neq\alpha'} \delta(\vec{x}_1 - \vec{x}_\alpha)\, \delta(\vec{x}_1 - \vec{x}_{\alpha'} - \vec{x}) \Big\rangle = \frac{1}{V} \Big\langle \sum_{\alpha\neq\alpha'} \delta(\vec{x} - \vec{x}_\alpha + \vec{x}_{\alpha'}) \Big\rangle$$

Since the sum over α' runs over all possible values of the difference $\vec{x}_\alpha - \vec{x}_{\alpha'}$ for each value of $\vec{x}_\alpha$, each term in the sum over α' is identical and we can write

$$g(\vec{x}) = \frac{1}{\langle n\rangle} \Big\langle \sum_{\alpha\neq 0} \delta(\vec{x} - \vec{x}_\alpha + \vec{x}_0) \Big\rangle \qquad (1)$$

A direct and intuitive method of determining $g(\vec{x})$ follows from this equation. Choose a configuration of particle positions in the ensemble of permitted configurations, and choose a coordinate system so that a particle, which we label with a 0, is at the origin. Then the integral of $\langle n\rangle g(\vec{x})$ over a volume element of size d^3x at $\vec{x}$ is simply the number of particles in that volume element. Thus $g(\vec{x})$ can be determined by counting the number of particles in a small volume d^3x at separation $\vec{x}$ from a particle at the origin. The average of this number over all (many) particles placed at the origin divided by $\langle n\rangle d^3x$ is $g(\vec{x})$.

In an uncorrelated system, such as an ideal gas, the probability of finding a particle at any position is uniform and is independent of the positions of other particles. In this case, $g(\vec{x})$ does not depend on $\vec{x}$, and since

$$\int d^3x \; \langle n\rangle\, g(\vec{x}) = N - 1 \qquad (2)$$

we get

$$g(\vec{x}) = 1 - \frac{1}{N} \rightarrow 1 \qquad (3)$$

As interparticle interactions are increased, spatial correlations build up and lead to nontrivial structure in $g(\vec{x})$. Sometimes the uncorrelated part is explicitly written as

$$g(\vec{x}) \equiv 1 + h(\vec{x})$$

where $h(\vec{x})$ is the pair correlated function. From (7.1), the Fourier transform of $g(\vec{x})$ is

$$g(\vec{q}) = \frac{1}{(2\pi)^{3/2}} \int d^3x \; g(\vec{x})\, e^{-i\vec{q}\cdot\vec{x}} = \frac{1}{(2\pi)^{3/2}} \frac{1}{\langle n \rangle} \Big\langle \sum_{\alpha \neq 0} e^{-i\vec{q}\cdot(\vec{x}_\alpha - \vec{x}_0)} \Big\rangle$$

$$= \frac{1}{(2\pi)^{3/2}} \frac{1}{\langle n \rangle} \Big\{ \Big\langle \sum_{\alpha} e^{-i\vec{q}\cdot(\vec{x}_\alpha - \vec{x}_0)} \Big\rangle - 1 \Big\} =$$

$$= \frac{1}{(2\pi)^{3/2}} \frac{1}{\langle n \rangle} \Big\{ \frac{1}{N} \Big\langle \sum_{\alpha,\alpha'} e^{-i\vec{q}\cdot(\vec{x}_\alpha - \vec{x}_{\alpha'})} \Big\rangle - 1 \Big\} =$$

$$= \frac{1}{(2\pi)^{3/2}} \frac{1}{\langle n \rangle} \Big\{ \frac{(2\pi)^3}{N} \langle n(\vec{q})\, n(-\vec{q}) \rangle - 1 \Big\} \tag{1}$$

and hence

$$\langle n(\vec{q})\, n(-\vec{q}) \rangle = \frac{V \langle n \rangle}{(2\pi)^3} \Big\{ 1 + (2\pi)^{3/2} \langle n \rangle\, g(\vec{q}) \Big\} \tag{2}$$

and hence

$$\frac{1}{V} I(\vec{q}) = \Big\{ 1 + (2\pi)^{3/2} \langle n \rangle\, g(\vec{q}) \Big\} \langle n \rangle \tag{3}$$

Note that $g(\vec{x}) = 1$ in an ideal gas. This leads to

$$\frac{1}{V} I(\vec{q}) = \langle n \rangle \Big\{ 1 + (2\pi)^3 \langle n \rangle\, \delta(\vec{q}) \Big\} \tag{4}$$

In general, when the system is, in addition, isotropic $g(\vec{x}) \to g(r)$, where $r \equiv |\vec{x}|$. In this case, $g(r)$ is known as the radial distribution function.

Liquids and Gases

Both liquids and gases are fluids. Fluids are spatially homogeneous and rotationally isotropic. This means that the average environment of any point in a fluid is identical to that of any other point and independent of direction. Thus the average properties of a fluid are invariant with respect to spatially uniform translations through any vector $\vec{R}$ and with respect to arbitrary rotations about any axis. It is instructive to see how these two invariance properties imply that densities are spatially uniform and that two point correlation functions depend only of the magnitude of the difference between two spatial coordinates. Translation invariance implies

$$\langle m(\vec{x})\rangle = \langle m(\vec{x}+\vec{R})\rangle \qquad \forall\, \vec{R}, \vec{x} \tag{1}$$

In particular we can choose $\vec{R} = -\vec{x}$ and hence $\langle m(\vec{x})\rangle = \langle m(\vec{0})\rangle$, $\forall \vec{x}$ and therefore $\langle m(\vec{x})\rangle$ is independent of $\vec{x}$: $\langle m(\vec{x})\rangle = \langle m\rangle$. Similarly

$$C_{mm}(\vec{x}_1, \vec{x}_2) = C_{mm}(\vec{x}_1+\vec{R}, \vec{x}_2+\vec{R}) \qquad \forall\, \vec{R}, \vec{x}_1, \vec{x}_2 \tag{2}$$

Here the choice $\vec{R} = -\vec{x}_2$ implies

$$C_{mm}(\vec{x}_1, \vec{x}_2) = C_{mm}(\vec{x}_1-\vec{x}_2, 0) \equiv \frac{1}{(2\pi)^{3/2}}\, C_{mm}(\vec{x}_1-\vec{x}_2) \qquad \forall\, \vec{x}_1, \vec{x}_2 \tag{3}$$

Rotational invariance implies

$$C_{mm}(\vec{x}_1-\vec{x}_2) = C(R(\vec{x}_1-\vec{x}_2)) \qquad \forall\, R, \vec{x}_1-\vec{x}_2 \tag{4}$$

and thus

$$C_{mm}(\vec{x}_1-\vec{x}_2) = C(|\vec{x}_1-\vec{x}_2|) \tag{5}$$

Notice that these symmetries imply (4.7)

$$\langle m(\vec{q}_1)\, m(\vec{q}_2)\rangle = \frac{1}{(2\pi)^3}\int d^3x_1\, d^3x_2\; C_{mm}(\vec{x}_1, \vec{x}_2)\, e^{-i\vec{q}_1\cdot\vec{x}_1}\, e^{-i\vec{q}_2\cdot\vec{x}_2} =$$

$$= \frac{1}{(2\pi)^{9/2}}\int d^3x_1\, d^3x_2\; C_{mm}(\vec{x}_1-\vec{x}_2)\, e^{-i\vec{q}_1\cdot\vec{x}_1}\, e^{-i\vec{q}_2\cdot\vec{x}_2} =$$

$$= \frac{1}{(2\pi)^{9/2}}\int d^3x_1\, d^3x\; C_{mm}(|\vec{x}|)\, e^{-i(\vec{q}_1+\vec{q}_2)\cdot\vec{x}_1}\, e^{i\vec{q}_2\cdot\vec{x}} =$$

$$= \frac{1}{(2\pi)^{3/2}}\, \delta(\vec{q}_1+\vec{q}_2)\int d^3x\; C_{mm}(|\vec{x}|)\, e^{i\vec{q}_2\cdot\vec{x}} \Rightarrow$$

$$\langle m(\vec{q}_1)\, m(\vec{q}_2)\rangle = C_{mm}(q_1)\, \delta(\vec{q}_1+\vec{q}_2) \tag{6}$$

Thus for a fluid

$$I(\vec{q}) \equiv (2\pi)^3 \langle m(\vec{q})\, m(-\vec{q})\rangle = C_{mm}(q)\,[(2\pi)^3\, \delta(\vec{0})] = V\, C_{mm}(q) \tag{7}$$

since

$$\delta(\vec{0}) = \frac{1}{(2\pi)^3}\int d^3x\; e^{-i\vec{0}\cdot\vec{x}} = V/(2\pi)^3 \tag{8}$$

The set of operations that leave a system unchanged form a group called the symmetry group. The group of arbitrary translations, rotations and reflections is the Euclidean group. Fluids have the highest possible symmetry group: the Euclidean group. All other equilibrium phases of matter are invariant only under some subgroup of the Euclidean group.

What is conventionally meant by a liquid is a fluid phase with a high density. Unlike many of the other condensed phases tha we will study, it is not distinguished from its higher temperature gas phase by a symmetry change. In fact, it is possible to go continuously from the liquid to the gase phase by going around a critical point. Except for ideal gases (which do not exist), there are always interactions and correlations between particles and consequently a pair distribution function, $g(|\vec{r}|)$, that differs from unity and reflects those correlations. The usual distiction between gas and liquid comes only when the two coexist and a meniscus can be observed. In this case the phase separation between the dense and the less dense phases is caused by the presence of an attractive interaction. However, the correlations in the liquid (and the correlations which eventually break the symmetries of the liquid state) are primarily due to the repulsive interactions. A typical form for the interparticle is the Lennard-Jones potential

$$U(R) \equiv 4\epsilon \left\{ \left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6} \right\} \qquad , \quad \epsilon > 0 \qquad (1)$$

Hard-sphere Liquids

If in fact the repulsive part dominate the correlations, then the simplest physical model of a liquid we might take would involve an exclusion of the interpenetration of the particles. This is more easily represented by a hard-sphere interaction. Although this seems like an immense trivialization of the problem, there is a good deal of unusual and unexpected physics to be found in hard-sphere models

$$U(r) = \infty \quad , \; r < r_0 \qquad , \qquad U(r) = 0 \qquad r > r_0 \qquad (2)$$

What will the radial distribution function, $g(r)$, look like for such a potential? It is clear that $g(r) = 0$ for $r < r_0$ and $g(r)$ must rise above one at further distances to conserve the total density, but will there be further conditions? The Bernal model of random-close-packing of hard spheres is a useful model for a liquid (or equally for an amorphous solid or glass) for which the above questions can be easily adressed.

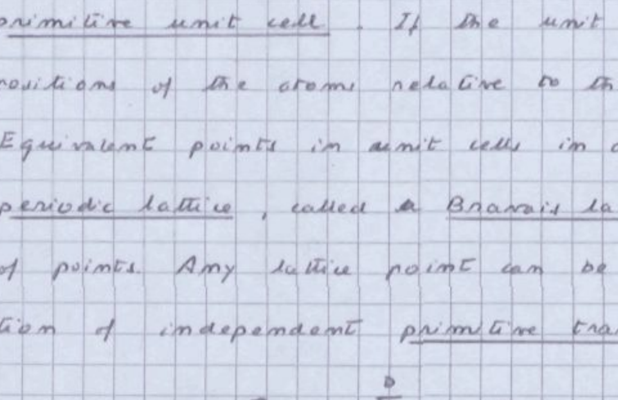
Crystalline Solids

A perfect crystal consist of a space-filling array of periodically repeated identical copies of a single structural unit containing some distribution of mass and charge. The repeated structural unit is called a unit cell. The unit cell with the smallest possible volume is called a primitive unit cell. If the unit cell contains more than one atom, the positions of the atoms relative to the center of the cell are called the basis. Equivalent points in unit cells in a D-dimensional perfect crystal lie on a periodic lattice, called a Bravais lattice, consisting of a mathematical array of points. Any lattice point can be specified by an integral linear combination of independent primitive translation vectors $\vec{a}_1, \vec{a}_2, \ldots, \vec{a}_D$

$$\vec{R}_{\vec{l}} = \sum_{i=1}^{D} l_i \vec{a}_i \qquad l_i = \text{integer} \qquad (1)$$

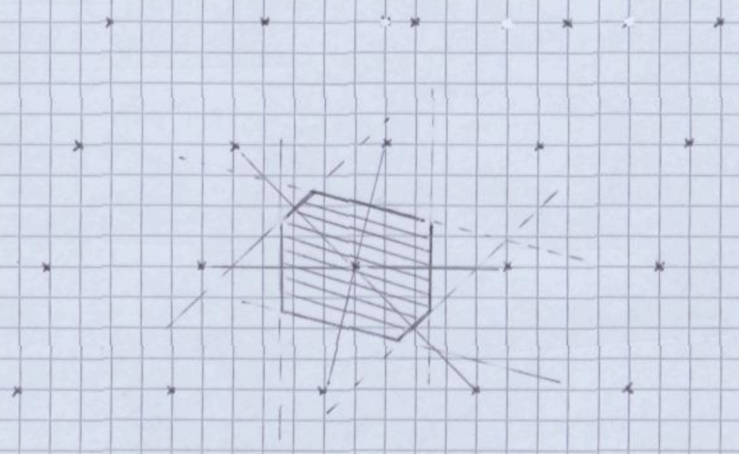
where $\vec{l} = (l_1, l_2, \ldots l_D)$ is a D-dimensional vector with components l_i ($\vec{l}$ indexes a particular unit cell, $\vec{R}_{\vec{l}}$ specifies its position in real space). The set of vectors $\vec{a}_1, \vec{a}_2, \ldots, \vec{a}_D$ completely define the mathematical lattice. A translation vector, or lattice vector, connects equivalent points in the lattice

$$\vec{T} = \vec{R}_{\vec{l}} - \vec{R}_{\vec{l}'} \qquad \forall \vec{l}, \vec{l}' \qquad (2)$$



The lattice of points in coordinate space is often called the direct lattice. All the vectors in the set defined by (1) have a magnitude greater than or equal to that of the shortest length vector connecting vertices in a primitive unit shell. As is shown in the figure, the set of primitive translation vectors for a lattice is not unique. It is always possible, however, to choose the set so that it contains the shortest vector in the lattice. The set of vectors $\vec{T}$ are closed under the operations of addition and multiplication by a minus sign; i.e. if vectors $\vec{T}_1$ and $\vec{T}_2$ are vectors in the periodic lattice, then the vectors $\pm\vec{T}_1$, $\pm\vec{T}_2$, $\vec{T}_1 \pm \vec{T}_2$ and $\pm\vec{T}_1 \mp \vec{T}_2$ are also.

There is no unique choice for a primitive unit cell of a Bravais lattice. One choice in $D=3$ is the parallelepiped whose edges are the primitive translation vectors and with volume $v_0 = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$. An alternative commonly used unit cell is the <u>Wigner-Seitz</u> unit cell obtained by constructing perpendicular bisectors to all lattice vectors emerging from a given lattice point. The smallest volume enclosed by the planes constructed in this way defines the Wigner-Seitz cell.



Construction of the Wigner-Seitz unit cell.

A compete description of a perfect crystal requires the specification of a periodic lattice and the distribution of mass in the unit cell surrounding each lattice point. In an ideal crystal consisting of a single type of pointlike atom located at each lattice site, the number density is simply

$$n(\vec{x}) = \sum_{\vec{\ell}} \delta(\vec{x} - \vec{R}_{\vec{\ell}}) \tag{1}$$

If the lattice has a basis with pointlike atoms of mass M_α located at $\vec{c}_\alpha$ in the unit cell, the mass density is

$$\rho(\vec{x}) = \sum_{\vec{\ell}} \sum_{\alpha} m_\alpha \, \delta(\vec{x} - \vec{R}_{\vec{\ell}} - \vec{c}_\alpha) \tag{2}$$

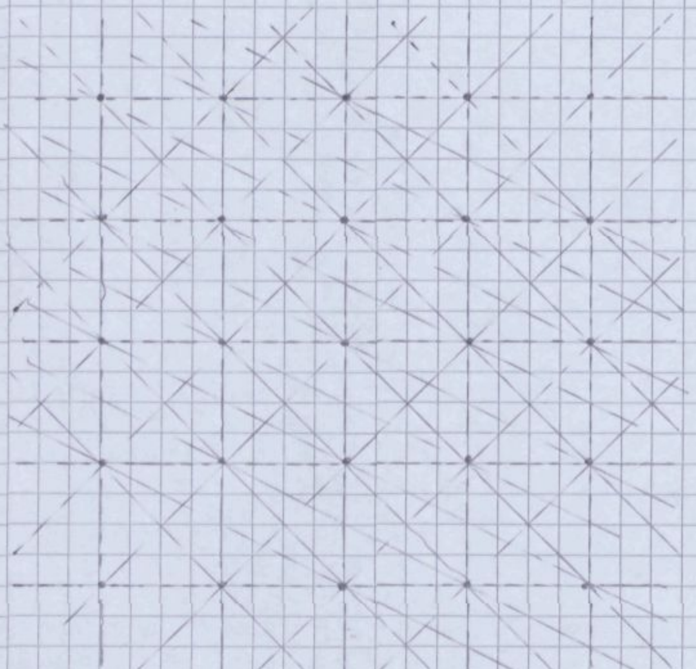
The mass density of a perfect crystal is invariant with respect to translations through a lattice vector

$$\rho(\vec{x}) = \rho(\vec{x} + \vec{T}) \tag{3}$$

There are no perfect crystals in nature with a mass density given precisely by (2). Thermal or quantum mechanical fluctuations cause instantaneous deviations from this ideal form. In addition any real crystal will have imperfections of various sorts (vacancies, dislocations, etc). Nevertheless, the average density

$$\langle \rho(\vec{x}) \rangle = \langle \rho(\vec{x} + \vec{T}) \rangle \tag{1}$$

has the periodicity of a perfect crystal. A physical crystal is a material whose average mass density is a periodic function of space.



Associated with any periodic lattice is a set of equispaced parallel planes containing all lattice points. Each set of these planes can be defined by its normal vector $\vec{G}$. Lattice vectors, in a given plane perpendicular to $\vec{G}$ satisfy $\vec{G}.\vec{T} = cte$. For this set of parallel plantes all lattice vectors lie in some plane which satisfies

$$\vec{G}\ \vec{T} = 2\pi m \tag{2}$$

for some m. The coefficient 2π is choosen so that

$$e^{i\vec{G}.\vec{T}} = 1 \tag{3}$$

Any point $\vec{x}_m$ (not just a lattice point) in the m-th plane associated with $\vec{G}$ satisfies $\vec{G}.\vec{x}_m = 2\pi m$. The difference $\vec{x}_m - \vec{x}_{m-1}$ between points in adjacent planes satisfies $\vec{G}.(\vec{x}_m - \vec{x}_{m-1}) = 2\pi$. The distance ℓ between adjacent planes is the component of $(\vec{x}_m - \vec{x}_{m-1})$ parallel to $\vec{G}$. Thus

$$\ell = \frac{2\pi}{|\vec{G}|} \tag{4}$$

For any set of primitive translation vectors $\vec{a}_1, \vec{a}_2, \ldots, \vec{a}_D$ it is always possible to construct a set of <u>reciprocal vectors</u> $\vec{b}_1, \vec{b}_2, \ldots, \vec{b}_D$ satisfying

$$\vec{a}_i . \vec{b}_j = 2\pi \delta_{ij} \qquad i, j = 1, 2, \ldots D \tag{5}$$

In three dimensions

$$\vec{b}_i = \frac{2\pi\ (\vec{a}_j \times \vec{a}_k)}{[\vec{a}_i . (\vec{a}_j \times \vec{a}_k)]} \qquad i, j, k = 1, 2, 3 \text{ cyclically} \tag{6}$$

Any vector satisfying (13.3) can be written as

$$\vec{G} = \sum_{i=1}^{D} m_i \vec{b}_i \tag{1}$$

where m_i are integer numbers. The vectors $\vec{G}$, therefore form a periodic lattice, called the <u>reciprocal lattice</u>, with primitive translation vectors $\vec{b}_1, \vec{b}_2 \ldots \vec{b}_D$. The Wigner-Seitz unit cell for the reciprocal lattice is called the first <u>Brillouin zone</u>.

Any periodic function of position

$$f(\vec{x}) = f(\vec{x} + \vec{T}) \tag{2}$$

can be decomposed with wave vectors in the reciprocal lattice

$$f(\vec{x}) = \sum_{\vec{G}} f_{\vec{G}}\, e^{i\vec{G}.\vec{x}} \tag{3}$$

This can be derived by taking the Fourier transform of $f(\vec{x})$

$$f(\vec{q}) = \frac{1}{(2\pi)^{D/2}} \int d^D x\, f(\vec{x})\, e^{-i\vec{q}.\vec{x}} = \frac{1}{(2\pi)^{D/2}} \sum_{\vec{T}} \int_0 d^D x\, f(\vec{x} + \vec{T})\, e^{-i\vec{q}.(\vec{x}+\vec{T})} =$$

$$= \left(\sum_{\vec{T}} e^{-i\vec{q}.\vec{T}} \right) \frac{1}{(2\pi)^{D/2}} \int_0 d^D x\, f(\vec{x})\, e^{-i\vec{q}.\vec{x}} \tag{4}$$

where $\int_0$ means an integral over a unit cell. The sum over $\vec{T}$ in the last expression can be easely computed

$$\sum_{\vec{T}} e^{-i\vec{q}.\vec{T}} = \sum_{l_1,\ldots,l_D} e^{-i\sum_{j=1}^{D} l_j (\vec{q}.\vec{a}_j)} \qquad l_i = \text{integer} \tag{5}$$

If $\vec{q}$ is a reciprocal lattice vector, $\vec{q} \equiv \sum_{i=1}^{D} m_i \vec{b}_i$ then the sum is equal to the number N_c of cells, and zero otherwise. Then we can write

$$f(\vec{q}) = N_c \sum_{\vec{G}} \delta_{\vec{q},\vec{G}} \frac{1}{(2\pi)^{D/2}} \int_0 d^D x\, f(\vec{x})\, e^{-i\vec{G}.\vec{x}} \tag{6}$$

Introducing the volume of a unit cell v_0 ($V = v_0 N_c$, $V \delta_{\vec{q},\vec{G}} \to (2\pi)^D \delta(\vec{q} - \vec{G})$)

$$f(\vec{q}) = \sum_{\vec{G}} (2\pi)^D \delta(\vec{q} - \vec{G}) \frac{1}{v_0} \frac{1}{(2\pi)^{D/2}} \int_0 d^3 x\, f(\vec{x})\, e^{-i\vec{G}.\vec{x}} \tag{7}$$

Then we can write

$$f(\vec{q}) = \sum_{\vec{G}} (2\pi)^{D/2}\, \delta(\vec{q} - \vec{G})\, f_{\vec{G}}$$

$$f_{\vec{G}} \equiv \frac{1}{v_0} \int_0 d^3x\, f(x)\, e^{-i\vec{G}.\vec{x}} \tag{1}$$

and hence

$$f(\vec{x}) = \frac{1}{(2\pi)^{D/2}} \int d^Dq\, f(\vec{q})\, e^{+i\vec{q}.\vec{x}} = \sum_{\vec{G}} \int d^Dq\, \delta(\vec{q} - \vec{G})\, f_{\vec{G}}\, e^{i\vec{q}.\vec{x}} = \sum_{\vec{G}} f_{\vec{G}}\, e^{i\vec{G}.\vec{x}} \qquad \text{Q.E.D.}$$

The Fourier representation of (14.3) applies to any periodic function. In particular

$$\langle n(\vec{x})\rangle = \sum_{G} \langle n_{\vec{G}}\rangle\, e^{i\vec{G}.\vec{x}} \tag{2}$$

Thus, the average number density in a periodic solid is fully specified by its Fourier components $\langle n_{\vec{G}}\rangle$ at reciprocal lattice vectors.

Let us consider the elastic scattering in the Born approximation assuming scatterers are rigidly fixes on a periodic lattice. (2.3)

$$\left(\frac{d\sigma(\vec{p}_i \to \vec{p}_f)}{d\Omega_f} \right)_B = \frac{1}{16\pi^2} \left| \int d^3x\, U(\vec{x})\, e^{-i\vec{q}.\vec{x}} \right|^2 \tag{3}$$

where $U(\vec{x}) = U(\vec{x} + \vec{T})$. Then using the results just obtained we can write

$$\left(\frac{d\sigma(\vec{p}_i \to \vec{p}_f)}{d\Omega_f} \right)_B = \frac{1}{16\pi^2} V^2 \sum_{\vec{G}} \delta_{\vec{q},\vec{G}}\, |U_{\vec{G}}|^2$$

$$U_{\vec{G}} \equiv \frac{1}{v_0} \int_0 d^3x\, U(x)\, e^{-i\vec{G}\vec{x}} \tag{4}$$

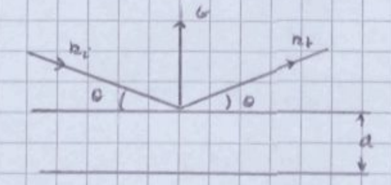
where $\vec{q} = (\vec{p}_f - \vec{p}_i)/\hbar$. Thus, there will be peaks in the scattering pattern at every reciprocal lattice vector with intensity proportional to the square of the volume of the sample and to the square of the Fourier component of the scattering potential at wave vector $\vec{G}$. These are the <u>Bragg scattering peaks</u> of the solid. In this case where we limit to elastic scattering we obtain a variation of Bragg's law, known as the <u>Laue condition</u>: In this case $|\vec{k}_f| = |\vec{k}_i|$ (where $\vec{k} = \vec{p}/\hbar$) and since $\vec{q} = \vec{G}$ we obtain

$$\vec{k}_i = \vec{k}_f - \vec{G} \quad \Rightarrow \quad \vec{k}_i^{\,2} = \vec{k}_f^{\,2} + \vec{G}^2 - 2\vec{k}_f \cdot \vec{G} \Rightarrow$$

$$\vec{k}_f \cdot (\vec{G}/2) = (\vec{G}/2)^2 \tag{1}$$

If we take into account that $|\vec{k}| = 2\pi/\lambda$, $|\vec{G}| = 2\pi/d$, where d is the distance between the scattering planes and, furthermore, we denote by θ the angle between θ and the scattering planes we obtain the famous

Bragg's law

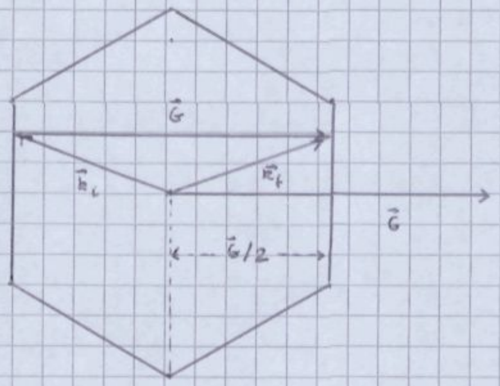


$$2d\sin\theta = \lambda \tag{2}$$

and in general

$$2d\sin\theta = n\lambda \qquad n = 1, 2, 3, \ldots \tag{3}$$

Notice that as a consequence of (1) when an incident wave lies on a Brillouin zone face it is Bragg scattered across the zone to the opposite face, as can be seen on the next figure



Let us now consider ~~in~~ this case the equation (6.6)

$$I(\vec{q}) = (2\pi)^3 \left\{ \langle n(\vec{q})\rangle \langle n(-\vec{q})\rangle + S_{nn}(\vec{q}, -\vec{q}) \right\} \tag{4}$$

and since $\langle n(\vec{x})\rangle = \langle n(\vec{x} + \vec{T})\rangle$ we obtain

$$\langle n(\vec{q})\rangle \langle n(-\vec{q})\rangle = \sum_{\vec{G}, \vec{G}'} (2\pi)^{3/2} \delta(\vec{q} - \vec{G}) \langle n_{\vec{G}}\rangle (2\pi)^{3/2} \delta(-\vec{q} - \vec{G}') \langle n_{-\vec{G}'}\rangle$$

$$= \frac{V^2}{(2\pi)^3} \sum_{\vec{G}, \vec{G}'} \delta_{\vec{q}, \vec{G}} \, \delta_{-\vec{q}, -\vec{G}'} \langle n_{\vec{G}}\rangle \langle n_{-\vec{G}'}\rangle = \frac{V^2}{(2\pi)^3} \sum_{\vec{G}} \delta_{\vec{q}, \vec{G}} \langle n_{\vec{G}}\rangle \langle n_{-\vec{G}}\rangle =$$

$$= V \sum_{\vec{G}} \delta(\vec{q} - \vec{G}) \langle n_{\vec{G}}\rangle \langle n_{-\vec{G}}\rangle = V \sum_{\vec{G}} \delta(\vec{q} - \vec{G}) |\langle n_{\vec{G}}\rangle|^2$$

and therefore

$$\frac{1}{V} I(\vec{q}) = \sum_{\vec{G}} (2\pi)^3 \delta(\vec{q}-\vec{G})|\langle m_{\vec{G}}\rangle|^2 + \frac{(2\pi)^3}{V} S_{mm}(\vec{q},-\vec{q}) \qquad (1)$$

and therefore the intensity of the Bragg peak at $\vec{G}$ is proportional to $|\langle m_{\vec{G}}\rangle|^2$. Along with the dominant scattering into Bragg peaks, there is also a <u>diffuse scattering</u> at non-Bragg angles given by $S_{mm}(\vec{q},-\vec{q})$. The simplest crystal is one in which there is a single atom rigidly fixed in each lattice site. In this case, since in general

$$m_{\vec{G}} = \frac{1}{v_0}\int_0 d^3x\, m(x)\, e^{-i\vec{G}\cdot\vec{x}} = \frac{1}{v_0} \qquad \forall \vec{G} \qquad (2)$$

and $S_{m,m}(\vec{q},-\vec{q}) \equiv 0$, and we have no diffuse scattering. Thus if the atomic form factor $U(\vec{q})$ were unity, the scattering pattern would consist of equally intense peaks at every reciprocal lattice vector. The atomic form factor generally dies off at large $\vec{q}$ so that the intensities of Bragg peaks would die off at large $\vec{q}$ even for this idealized model of rigid fixed atoms.

Symmetry and Crystal Structure

Consider a crystal fixed in some laboratory frame of reference. An observer in the same laboratory frame will identify the crystal by its spatially periodic density. If the crystal is now translated through a lattice vector $\vec{T}$, it will be absolutely indistinguishable from the untranslated crystal to the fixed observer. Translations by lattice vectors are symmetry operations that leave the density of the crystal invariant. The set of lattice translation form a group, and the crystal is said to be invariant under operations in this group. Crystals are also invariant under <u>point group</u> operations consisting of rotations, reflections, and inversions about special symmetry points. Molecules and finite size objects can have symmetry axis of arbitrary order. The requirement that a crystal be invariant under translations through any vector in the direct lattice, which, as we have seen, contains no vector shorter than some minimum lenght vector, places severe restrictions on possible rotational symmetries

To illustrate how this comes about we will prove that for bidimensional crystals it is impossible for a periodic crystal to have a five-fold symmetry, i.e. to be invariant with respect to rotations through $2\pi/5$. Assume that a crystal does have a five-fold symmetry and let $\vec{a}_0 = (1, 0)$ be the shortest vector in the lattice. Since the crystal is assumed to have a five-fold symmetry, the vectors

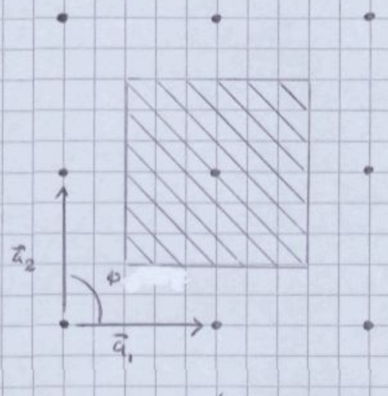
$$\vec{a}_m = (\cos(2\pi m/5) , \sin(2\pi m/5)) \qquad m = 0, 1, 2, \ldots \qquad (1)$$

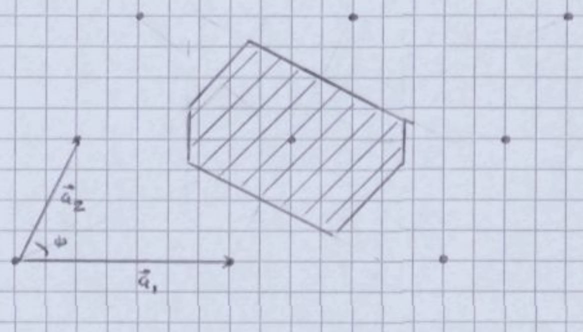
must also be in the direct lattice. But by the closure property of any lattice, the vector

$$\vec{T} = \vec{a}_4 + \vec{a}_1 = [\cos(8\pi/5) + \cos(2\pi/5) , \sin(8\pi/5) + \sin(2\pi/5)] =$$

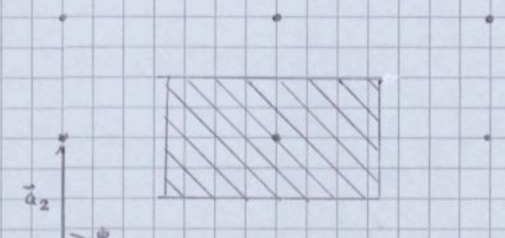
$$= (\tau^{-1}, 0) = \tau^{-1} \vec{a}_0 \qquad \tau = \frac{1+\sqrt{5}}{2} = 1.618033989$$

must also be in the direct lattice, but $\vec{T}$ is shorter that $\vec{a}_0$, contradicting the assumption that $\vec{a}_0$ was the shortest vector in the lattice. Thus, it is impossible for a periodic lattice in two dimensions to have five-fold symmetry. Similar arguments rule out all periodic lattices in two dimensions with other than two-, three-, four- or six-fold symmetry. These restrictions lead to only <u>five distinct types of Bravais lattices in two dimensions</u>

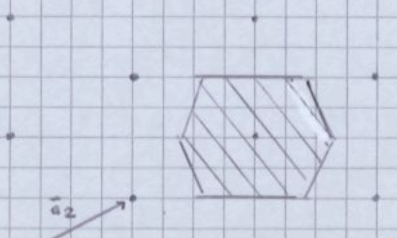




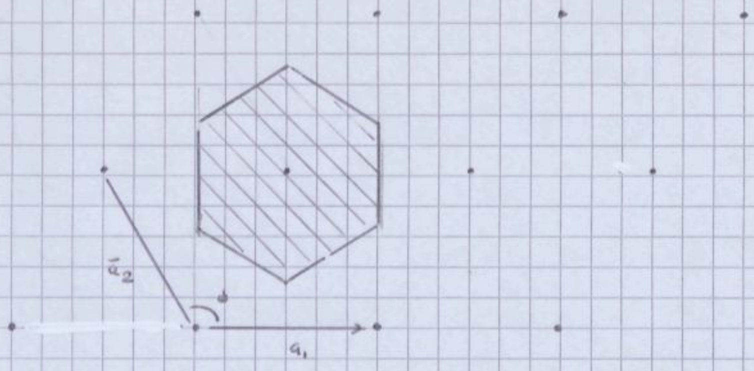
<u>Square</u> (Shaded region ≡ Wigner-Seitz unit cells) <u>Oblique</u>



<u>Rectangular</u>



<u>Centered Rectangular</u>



hexagonal

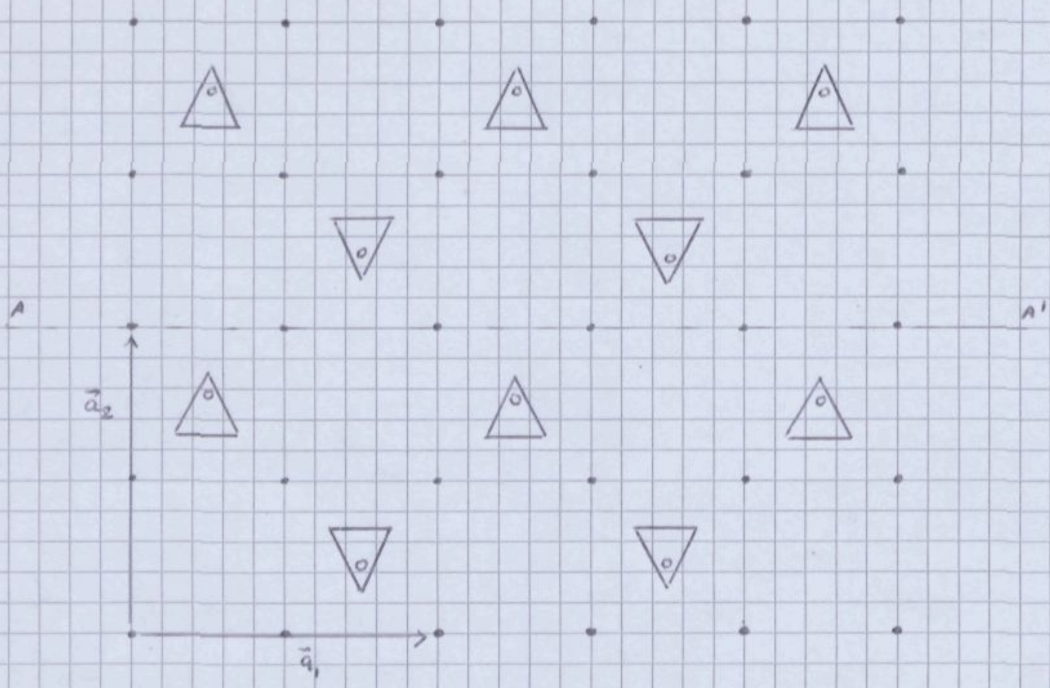
Points group that are compatible with periodic translational symmetry are called crystallographic point groups.

The triangular lattice with six-fold symmetry deserves special attention. It is the two-dimensional lattice with the highest rotational symmetry. In addition, the densest possible packing of hard circles of radius R is obtained by placing their centers on a triangular lattice with lattice parameter $a = 2R$. Note that each circle is tangent to six other circles. A lattice in D-dimensions that provides the densest possible packing of hard spheres is said to be close packed. The triangular lattice is the only close packed lattice in two dimensions. The fractional area occupied by the hard circles is the area of the circle divided by the area of the the hexagonal Wigner-Seitz cell with side of length $s = 2R/\sqrt{3}$:
$\pi R^2 / (3sR) = \pi\sqrt{3}/6 = 0.906900$

In three dimensions, there are 14 distinct Bravais lattices, as shown in the figure. They range from the highest symmetry cubic lattices with four three-fold and three four-fold axes and three mirror planes to the triclinic lattice whose point group consist only of the inversion operation.

The group of all translations and rotations that leave a crystal invariant is called the space group. Often the space group consists only of point group operations about symmetry points and translations by vectors in the direct lattice. In this case, the symmorphic case, the space group is a direct product of the point group and the translation group. In some cases, however, there may be operations in the space group consisting of a combination of point group and translation operations that individually are not in the space group. An example of such an operation is illustrate in the

next figure.



This is a lattice with a multi-atom basis and primitive translation vectors $\vec{a}_1 = (2,0)$, $\vec{a}_2 = (0,2)$. The lattice is not invariant under reflection about the line AA'. It is however, invariant under first a reflection through the line A'A followed by a translation through the vector $\vec{a}_1/2$ not in the direct lattice. The line AA' is a two-dimensional version of a *glide plane*. A symmetry operation involving a rotation about some symmetry axis followed by a translation through a vector not in the direct lattice along the symmetry axis gives rise to a *screw axis*. Space groups with glide planes or screw axes are called *nonsymmorphic*.

II - THERMODYNAMICS AND STATISTICAL MECHANICS

Condensed matter physics by its very nature deals with systems with a large number of degrees of freedom, i.e. systems for which a statistical description is essential.

Thermodynamics of Homogeneous Fluids

An isotropic, homogeneous fluid is the simplest state of matter. It is composed of mobile atoms or molecules whose kinetic energy dominates the structure. A fluid at finite temperature with a final number of particles cannot exist in equilibrium unless it is confined in some way to a finite volume V (otherwise particles will "evaporate" to less dense region of space). We will, therefore, consider for the moment a single-phase fluid (either a liquid or a gas) in a volume V. If the fluid is thermally isolated so that it cannot exchange energy with the outside world, its internal energy (kinetical plus potential energy) E is constant. If external forces do work W_{ext} on the fluid, its internal energy changes by an amount

$$\Delta E = W_{ext} \tag{1}$$

Work is done on a fluid by changing its volume V. Since the fluid in equilibrium always fills the volume to which it is confined, it must exert an outward force on the walls of its container. Conversely, the walls of the container exert an inward force on the fluid. A fluid contained in a volume surrounded by a surface A can only exert a force normal to A. Furthermore, the total force on a flat surface is proportional to its area. The outward force per unit area exerted by a fluid through its containing surface is called the pressure P. The force exerced on a surface element of area dA by the fluid is $P\,(dA)\,\hat{n}$, where $\hat{n}$ is the local outward unit normal to the surface. The force exerted by container walls on a surface element is $-P\,(dA)\,\hat{n}$. The work done by external forces in displacing a particular surface element a distance dx along $\hat{n}$ is thus

$$\delta W_{ext} = -P\,(dA)\,(dx) = -P\,dV \tag{2}$$

The total work in changing the volume is the integral of (1.2) between the initial and final volumes. Since the force exerted by the walls on the fluid is just the negative of the force exerted by the fluid on the walls, W_{ext} is minus the work W done by the fluid.

If the fluid is thermally isolated, its internal energy can also be increased by the addition of heat. In this case, the general equation for the changes in E becomes

$$\Delta E = Q - W \tag{1}$$

where Q is the added heat and W the work done by the fluid. More generally, Q is the amount of energy received by the system in forms which cannot be identified as the negative work done by the system.

Processes that occur sufficiently slowly that thermal equilibrium is maintained are called *quasi-static*. In quasi-static processes, the heat $\bar{d}Q$ added to the system is equal to its *absolute temperature T* times the change in *entropy S*:

$$\bar{d}Q = T\,dS \tag{2}$$

S, like the internal energy, is completely determined by the volume and temperature of the fluid if the number of particles remains fixed. Thus, a fluid, initially in equilibrium at temperature T_i and volume V_i with entropy S_i, subjected to a sequence of changes that terminate at final temperature T_f and volume V_f will have an entropy S_f that depends only on T_f and V_f. If the changes run through a cycle, $T_f = T_i$ and $V_f = V_i$ then $S_f - S_i = \int_i^f dS = 0$. The total heat added, $\int_i^f \bar{d}Q$, need not, however, be zero in going about the cycle. dE and dS are perfect differentials, but $\bar{d}Q$ is not.

The *first law of thermodynamics* can be written as

$$dE = T\,dS - P\,dV \tag{3}$$

for quasi-static processes. This equation implies that

$$T = \left.\frac{\partial E}{\partial S}\right)_V , \qquad P = -\left.\frac{\partial E}{\partial V}\right)_S \tag{4}$$

Similarly

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right)_V \qquad \frac{P}{T} = \left.\frac{\partial S}{\partial V}\right)_E \tag{1}$$

Thus the functions $E(S, V)$ or $S(E, V)$ completely determine the thermodynamic state of a fluid with a fixed number of particles.

Changing the number N of particles in a fluid will lead to a change in the internal energy even if the entropy and volume are fixed. The chemical potential μ is the change in internal energy produced by the addition of one particle. The first law for quasi-static processes for a one-component fluid in which the number of particles can change is thus

$$dE = T\,dS - P\,dV + \mu\,dN \tag{2}$$

A complete thermodynamic description of the fluid is contained in the function $E(S, V, N)$.

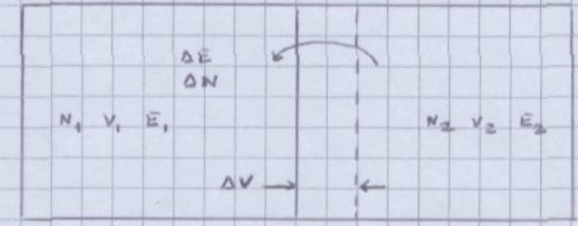
Temperature, pressure and chemical potential are sometimes referred to as generalized forces (they are the first derivatives of the energy). There is an important distinction between the generalized forces and the variables E, S, V and N. Imagine dividing a fluid with energy E, entropy S, volume V, and particle number N into two equal parts. In each part E, V, S and N are divided by two, but the generalized forces are the same as before. Variables such as E, S, V and N whose magnitudes increases upon increasing the size of the sample are called extensive variables, variables such as T, P and μ whose values remain constant upon increasing the size of the sample are called intensive variables. Associated with each extensive variable, there is a generalized force such that the change in internal energy is the generalized force times the change in the extensive variable. The extensive variable and its associated generalized force are called conjugate variables:

$$(T, S) \quad ; \quad (-P, V) \quad ; \quad (\mu, N) \qquad \text{conjugate variables} \tag{3}$$

The first law of thermodynamics is merely a statement of the conservation of energy. The second law describes the nature of changes that occur in statistical systems. It can be stated in various way, the most physically intuitive of which is that heat cannot spontaneously flow "uphill" from a cold body to a hot body. An equivalent statement is that any changes in a closed system arising from removal of constraints will lead to an increase in the entropy, i.e.

$$\Delta S \geqslant 0 \tag{1}$$

An immediate consequence of this law is that the entropy of a closed system will be a maximum with respect to any changes of internal unconstrained variables. Consider, for example, a fluid isolated from the outside world in a container divided into two parts (labeled 1 and 2) by a movable partition that permits the exchange of energy and particles, as depicted in the figure. The total entropy S must be a maximum with respect to changes in volume, energy, and number of particles in the fluid on the two sides of the partition. The total energy, particle number, and volume cannot change since the system is isolated from the outside world. Thus, changes in particle number, volume, and internal energy in the fluid on one side of the partition must be accompanied by equal and opposite changes in the fluid on the other side:



$$\Delta E_1 = -\Delta E_2 = \Delta E \quad , \quad \Delta V_1 = -\Delta V_2 = \Delta V \quad , \quad \Delta N_1 = -\Delta N_2 = \Delta N \tag{2}$$

Since the entropy is a maximum, it must be stationary with respect to these changes, i.e.

$$\Delta S = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\Delta E + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right)\Delta V - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right)\Delta N = 0 \tag{3}$$

implying $T_1 = T_2$, $P_1 = P_2$ and $\mu_1 = \mu_2$. The interface between two coexisting phases is essentially a movable partition that allows interchange of particle and energy. Thus, the above considerations imply that the temperatures, pressures and chemical potentials of coexisting phases must be equal.

The third law of thermodynamics (or Nerst theorem) relates to the behavior of systems as they approach the absolute zero of temperature. Nerst suggested that the entropy of physical systems would tend to zero as T → 0. (Within quantum statistical mechanics this is equivalent to having a non-infinite ground state degeneracy hence a nonextensive or zero entropy). The consequences of this law are the most temperature derivatives of thermodynamic quantities go to zero at least as fast as T, and in particular the specific heat (see later) should go to zero with T. There are presently several interesting physical and model systems which appear at first glance to violate this theorem, especially glasses and systems with "frustrated" ground states, retaining considerable entropy to quite low temperatures.

As we saw above, all thermodynamic quantities can be obtained from the internal energy, E, provided the latter is expressed as a function of its associated *natural variables*, S, V and N. Functions that contain all thermodynamic information are called *thermodynamic potentials*. E is an extensive variable that is a natural function of extensive variables only. It is often desirable to consider other thermodynamic potentials that are natural functions of one or more of the extensive parameters that can be controlled by establishing contact with an appropriate reservoir as implied by eq (4.3) (Either side of the figure of last page can be a reservoir if it is made sufficiently large so that its T, P or μ do not change significantly when energy, volume or particles are removed). These potentials are Legendre transforms of E.

The *Helmholtz free energy*

$$F = E - TS \tag{1}$$

is a natural function of T, V, N, as can be seen by the differential relation

$$\begin{aligned} dF &= dE - TdS - SdT = \\ &= -SdT - PdV + \mu dN \end{aligned} \tag{2}$$

it satisfy.

The *Gibbs free energy* is a natural function of T, P and N

$$G = E - TS + PV = F + PV \tag{3}$$

$$dG = -SdT + VdP + \mu dN \tag{4}$$

The <u>enthalpy</u> is a natural function of S, P and N

$$H = E + PV \tag{1}$$

$$dH = -TdS + VdP + \mu dN \tag{2}$$

Finally, <u>the grand potential</u>

$$\mathcal{A} = E - TS - \mu N = F - \mu N \tag{3}$$

$$d\mathcal{A} = -SdT - PdV - N d\mu \tag{4}$$

is a natural function of T, V and μ. Like E, all the thermodynamic potentials just introduced contain all thermodynamic information, provided they are expressed as functions of their associated natural variables. For example, the entropy is given by

$$S = -\left.\frac{\partial F}{\partial T}\right)_{V,N} = -\left.\frac{\partial G}{\partial T}\right)_{P,N} = -\left.\frac{\partial \mathcal{A}}{\partial T}\right)_{V,\mu} \tag{5}$$

In equilibrium, the entropy is a maximum with respect to changes of unconstrained parameters as demostrated below. In equilibrium, the free energies just introduced are minima with respect to similar changes. Consider a fluid in thermal and mechanical contact with a reservoir, whose variables will be indicated by a zero. The fluid and reservoir together form a closed system with constant total volume. The reservoir is at temperature T_0 and pressure P_0. The change $\Delta S_T = \Delta S + \Delta S_0$, in the total entropy occurring when any constraints are removed must be positive. The heat Q transferred from the reservoir to the fluid is, by the first law, equal to the change ΔE in the internal energy of the fluid plus the work done by the fluid. The work done by the fluid in changing its volume by ΔV is $P_0 \Delta V$. Thus $Q = \Delta E + P_0 \Delta V$. The temperature of the reservoir does not change in transferring heat to the fluid. The change in entropy of the reservoir is, therefore, $\Delta S_0 = -Q / T_0$, and

$$\Delta S_T = \Delta S - \frac{\Delta E + P_0 \Delta V}{T_0} \geqslant 0 \quad \Rightarrow \tag{6}$$

$$\Delta(E - T_0 S + P_0 V) \leq 0 \tag{7}$$

Thus, in absence of external forces, changes in the quantity $E - T_0 S + P_0 V$ resulting from the removal of constraints will be negative. If the volume and temperature of the fluid are fixed, then

$$\Delta F \leq 0 \qquad V, T = \text{fixed} \tag{1}$$

and if the pressure and temperature are fixed, eq (6.7) implies

$$\Delta G \leq 0 \qquad P, T = \text{fixed} \tag{2}$$

when there are not external forces. Thus the removal of constraints at constant volume and temperature leads to a decrease in Helmholtz free energy, and the removal of constraint at constant temperature and pressure lead to a decrease of the Gibbs free energy. In other words, to attain equilibrium nature ajust any free variable

to maximize S for fixed E and T
to minimize F for fixed V and T (3)
to minimize G for fixed P and T

Since in equilibrium $E - T_0 S + P_0 V$ is a minimum, its deviation from thermodynamic equilibrium will be positive. Thus

$$\delta E - T_0\, \delta S + P_0\, \delta V \geq 0 \tag{4}$$

where δE, δS and δV are, respectively, the deviations of the internal energy, entropy, and volume from their equilibrium values in contact with the reservoir at temperature T_0 and pressure P_0. Eq (4) is valid for arbitrary values δE, δS and δV. When applied to infinitesimal values of these parameters, eq (4) leads to positivity constraints on equilibrium derivatives. If $\delta E(\delta S, \delta V)$ is expanded in a power series, the first order terms in δS and δV on the left hand side of (4) will vanish because the equilibrium temperature and pressure of the fluid are equal to those of the reservoir. Thus, to second order in δS and δV, eq (4) becomes

$$\frac{1}{2} \frac{\partial^2 E}{\partial S^2} (\delta S)^2 + \frac{\partial^2 E}{\partial S \partial V} \delta S\, \delta V + \frac{1}{2} \frac{\partial^2 E}{\partial V^2} (\delta V)^2 \geq 0 \tag{5}$$

which must be true for arbitrary values of dS and dV and therefore this implies (using (2.4))

$$\frac{\partial^2 E}{\partial S^2} = \left.\frac{\partial T}{\partial S}\right)_V \geq 0$$

$$\frac{\partial^2 E}{\partial V^2} = -\left.\frac{\partial P}{\partial V}\right)_S \geq 0 \tag{1}$$

$$\frac{\partial^2 E}{\partial S^2}\frac{\partial^2 E}{\partial V^2} - \left(\frac{\partial^2 E}{\partial S \partial V}\right)^2 = -\left\{ \left.\frac{\partial T}{\partial S}\right)_V \left.\frac{\partial P}{\partial V}\right)_S - \left.\frac{\partial T}{\partial V}\right)_S \left.\frac{\partial P}{\partial S}\right)_V \right\} =$$

$$= -\frac{(\partial P/\partial V)_T}{(\partial S/\partial T)_V} \geq 0$$

Hence, in thermodynamical equilibrium, the heat capacity at constant volume C_V, the isothermal compressibility k_T and the isentropic compressibility k_S must be non negative

$$C_V \equiv T \left.\frac{\partial S}{\partial T}\right)_V \geq 0 \quad , \quad k_T \equiv -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right)_T \geq 0 \quad , \quad k_S \equiv -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right)_S \geq 0 \tag{2}$$

Furthermore, a straightforward exercise in partial derivatives yields the relation

$$C_p \equiv T \left.\frac{\partial S}{\partial T}\right)_p = C_V + T\,\frac{1}{V k_T}\left[\left(\frac{\partial V}{\partial T}\right)_p\right]^2 \tag{3}$$

implying that in thermodynamical equilibrium

$$C_p \geq C_V \geq 0 \tag{4}$$

Note that heat capacities are extensive. It is often useful to consider an intensive measure of heat capacity obtained by dividing C_V or C_p by an extensive measure of the quantity of matter such as the volume V, the particle number N, or the mass M, and one introduces in this way the specific heats

The fact that extensive parameters increase in proportion to the size of the system leads to simple but important constraints on the thermodynamic potentials. The internal energy is a function $Y(S, V, N)$ of the extensive variables S, V and N. If the size of the system increases by a factor b, all the extensive parameters increase by a factor b, but the function Y does not change. Therefore

$$E = Y(S, V, N) \qquad bE = Y(bS, bV, bN) \tag{1}$$

A function f(x) is said to be <u>homogeneous of degree k</u> if it satisfies $f(x) = b^k f(bx)$. E is a homogeneous function of S, V and N of degree -1. Eq (1) is true for arbitrary b, and in particular for $b = V^{-1}$, leading to

$$E = V\,Y(S/V, 1, N/V) \tag{2}$$

Introducing ϵ, n, s which are defined as

$$\epsilon = \frac{E}{V} \quad , \quad n = \frac{N}{V} \quad , \quad s = \frac{S}{V} \tag{3}$$

and represent, respectively, the density of energy, particles and entropy we have

$$\epsilon = \epsilon(s, n) \tag{4}$$

Similar arguments lead to

$$F(T, V, N) = V f(n, T) \quad , \quad G(T, p, N) = N g(p, T)$$
$$\mathcal{A}(T, V, \mu) = V a(T, \mu) \tag{5}$$

where $f \equiv F/V$ is the Helmholtz free energy density, $g \equiv G/N$ is the Gibbs free energy per particle and $a \equiv \mathcal{A}/V$ is the grand potential density.

Eqs (1) to (5) show that the extensive thermodynamical potentials have a trivial dependence on one of the extensive parameters that lead to an identification of the free energy densities with intensive generalized forces:

$$\left.\frac{\partial G}{\partial N}\right)_{T,p} \equiv g(p, T) = \mu \tag{6}$$

$$\left.\frac{\partial \mathcal{A}}{\partial V}\right)_{T,\mu} \equiv a(T, \mu) = -p = f - n\mu$$

Note that the volume density of the extensive internal energy is a function only of the volume densities of the extensive quantities S and N, whereas the intensive pressure is a function only of the intensive parameters T and μ

Quasi-static changes in these quantities are related by differential relations

$$d\epsilon = T\,ds + \mu\,dn \qquad (1)$$

$$dp = n\,d\mu + s\,dT \qquad (2)$$

as can be seen using $E = V\epsilon$ in eq (3.2) and $\Omega = -Vp$ in eq (6.4). Eq (1) says that the energy density changes in response to changes in the density and entropy density rather than to particle number, volume and entropy separately. This allows us to discuss the properties of a system by considering some fixed sub-volume that is able to exchange particles and energy with the rest of the system through some imaginary wall. Eq (2) says that changes in pressure at constant temperature are equivalent to the density times changes in the chemical potential. This implies, for instance, that the isothermal compressibility can be expressed

$$k_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right)_{T,N} = -\frac{1}{V}\frac{\partial (N/n)}{n\,\partial\mu} = \frac{1}{n^2}\frac{\partial n}{\partial\mu} \qquad (3)$$

Thus $n^2 k_T$ is the derivative of the density with respect to the thermodynamically conjugate potential μ.

Generalized forces and extensive parameters or their derivatives are related via <u>equations of state</u> obtained by the appropriate derivative of the thermodynamic potentials. For example, the pressure P as a function of T, V and N is obtained differentiating F with respect to V

$$\underline{P}(T, V, N) = -\left.\frac{\partial F}{\partial V}\right)_{T,N} \qquad (4)$$

Since $\underline{P}$ is an intensive function of the extensive variable V and N, it must be a function of the density only since

$$P(T, V, N) = p(T, bV, bN) = p(T, n) \qquad (5)$$

where the last expression has been obtained taking $b = V^{-1}$. An alternative equation of state expresses

$$\mu(T, n) = \left.\frac{\partial F}{\partial N}\right)_{T,V} = \left.\frac{\partial f}{\partial n}\right)_{T} \qquad (6)$$

Note that (4) implies (6) and viceversa since $-p = f - \mu n$

Notice that $-p = f - \mu n$ and eq (10.6) imply that the pressure as a function of μ and T can be expressed as a minimum over n of the function

$$w(\mu, T, n) \equiv f(T, n) - \mu n \tag{1}$$

i.e.

$$-p(\mu, T) = [f(T, n) - \mu n]_{\min\, n} = w(\mu, T, n)\Big|_{\min,\, n} \tag{2}$$

Statistical mechanics : phase space and ensembles

Thermodynamics is an empirically based science that requires no knowledge of microscopic interactions. Statistical mechanics establishes a connection between the microscopic and macroscopic thermodynamic description of a system. We are going to study now statistical mechanics of homogeneous fluids.

The state of a closed system consisting of N classical point particles in a D-dimensional space at time t is specified by the coordinates $\vec{x}_\alpha(t)$ and momenta $\vec{p}_\alpha(t)$, $\alpha = 1, 2, \ldots, N$, or equivalently by a vector $\vec{R} = [\vec{x}_\alpha(t), \vec{p}_\alpha(t)]$ in a $2ND$-dimensional phase space. $\vec{x}_\alpha(t)$ and $\vec{p}_\alpha(t)$ evolve in time according to Newton's laws along a trajectory in phase space. In quantum mechanical systems $\vec{R}$ is an operator, and the state of the system is specified by an N-particle wave function. If the state of the system is precisely known at some time t_0, its state at future times is, in principle, determined by its Hamiltonian H. It is impossible, however, to have complete knowledge of the state of a system consisting of 10^{23} particles. In practice, detailed knowledge of only a few macroscopic properties such as volume or energy is possible and a statistical description is the only reasonable one.

In an isolated fluid, the internal energy E is fixed. The Hamiltonian H depends on $\vec{x}_\alpha$, $\vec{p}_\alpha$, on the volume V, and possibly of other external controllable parameters, which will be not considered at present. In the absence of any other knowledge about the system, there is no reason to favor any state (i.e. point in phase space) with energy E over any other. It is, therefore, postulated that all points in phase space with a given energy are equally likely and that the macroscopic properties of the fluid can be obtained by averaging over the ensemble of states with fixed energy. This is the <u>microcanonical ensemble</u>. In this ensemble, the probability of occurrence of a given point in phase space is

$$P_{micro}(\vec{R}) = \frac{\delta\left[E - H(\vec{R}, V)\right]}{\omega(E, V)} \tag{1}$$

where $\omega(E, V)$ is the density of states so that the sum of $P_{micro}(\vec{R})$ over all states $\vec{R}$ is unity:

$$\omega(E, V) = \mathrm{Tr}\ \delta\left[E - H(\vec{R}, V)\right] \tag{2}$$

In quantum mechanical systems, $\delta(E - H)$ is an operator or matrix called the <u>microcanonical density matrix</u>. The trace (2) is over all states of the system. In classical systems, it is an integral over phase space

$$\mathrm{Tr} \equiv \frac{1}{N!} \prod_{\alpha} \int \frac{d^D x_\alpha\, d^D p_\alpha}{(2\pi\hbar)^{DN}} \tag{3}$$

The factor $[N!(2\pi\hbar)^{DN}]^{-1}$ arises when classical limit of the quantum mechanical trace operation is taken. It is, strictly speaking, not necessary in classical statistical mechanics for a fixed number of particles, but is needed for a proper definition of entropy and evaluation of the chemical potential. The absence of this term leads to the Gibbs paradox in which the entropy of a classical gas is not extensive.

The entropy of a system in equilibrium is simply the logarithm of the number of configurations available at energy E

$$S = \ln\left[\omega(E, V)\,\Delta E\right] \tag{4}$$

where ΔE is some energy interval representing, for example, the precision with which the energy of the system can actually be determined. Eqs (4) and (1) provide a statistical mechanical interpretation of the second law. There are more configurations available to a system whenever constraints are removed. Thus the entropy increases. The most likely state of the system is one which occurs with maximum probability. If constraints are removed, the new equilibrium will have higher entropy and thus higher probability than that with the constraints in effect.

The microcanonical ensemble is not the most useful ensemble for doing calculations because involves difficult sums over states with constrained energies. Two other ensembles are far more useful. In the *canonical ensemble* the density matrix is $\exp(-\beta H)$, where $\beta = T^{-1}$ (we use units in which the Boltzmann constant k_B is equal to one) and the probability matrix is

$$P_c = \frac{1}{Z_N(T,V)} e^{-\beta H} \tag{1}$$

where

$$Z_N(T,V) = \mathrm{Tr}\left[e^{-\beta H} \right] = \frac{1}{N!\,(2\pi\hbar)^{ND}} \int d\vec{R}\; e^{-\beta H} \quad \text{(classical)} \tag{2}$$

is the *partition function*. In the *grand canonical ensemble*, the number of particles is allowed to vary, and the probability of a given state is

$$P_{gc} = \frac{1}{\Xi(T,\mu,V)} e^{-\beta(H-\mu N)} \tag{3}$$

where

$$\Xi(T,\mu,V) = \mathrm{Tr}\left[e^{-\beta(H-\mu N)} \right] \tag{4}$$

is the *grand partition function*. The trace is over all states with all possible numbers of particles. For classical systems

$$\Xi(T,\mu,V) = \sum_N e^{\beta\mu N} Z_N(T,V) \quad \text{(classical)} \tag{5}$$

In neither the canonical nor the grand canonical ensemble the energy is fixed. The average energy is the average of the Hamiltonian over the ensemble

$$\langle E \rangle \equiv \langle H \rangle = \mathrm{Tr}\left[\rho H \right] \tag{6}$$

where ρ is either P_c or P_{gc}. $\langle E \rangle$ can be obtained in either ensemble by differentiation of the partition function with respect to β.

$$\langle E \rangle = -\frac{1}{Z_N} \left.\frac{\partial Z_N}{\partial \beta}\right|_{N,V} = -\left.\frac{\partial \ln Z_N}{\partial \beta}\right|_{N,V} \tag{7}$$

$$\langle E \rangle = -\frac{1}{\Xi} \left.\frac{\partial \Xi}{\partial \beta}\right|_{\beta\mu, V} = -\left.\frac{\partial \ln \Xi}{\partial \beta}\right|_{\beta\mu, V} \tag{8}$$

Fluctuations in H can similarly be calculated

$$\langle E^2 \rangle = \frac{1}{Z_N} \operatorname{Tr}\left[e^{-\beta H} H^2 \right] = \frac{1}{Z_N} \frac{\partial^2 Z_N}{\partial \beta^2} \tag{1}$$

and

$$\langle (\delta E)^2 \rangle \equiv \langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial^2 \ln Z_N}{\partial \beta^2} = - \frac{\partial \langle E \rangle}{\partial \beta} \tag{2}$$

Similar expressions apply for the grand canonical ensemble. In the grand canonical ensemble, the number of particles is not fixed. We have

$$\langle N \rangle = \frac{1}{\Xi} \operatorname{Tr}\left[e^{-\beta (H - \mu N)} N \right] \tag{3}$$

$$\langle (\delta N)^2 \rangle \equiv \langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{\Xi} \operatorname{Tr}\left[e^{-\beta (H - \mu N)} (N - \langle N \rangle)^2 \right] \tag{4}$$

The first of this expression can always be written

$$\langle N \rangle = \frac{\partial \ln \Xi}{\partial \beta \mu} \tag{5}$$

if $[H, N] = 0$ we can also write

$$\langle (\delta N)^2 \rangle = \frac{\partial^2 \ln \Xi}{\partial (\beta \mu)^2} = \frac{\partial \langle N \rangle}{\partial \beta \mu} \qquad \text{if } [H, N] = 0 \tag{6}$$

Both $\langle E \rangle$ and $\langle N \rangle$ are extensive quantities. It is clear from (2) and (4) that the fluctuations in E and N are also extensive quantities. Therefore

$$\langle (\delta E)^2 \rangle^{1/2} / \langle E \rangle \sim N^{-1/2} \quad , \quad \langle (\delta N)^2 \rangle^{1/2} / \langle N \rangle \sim N^{-1/2} \tag{7}$$

so that, in large systems, the distinction between the fixed energy of the microcanonical ensemble and the average energy of the canonical ensemble is unimportant. The energy E of the microcanonical ensemble or the average energy $\langle E \rangle$ of the canonical and grand canonical ensembles is the thermodynamic internal energy. In the future, we will only distinguish between $\langle E \rangle$ and E when necessary.

The partition functions Z_N and Ξ are related to the thermodynamic potentials F and Ω introduced before by

$$F(T, N, V) = -T \ln Z_N(T, V) \tag{1}$$

$$\mathcal{A}(T, \mu, V) = -T \ln \Xi(T, \mu, V) \tag{2}$$

The first of these results is most easily obtained by recognizing that $\omega(E)\, e^{-\beta E}$ is strongly peaked function in the vicinity of $E = \langle E \rangle$:

$$Z_N = \int dE\, \omega(E)\, e^{-\beta E} \sim e^{-\beta(\langle E \rangle - TS)} \tag{3}$$

Similar expressions apply for Ξ.

The heat capacity and compressibility are related, respectively, to fluctuations in the energy and particle number

$$C_V = -T \frac{\partial^2 F}{\partial T^2} = T^{-2} \frac{\partial^2 \ln Z_N}{\partial \beta^2} = \frac{\langle (\delta E)^2 \rangle}{T^2} \geq 0 \tag{4}$$

and

$$k_T = \langle n \rangle^{-2} \frac{\partial \langle n \rangle}{\partial \mu} = \frac{V}{T} \frac{\langle (\delta N)^2 \rangle}{\langle N \rangle^2} \geq 0 \tag{5}$$

Thus, we see that the positivity of C_V and k_T, which emerged as a condition for equilibrium in the thermodynamic analysis, emerges in a statistical mechanical analysis as a result of the positivity of the variances of random variables

The Ideal Gas

One of the simplest statistical systems is the gas of non-interacting particles of mass M in a volume V. The Hamiltonian is

$$H = \sum_{\alpha=1}^{N} \frac{\vec{p}_\alpha^{\,2}}{2M} \tag{6}$$

Now

$$Z_N(T, V) = \frac{1}{N!\,(2\pi\hbar)^{DN}} \int \prod_{\alpha=1}^{N} d^D x_\alpha\, d^D p_\alpha\, e^{-\beta \sum_{\alpha=1}^{N} \frac{\vec{p}_\alpha^{\,2}}{2M}} =$$

$$= \frac{V^N}{N!\,(2\pi\hbar)^{DN}} \left(\int_{-\infty}^{+\infty} dp\, e^{-\beta p^2/2M} \right)^{ND} =$$

$$= \frac{V^N}{N!\,(2\pi\hbar)^{DN}} \left(\frac{2M}{\beta} \right)^{ND/2} \left(\int_{-\infty}^{+\infty} dx\, e^{-x^2} \right)^{ND} = \frac{V^N}{N!\,(2\pi\hbar)^{DN}} \left(\frac{2M\pi}{\beta} \right)^{ND/2} \tag{7}$$

If we introduce

$$\lambda \equiv \frac{2\pi\hbar}{\sqrt{2M\pi/\beta}} = \frac{2\pi\hbar}{\sqrt{2M\pi k_B T}} \qquad \text{(thermal wave length)} \qquad (1)$$

and we obtain

$$Z_N(T,V) = \frac{1}{N!}\,\frac{V^N}{(\lambda)^{DN}} \qquad (2)$$

From (15.1) the Helmholtz free energy density is

$$f(n,T) = -\frac{T}{V}\ln Z_N = -\frac{T}{V}\left[+N\ln V - \ln N! - N\ln\lambda^D\right]$$

$$= -\frac{T}{V}\left\{ N\ln V - N\ln\lambda^D + N - N\ln N \right\} \Rightarrow$$

$$f(n,T) = T n \left\{ \ln(n\lambda^D) - 1 \right\} \qquad (3)$$

Now from eqs. (13.7), (10.6), (10.4) and (6.5) we obtain

$$E = \frac{D}{2} N T \qquad (4)$$

$$\mu = T \ln(n\lambda^3) \qquad (5)$$

$$P = n T \qquad (6)$$

$$S = N\left\{ \frac{D+2}{2} - \ln(n\lambda^D) \right\} \qquad (7)$$

Eq (6) is the familiar equation of state for an ideal gas. Also

$$C_V = \frac{D}{2} N \qquad C_P = \frac{D+2}{2} N \qquad (8)$$

$$k_T = \frac{1}{nT} = p \qquad (9)$$

All this are classical results valid only when

$$n\lambda^D \ll 1 \qquad (10)$$

When $n\lambda^D \gtrsim 1$ the quantum mechanical effects are important.

Spatial Correlations in Classical Systems

We have seen before that we are able to find the average energy and average particle number in the grand canonical ensemble by differentiating the partition function respect to β or $(\beta\mu)$. It is extremely useful to be able to generate the spatially dependent density and its correlation functions by a similar process. In order to do so, it is necessary to introduce external potentials that depend on position. Let $u(\vec{x})$ be an externally controlled one-body potential. The potential energy must be augmented by a term

$$U_{ext} = - \sum_{\alpha} u(\vec{x}_\alpha) \equiv - \int d^3x \, u(\vec{x}) \, n(\vec{x}) \tag{1}$$

so that the total Hamiltonian becomes

$$H = K + U + U_{ext} \tag{2}$$

where K is the kinetic energy and U is the potential energy associated with interactions among the constituent particles of the fluid. If $u(\vec{x})$ is changed by an amount $\delta u(\vec{x})$, U_{ext} changes according to

$$\delta U_{ext} = - \int d^3x \, \delta u(\vec{x}) \, n(\vec{x}) \tag{3}$$

The partition function can be expanded in powers of δu:

$$Z_N [T, V, u(\vec{x}) + \delta u(\vec{x})] = \mathrm{Tr} \; | \; e^{-\beta H} \Big\{ 1 + \int d^3x \, \beta \, \delta u(\vec{x}) \, n(\vec{x})$$

$$+ \frac{1}{2} \int d^3x \, d^3x' \, \beta \, \delta u(\vec{x}) \, \beta \, \delta u(\vec{x}') \, n(\vec{x}) \, n(\vec{x}') + \cdots \Big\} \Rightarrow$$

$$\frac{Z_N [T, V, u(\vec{x}) + \delta u(\vec{x})]}{Z_N [T, V, u(\vec{x})]} = 1 + \int d^3x \, \beta \, \delta u(\vec{x}) \langle n(\vec{x}) \rangle +$$

$$+ \frac{1}{2} \int d^3x \, \beta \, \delta u(\vec{x}) \, \beta \, \delta u(\vec{x}') \langle n(\vec{x}) \, n(\vec{x}') \rangle + \cdots \tag{4}$$

where is understood that H is evaluated at $\delta u(x) = 0$. Then we obtain

$$\langle n(\vec{x}) \rangle = \frac{1}{Z_N} \left. \frac{\delta Z_N}{\beta \, \delta u(\vec{x})} \right)_{T,V,N} = \left. \frac{\delta \ln Z_N}{\delta \, \beta u(\vec{x})} \right)_{T,N,V} = - \left. \frac{\delta F}{\delta u(\vec{x})} \right)_{T,N,V} \tag{5}$$

and

$$C_{nn}(\vec{x},\vec{x}') = \frac{1}{Z_N}\,\frac{\delta^2 Z_N}{\beta\,\delta u(\vec{x})\;\beta\,\delta u(\vec{x}')}\Bigg)_{T,V,N} \qquad (1)$$

and similarly

$$S_n(\vec{x},\vec{x}') = \frac{\delta^2 \ln Z_N}{\beta\,\delta u(\vec{x})\;\beta\,\delta u(\vec{x}')}\Bigg)_{T,V,N} = \frac{\delta\langle n(\vec{x})\rangle}{\delta\,\beta\, n(\vec{x}')}\Bigg)_{T,V,N} = -\,T\,\frac{\delta^2 F}{\delta u(\vec{x})\,\delta u(\vec{x}')}\Bigg)_{T,V,N} \qquad (2)$$

To gain familiarity with the functional derivatives, it is useful to derive the pair distribution function for the non-interacting classical gas from $Z_N[T,V,u(\vec{x})]$, which can be easily evaluated

$$Z_N[T,V,u(\vec{x})] = \frac{1}{N!\,(2\pi\hbar)^{DN}}\int\prod_{\alpha=1}^{N} d^Dx_\alpha\, d^Dp_\alpha\; e^{-\beta\sum_{\alpha=1}^{N}\frac{p_\alpha^2}{2M}}\; e^{+\beta\sum_{\alpha=1}^{N}u(\vec{x}_\alpha)} \Rightarrow$$

$$Z_N[T,V,\bar{u}(x)] = \frac{1}{N!}\left[q\,\lambda^{-D}\right]^N \qquad (3)$$

$$\lambda \equiv \frac{2\pi\hbar}{\sqrt{2\pi M T}} \qquad\qquad q \equiv \int d^Dx\; e^{\beta u(\vec{x})} \xrightarrow[u(x)\to 0]{} V$$

Thus we have

$$\langle n(\vec{x})\rangle = \frac{\delta \ln Z_N}{\delta\,\beta u(x)} = N\,\frac{\delta \ln q}{\delta\,\beta u(\vec{x})} = N\,\frac{1}{q}\,e^{\beta u(x)} \xrightarrow[u(x)\to 0]{} \frac{N}{V} \qquad (4)$$

and

$$S_n(\vec{x},\vec{x}') = \frac{\delta^2 \ln Z_N}{\delta\beta u(\vec{x})\,\delta\beta u(\vec{x}')} = N\,\frac{\delta^2 \ln q}{\delta\beta u(\vec{x})\,\delta\beta u(\vec{x}')} = N q^{-1}\, e^{\beta u(\vec{x})}\,\delta(\vec{x}-x') - N q^{-2}\, e^{\beta u(\vec{x})}\, e^{\beta u(\vec{x}')}$$

$$= \langle n(\vec{x})\rangle\,\delta(\vec{x}-\vec{x}') - \frac{1}{N}\,\langle n(\vec{x})\rangle\langle n(\vec{x}')\rangle \xrightarrow[N\to\infty]{} \langle n(\vec{x})\rangle\,\delta(\vec{x}-\vec{x}') \qquad (5)$$

If $u(\vec{x})$ is nonzero and nonuniform, the equilibrium density is nonuniform. External nonuniform potentials provide a natural way to discuss inhomogeneous systems. It should be noted that (5) with (I.5.5) and (I.6.7) yield

$$g(\vec{x},\vec{x}') = 1 - \frac{1}{N} \xrightarrow[N\to\infty]{} 1.$$

Thus the formal manipulations presented here yield the result discussed before.

The introduction of an external inhomogeneous potential is in many ways simpler and more instructive in the grand canonical ensemble. The external potential, like the chemical potential, couples linearly to the density, and one can interpret the external potential as a shift in the chemical potential

$$\mu \longrightarrow \mu(\vec{x}) = \mu + u(\vec{x}) \qquad (1)$$

The grand partition function is now a functional of $\mu(\vec{x})$

$$\Xi[T, V, \mu(\vec{x})] = \mathrm{Tr}\left\{ \exp\left[-\beta \left(H - \int d^D x \, \mu(\vec{x})\, n(\vec{x}) \right) \right] \right\} \qquad (2)$$

Following the same steeps as before

$$\langle n(\vec{x}) \rangle = \frac{\partial \ln \Xi[\mu(\vec{x})]}{\beta \, \partial \mu(\vec{x})} = - \frac{\partial \mathcal{A}[\mu(\vec{x})]}{\partial \mu(\vec{x})} \qquad (3)$$

$$\beta S_{nn}(\vec{x}, \vec{x}') = - \frac{\partial^2 \mathcal{A}[\mu(\vec{x})]}{\partial \mu(\vec{x}) \, \partial \mu(\vec{x}')} = \frac{\partial \langle n(\vec{x}) \rangle}{\delta \mu(\vec{x}')} \qquad (4)$$

The last expression can be used to derive an important relation between the Ursell function and the compressibility. In eq (3) $\langle n(\vec{x}) \rangle$ is a functional of $\mu(x)$ and can be expanded in a Taylor series.

$$\langle n(\vec{x}) \rangle - \langle n(\vec{x}) \rangle_0 = \int d^D x' \, \frac{\partial \langle n(\vec{x}) \rangle}{\partial \mu(\vec{x}')} \, \delta\mu(\vec{x}') + \cdots$$

$$= \int d^D x' \, \beta \, S_{nn}(\vec{x}, \vec{x}') \, \delta\mu(\vec{x}') + \cdots \qquad (5)$$

Where $\langle n(\vec{x}) \rangle_0$ is the density at $d\mu(\vec{x}) = 0$. The compressibility is related to the derivative of n with respect to a spatially constant chemical potential (10.3). If $d\mu$ is spatially constant, then $d\mu(\vec{x}) = d\mu$ is independent of $\vec{x}$. Then, using (10.3) and (5), we obtain

$$\frac{\partial \langle n \rangle}{\partial \mu} = \langle n \rangle^2 \kappa_T = \beta \int d^D x' \, S_{nn}(\vec{x}, \vec{x}') = (2\pi)^D \beta \, S_{nn}(\vec{q} = 0) \qquad (6)$$

This is a very important and general relation relating the derivative of the density of an extensive parameter with respect to its conjugate field to the zero wave number fluctuations of the density of the same parameter.

We close this section with the observation that a Helmholtz free energy functional of the density $n(\vec{x})$ can be obtained via a generalized Legendre transformation of the grand potential $\mathcal{A}[\mu(\vec{x})]$ with a spatially varying chemical potential. Let us generalize (6.3)

$$F[T, V, \langle m(\bar{x})\rangle] = \mathcal{A}[T, V, \mu(\bar{x})] + \int d^d x \, \langle m(\bar{x})\rangle \mu(\bar{x}) \qquad (1)$$

then

$$\frac{\delta F[T, V, \langle m(\bar{x})\rangle]}{\delta \langle m(\bar{x})\rangle} = \mu(\bar{x}) \qquad (2)$$

This is a generalization of the equation of state (10.6) to spatially inhomogeneous situations. If $\mu(\bar{x})$ is spatially uniform, F can be expressed as the volume integral of a local free energy functional of $\langle m(\bar{x})\rangle \equiv \langle m\rangle$,

$$F = \int d^d x \; f(T, \langle m\rangle) \qquad (3)$$

and eq (2) reduces to (10.6). More generally, as we shall see, later on, F can depend on $\langle m(\bar{x})\rangle$ at different points in space. The concept that free energies can be functions of spatially varying densities of extensive variables is a very important one that has many applications to many problems in condensed matter systems.

The expression (11.2) for the pressure as a minimum over m of the function $f(T, m) - \mu m$ has a straightforward generalization to situations in which $\langle m(\bar{x})\rangle$ is allowed to vary in space. Let

$$W[T, V, \mu(\bar{x}), \langle m(\bar{x})\rangle] = F[T, V, \langle m(\bar{x})\rangle] - \int d^d x \, \langle m(\bar{x})\rangle \mu(\bar{x}) \qquad (4)$$

Then, when $\mu(\bar{x}) = \mu$ is independent of $\bar{x}$

$$p(\mu, T) = - \lim_{V \to \infty} \frac{1}{V} W[T, V, \mu, \langle m(\bar{x})\rangle]_{\min \langle m(\bar{x})\rangle} = - \frac{1}{V} \mathcal{A}(T, V, \mu) \qquad (5)$$

This relation is useful to discuss the equations of state of fluids and solids.

Ordered Systems

We have discussed homogeneous, isotropic fluids. The only macroscopic variables needed to characterize the thermodynamic state of fluids are their volume, particle number and internal energy. As we have seen before condensed matter exhibit a wide variety of rotational and positional order not described by the above variables. Clearly, a complete description of ordered phases requires the introduction of new variables quantifying the degree of order and a modification of thermodynamics and statistical mechanics to describe the effects of these variables on energies and entropies.

The simplest order to describe is magnetic order. Consider an ideal gas in which each particle α carries a spin $\vec{S}_\alpha$ and an associated magnetic moment $\mu_s \vec{S}_\alpha$. In the presence of an external magnetic field $\vec{h}$, the gas will develop a magnetic moment

$$\vec{M} = \langle \sum_\alpha \mu_\alpha \vec{S}_\alpha \rangle \qquad (1)$$

proportional to the total number of particles. It is an extensive variable whose density is the intensive magnetization

$$\langle \vec{m}(\vec{x}) \rangle = \langle \sum_\alpha \mu_\alpha \vec{S}_\alpha \, \delta(\vec{x} - \vec{x}_\alpha) \rangle \qquad (2)$$

This equation shows that the magnetization $\vec{m}(\vec{x})$ is an operator analogous to the density operator: particle α contributes to $\vec{m}(\vec{x})$ only at its position $\vec{x}_\alpha$. The integral of $\vec{m}(\vec{x})$ over all $\vec{x}$ is the total magnetic moment. If the magnetization is spatially uniform, then $\langle \vec{m}(\vec{x}) \rangle = \vec{M}/V$. The internal energy and entropy clearly depend on the variable $\langle \vec{m} \rangle$, and it must be included along with the density for a complete thermodynamic description of the classical gas of magnetic particles.

The interaction between spins in the ideal gas just discussed is essentially zero (ignoring dipolar forces), and the magnetization is nonzero only in the presence of an external aligning magnetic field. If there are interactions among spins, it is possible to have a nonzero $\langle \vec{m} \rangle$ even when $\vec{h}$ is zero. To see how this can come about, it is useful to consider a model in which spins confined to sites on a regular periodic lattice (i.e. the spin positions $\vec{x}_\alpha$ are confined to sites $\vec{R}_{\vec{\ell}}$ on a periodic lattice) interact via a nearest neighbor exchange interaction. This model is called the Heisenberg model of ferromagnetism, and its Hamiltonian can be expressed as

$$H_{Heis} = -2J \sum_{\langle \vec{\ell}, \vec{\ell}' \rangle} \vec{S}_{\vec{\ell}} \cdot \vec{S}_{\vec{\ell}'} \quad , \quad J > 0 \qquad (3)$$

where the sum is over nearest neighbor sites on the lattice. When $\vec{h}$ is zero, the spin represent internal degrees of freedom, which will seek configurations that, at constant T, will minimize the Helmholtz free energy $F = E - TS$. At high T, F is clearly minimized by maximizing the entropy.

The maximally disordered state has the highest entropy, implying that the equilibrium state at high temperature is the <u>paramagnetic state</u> with no average alignment of spins, i.e. no magnetization. At low temperature, the internal energy dominates over TS and the state that minimizes F is one that minimizes E. The ground state of H_{Heis} are clearly states in which all of the spins are aligned along a common axis. Thus, states which minimize E have a non vanishing magnetization, and the low temperature equilibrium phase is the <u>ferromagnetic phase</u> with nonzero average spin $\langle \vec{S} \rangle = \langle S_{\vec{\ell}} \rangle$ independent of the site $\vec{\ell}$ or equivalently a magnetization $\langle \vec{m} \rangle = v_0^{-1} \mu_S \langle \vec{S} \rangle$, where v_0 is the volume of the unit cell. At some temperature T_c, there is a phase transition from the entropy dominated paramagnetic state to the energy dominated ferromagnetic state. The magnetization $\langle \vec{m} \rangle$ is called the <u>order parameter</u> of the ferromagnetic phase.

The Heisenberg Hamiltonian is invariant with respect to arbitrary rotations of every spin $\vec{S}_{\vec{\ell}}$. Thus there is no preferred direction for the magnetization in the ferromagnetic state. In order to obtain an unambiguous statistical mechanical characterization of the ferromagnetic state with $\langle \vec{m} \rangle$ pointing along a given direction, it is necessary to add an external magnetic field $\vec{h}$. The Hamiltonian describing the interaction of spins with a spatially varying external field $\vec{h}(\vec{x})$ is

$$H_{ext} = - \sum_{\alpha} \mu_S \vec{S}_\alpha \cdot \vec{h}(\vec{x}_\alpha) = - \sum_{\vec{\ell}} \mu_S \vec{S}_{\vec{\ell}} \cdot h(\vec{R}_\ell) = - \int d^d x \; \vec{h}(\vec{x}) \cdot \vec{m}(\vec{x}) \tag{1}$$

The partition function for a lattice of N spins in the presence of $\vec{h}$ becomes

$$Z_N [T, \vec{h}(\vec{x})] = \mathrm{Tr} \left\{ e^{-\beta [H - \int d^d x \; \vec{h}(\vec{x}) \cdot \vec{m}(\vec{x})]} \right\} \tag{2}$$

where H is the total $\vec{h}$-independent part of the Hamiltonian (which for the Heisenberg model would be simply H_{Heis}). The equilibrium magnetization in the thermodynamic limit is

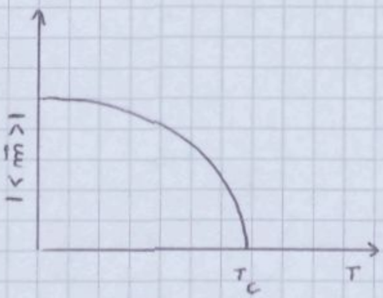
$$\langle \vec{m} [T, \vec{h}(\vec{x}), \vec{x}] \rangle = \lim_{N \to \infty} \frac{1}{Z_N [T, \vec{h}(\vec{x})]} \mathrm{Tr} \left\{ e^{-\beta [H - \int d^d x \; \vec{h}(\vec{x}) \cdot \vec{m}(\vec{x})]} \vec{m}(\vec{x}) \right\} \equiv$$

$$\equiv \lim_{N \to \infty} \langle \vec{m}_N [T, \vec{h}(\vec{x}), \vec{x}] \rangle \tag{3}$$

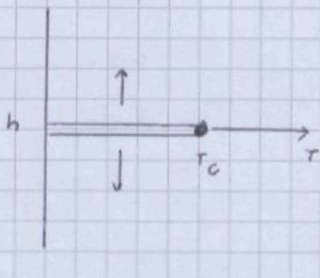
In the limit $N \to \infty$, $\langle m(T, \vec{h}, \vec{x})\rangle$ will align along the spatial uniform field $\vec{h}$ even for infinitesimally small fields. A zero-field ferromagnetic state with a given direction of $\langle \vec{m}\rangle$ can thus be obtained by taking the limit $\vec{h} \to 0$ after the thermodynamic limit:

$$\langle \vec{m}(T)\rangle = \lim_{\vec{h}\to 0} \lim_{N\to\infty} \langle \vec{m}_N(T, \vec{h})\rangle \qquad (1)$$

The spatial index $\vec{x}$ has been supressed because $\vec{h}$ and thus $\langle \vec{m}\rangle$ are spatially uniform.



(a)



(b)

The phase diagram for a Heisenberg magnet in the $h-T$ plane for a field $\vec{h} = h\hat{e}$ along a particular direction specified by the unit vector $\hat{e}$ is shown in (b). For T less that the critical temperature T_c there will be a spontaneous magnetization $\langle \vec{m}(T)\rangle$ defined by (1) aligned parallel to $\hat{e}$ for $h \to 0^+$ and antiparallel to $\hat{e}$ for $h \to 0^-$. At $h = 0$, there is a coexistence line along which all directions of $\langle \vec{m}\rangle$ are energetically equivalent. The coexistence line terminates at the critical point $T = T_c$, $h = 0$. Along the coexistence line, there is no reason to choose one direction of $\langle \vec{m}\rangle$ over another, and an average over all possible directions of $\langle \vec{m}\rangle$ will yield a zero magnetization. The magnitude of $\langle m\rangle$, or equivalently $\langle m\rangle^2 = \langle \vec{m}\rangle \cdot \langle \vec{m}\rangle$, however, has the same value whether a particular direction or an average over all possible directions of $\langle \vec{m}\rangle$ is taken. Thus, an alternative characterization of the existence of ferromagnetic order is that $\langle m\rangle^2$ be nonzero. Another property that we intuitively associate with an ordered state is spatial correlation or "long-range order". For the ferromagnet, we expect that if we know the direction of the spin at one side we will find the spins at distant sites aligned in the same direction. In contrast, for the disordered or paramagnetic state, we suspect that the orientation of a spin at one site tells us little about the orientations of spins just a few sites away. The spatial correlations are quantified by the spin-spin (magnetization-magnetization) correlation function

$$C_{mm}(\vec{x}, \vec{x}') = \langle \vec{m}(\vec{x}) \cdot \vec{m}(\vec{x}')\rangle \qquad (2)$$

In the paramagnetic phase, $C_{mm}(\vec{x}, \vec{x}')$ dies exponentially to zero in the large separation limit, $|\vec{x} - \vec{x}'| \to \infty$. In the ferromagnetic phase, it tends to $\langle m \rangle^2$

$$C_{mm}(\vec{x}, \vec{x}') \xrightarrow[|\vec{x} - \vec{x}'| \to \infty]{} \langle m \rangle^2 \qquad \text{(ferromagnetic phase)} \tag{1}$$

and we see that the large-separation behavior of a correlation function determines the existence of ferromagnetic order. A nonvanishing of the magnetization and long-range order go hand in hand.

The partition function defined in eq (22.2) has explicit dependence on the number of particles N but not on the volume of the sample, which might change, for example, if the lattice parameter changed. More generally, one should consider a generalization $Z_N[T, V, \vec{h}(\vec{x})]$ of the partition function of the canonical ensemble that is a function of $T, N, V, \vec{h}(\vec{x})$ or the partition function $\Xi[T, V, \mu(\vec{x}), \vec{h}(\vec{x})]$ of the grand canonical ensemble that is a function of $T, V, \mu(\vec{x})$ and $\vec{h}(\vec{x})$

In what follows, we will assume that the number of particles and volume remain fixed and supress any explicit reference to them in partition functions and free energies. $Z[T, \vec{h}(\vec{x})]$ in eq (22.2) has exatly the same form as the grand canonical partition function, (19.2), with $\vec{h}(\vec{x})$ replacing the spacially varying chemical potential. Thermodynamic potentials as a function of $\vec{h}(\vec{x})$ or $\langle \vec{m}(\vec{x}) \rangle$ and correlation functions of $\vec{m}(\vec{x})$ follow by a straightforward generalization of the discussion in the part starting on pag. 17. The magnetic thermodynamic potential associated with $Z[T, \vec{h}(\vec{x})]$ is (15.2)

$$\mathcal{A}[T, \vec{h}(\vec{x})] = -T \ln Z[T, \vec{h}(\vec{x})] \tag{2}$$

The magnetization, Eq (22.3), is obtained by differentiating $\ln Z$ with respect to $\vec{h}(\vec{x})$

$$\langle m_i(\vec{x}) \rangle = \frac{1}{Z} \frac{\delta Z}{\delta \beta h_i(\vec{x})} = -\frac{\delta \mathcal{A}}{\delta h_i(\vec{x})} \tag{3}$$

where $\langle m_i \rangle$ and h_i are respectively the ith cartesian components of the vectors $\langle \vec{m} \rangle$ and $\vec{h}$. The potential $\mathcal{A}$ obeys the differential thermodynamic relation

$$d\mathcal{A} = -S\,dT - \int d^D x \, \langle \vec{m}(\vec{x}) \rangle \cdot d\vec{h}(\vec{x}) \tag{4}$$

The generalized susceptibility measuring the change in $\langle m_i \rangle$ in response to an external field at $\vec{x}'$ is

$$\chi_{ij}(\vec{x}, \vec{x}') = \frac{\partial \langle m_i(\vec{x}) \rangle}{\partial h_j(\vec{x}')} \tag{1}$$

In classical systems, the order parameter correlation function is the derivative of $\langle m_i(\vec{x}) \rangle$ with respect to $\beta h_j(\vec{x}')$ and is, therefore, T times $\chi_{ij}(\vec{x}, \vec{x}')$

$$G_{ij}(\vec{x}, \vec{x}') = \langle [m_i(\vec{x}) - \langle m_i(\vec{x}) \rangle][m_j(\vec{x}') - \langle m_j(\vec{x}') \rangle] \rangle =$$

$$= \langle \delta m_i(\vec{x}) \, \delta m_j(\vec{x}') \rangle = \frac{\partial \langle m_i(\vec{x}) \rangle}{\partial \beta h_j(\vec{x}')} = T \chi_{ij}(\vec{x}, \vec{x}') \tag{2}$$

This equation is the analog of (19.4) for the Ursell function of a fluid. When we consider many fields, and when there is a possibility of ambiguity in the interpretation of the subscripts ij, we will use the notation G_{m_i, m_j} rather than G_{ij} for the $\delta m_i(\vec{x}) - \delta m_j(\vec{x}')$ correlation function. The uniform magnetic susceptibility is the derivative of the magnetization with respect to the external magnetic field. It is analog of the compressibility in fluids systems and is proportional to the $\vec{q} = 0$ limit of the Fourier transform of $G_{ij}(\vec{x}, \vec{x}')$ (see 16.6)

$$\chi_{ij} = \frac{\partial \langle m_i \rangle}{\partial h_j} = \lim_{q \to 0} (2\pi)^D \beta \, G_{ij}(\vec{q}) \tag{3}$$

Because the magnetization is a conserved quantity

$$\frac{\partial}{\partial t} \int d^D x \, \vec{m}(\vec{x}) = 0 \tag{4}$$

eq (3) is valid for both classical and quantum mechanical system even though (2) is not valid for quantum mechanical systems. We will discuss this latter on.

In many cases we will prefer to express thermodynamic quantities in terms of the order parameter $\langle \vec{m}(\vec{x}) \rangle$ rather than in term of the field $\vec{h}(\vec{x})$. The thermodynamic potential that is a natural function of $\langle \vec{m}(\vec{x}) \rangle$ is obtained from $\mathcal{A}[T, \vec{h}(\vec{x})]$ by a Legendre transformation

$$F[T, \langle \vec{m}(\vec{x}) \rangle] = \mathcal{A}[T, \vec{h}(\vec{x})] + \int d^D x \, \vec{h}(\vec{x}) \cdot \langle \vec{m}(\vec{x}) \rangle \tag{5}$$

We will usually refer to F as the free energy. It satisfies the differential relation

$$dF = -S\,dT + \int d^Dx\ \vec h(\vec x)\cdot d\langle \vec m(\vec x)\rangle \qquad (1)$$

The magnetic equation of state is, therefore

$$\frac{\delta F}{\delta \langle m_i(\vec x)\rangle} = h_i(\vec x) \qquad (2)$$

When $\langle \vec m(\vec x)\rangle = \langle \vec m\rangle$ is spatially uniform, F, like the Helmholtz free energy as a fuction of density, can be written as a volume integral of a free energy density that is a function of $\langle \vec m\rangle$

$$F = \int d^Dx\ f\,[T, \langle m\rangle] \qquad (3)$$

In this case the equation of state becomes

$$\frac{\delta f}{\delta \langle m_i\rangle} = h_i \qquad (4)$$

This is analog of (10.6). It is clear now how the appearance of order is described mathematically. When $\vec h$ is zero, the equilibrium state is one which minimizes f. If solutions of (4) for $\vec h = 0$ with nonzero $\langle \vec m\rangle$ exits, there can be spontaneous order provided the free energy of the state with nonzero $\langle \vec m\rangle$ is lower than that with $\langle \vec m\rangle = 0$

The magnetization correlation function can be obtained by differentiating A with respect to $\beta h_i(\vec x)$ as indicated by eqs (25.1) and (25.2). Its inverse can be obtained directly by differentiating F with respect to $\langle m_i(x)\rangle$. To see this, we differentiate $\langle m_i(\vec x)\rangle$ with respect to $\langle m_k(\vec x'')\rangle$ to obtain

$$\frac{\delta \langle m_i(\vec x)\rangle}{\delta \langle m_k(\vec x'')\rangle} = \delta_{ik}\,\delta(\vec x - \vec x'') = \int d^Dx'\ \frac{\delta \langle m_i(\vec x)\rangle}{\delta h_j(\vec x')}\ \frac{\delta h_j(\vec x')}{\delta \langle m_k(\vec x'')\rangle} \qquad (5)$$

The inverse $\chi^{-1}_{ij}(\vec x, \vec x')$ satisfies

$$\int d^Dx'\ \chi_{ij}(\vec x, \vec x')\,\chi^{-1}_{jk}(\vec x', x'') = \delta_{ik}\,\delta(\vec x - \vec x'') \qquad (6)$$

From (5) and (6) and taking into account (25.1) and (2)

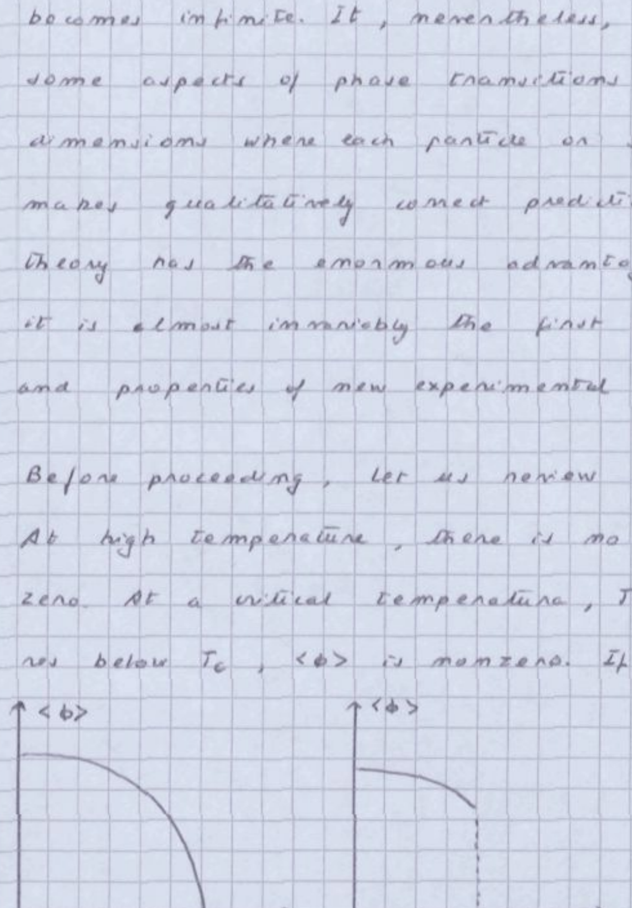
$$\chi^{-1}_{ij}(\vec x, \vec x') = \frac{\delta h_i(\vec x)}{\delta \langle m_j(\vec x')\rangle} = \frac{\delta^2 F}{\delta \langle m_i(\vec x)\rangle\,\delta \langle m_j(\vec x')\rangle} \qquad (7)$$

which gives an efficient way for computing $\chi_{ij}(\vec x, \vec x')$.

III - MEAN-FIELD THEORY

We will use mean-field theory to study phase transitions and the properties of various ordered phases. Mean-field theory is an approximation for the thermodynamic properties of a system based on treating the order parameter as spatially constant. It is a useful description if spatial fluctuations are not important. It becomes an exact theory only when the range of interactions becomes infinite. It, nevertheless, makes quantitatively correct predictions about some aspects of phase transitions (e.g. critical exponents) in high spatial dimensions where each particle or spin has many nearest neighbors, and it makes qualitatively correct predictions in physical dimensions. Mean-field theory has the enormous advantage of being mathematically simple, and it is almost invariably the first approach taken to predict phase diagrams and properties of new experimental systems.

Before proceeding, let us review some simple facts about phase transitions. At high temperature, there is no order, and the order parameter $\langle\phi\rangle$ is zero. At a critical temperature, T_c, order sets in so that, for temperatures below T_c, $\langle\phi\rangle$ is nonzero. If $\langle\phi\rangle$ rises continuously from zero, as shown in (a) the transition is <u>second order</u>. If $\langle\phi\rangle$ jumps discontinuously to a nonzero value just below T_c, (b), the transition is <u>first order</u>. The entropy is also continuous at a second-order and discontinuous at a first-order transition. In the first-order transition, heat is absorbed by the system in going from low-temperature to high-temperature phase. This heat is the latent heat $Q_L = T_c \Delta S$ of the transition, where ΔS is the entropy change and T_c is the transition temperature.



(a) (b)

Braggs-Williams Theory

The free energy F is the difference between the internal energy $E = \langle H\rangle$, and TS. Thus, F can be obtained if E and TS can be calculated separately as a function of the order parameter. The simplest of all models is the

Ising model with a global Z_2 symmetry (The simplest discrete group is the group Z_2 consisting only two elements: the identity and an element whose square is the identity). At each site $\vec{R}_{\vec{\ell}}$ on a lattice, there is a spin variable $\sigma_{\vec{\ell}}$ that can take on only the values +1 or -1. The spins interact via a nearest neighbor exchange interaction so that the Ising Hamiltonian is

$$H_{Ising} = - J \sum_{\langle \vec{\ell}, \vec{\ell}' \rangle} \sigma_{\vec{\ell}} \sigma_{\vec{\ell}'} \qquad , \quad J > 0 \tag{1}$$

where the sum is over nearest neighbor bonds $\langle \vec{\ell}, \vec{\ell}' \rangle$ in the lattice. As in the Heisenberg model, there is a high-temperature paramagnetic phase with $\langle\sigma\rangle = 0$ and a low-temperature ferromagnetic phase with $\langle\sigma\rangle \neq 0$. The low-temperature phase breaks Z_2 symmetry. In the Ising model the order parameter is $m = \langle\sigma\rangle$ is the average of spin The entropy for a given spatially uniform m can be calculated exactly. The total magnetic moment is simply the number $N_\uparrow$ of up spins minus the number $N_\downarrow$ of down spins, and

$$m = \frac{1}{N} \left(N_\uparrow - N_\downarrow \right) \qquad , \quad N \equiv N_\uparrow + N_\downarrow \quad \Rightarrow \quad |m| \leq 1 \tag{2}$$

The entropy for a given m is the logarithm of the number of configurations with a given $N_\uparrow$ and $N_\downarrow$

$$S = \ln \binom{N}{N_\uparrow} = \ln \binom{N}{N(1+m)/2} = \ln \left\{ \frac{N!}{[N(1+m)/2]!\,[N(1-m)/2]!} \right\}$$

$$= \ln N! - \ln [N(1+m)/2]! - \ln [N(1-m)/2]!$$

and since

$$\ln \Gamma(z) = z \ln z - z - \frac{1}{2} \ln z + \ln \sqrt{2\pi} + \ldots \qquad |\arg z| < \pi \tag{3}$$

$\Rightarrow$

$$\ln \Gamma(z+1) = z \ln z - z + \frac{1}{2} \ln z + \ln \sqrt{2\pi} + \ldots$$

$$S = N \ln N - N + \frac{1}{2} \ln N - \frac{1}{2} N(1+m) \ln \frac{1}{2} N(1+m) + \frac{1}{2} N(1+m) - \frac{1}{2} \ln \frac{1}{2} N(1+m)$$

$$- \frac{1}{2} N(1-m) \ln \frac{1}{2} N(1-m) + \frac{1}{2} N(1-m) - \frac{1}{2} \ln \frac{1}{2} N(1+m) + \ldots =$$

$$= N \ln 2 - \frac{1}{2} N(1+m) \ln(1+m) - \frac{1}{2} N(1+m) \ln(1-m) + \ldots$$

Hence

$$\frac{S}{N} = s(m) = \ln 2 - \frac{1}{2}(1+m)\ln(1+m) - \frac{1}{2}(1-m)\ln(1-m) \qquad (1)$$

This entropy is often called the entropy of mixing

To evaluate E, one should calculate

$$\langle H \rangle = Z_m^{-1}\, Tr_m \left[e^{-\beta H} H \right] \qquad (2)$$

where Tr_m is a trace over all configurations with fixed m and

$$Z_m = Tr_m \left[e^{-\beta H} \right] \qquad (3)$$

An exact evaluation of this average would constitute an exact solution of the Ising model and is quite complicated. In Bragg-Williams theory, $\langle H \rangle$ is approximated by replacing $\sigma_{\vec{\ell}}$ in H by its position independent average m:

$$E = -J \sum_{\langle \vec{\ell}, \vec{\ell}' \rangle} m^2 = -\frac{1}{2} J N z\, m^2 \qquad (4)$$

where z is the number of nearest neighbor sites in the lattice ($z = 2D$ for a D-dimensional hypercubic lattice)

The complete Bragg-William free energy is thus

$$f(T, m) = (E - TS)/N =$$

$$= -\frac{1}{2} J z\, m^2 + \frac{1}{2} T \left[(1+m)\ln(1+m) + (1-m)\ln(1-m) \right] - T \ln 2 \qquad (5)$$

Notice that $f(T, m) = f(T, -m)$. Notice

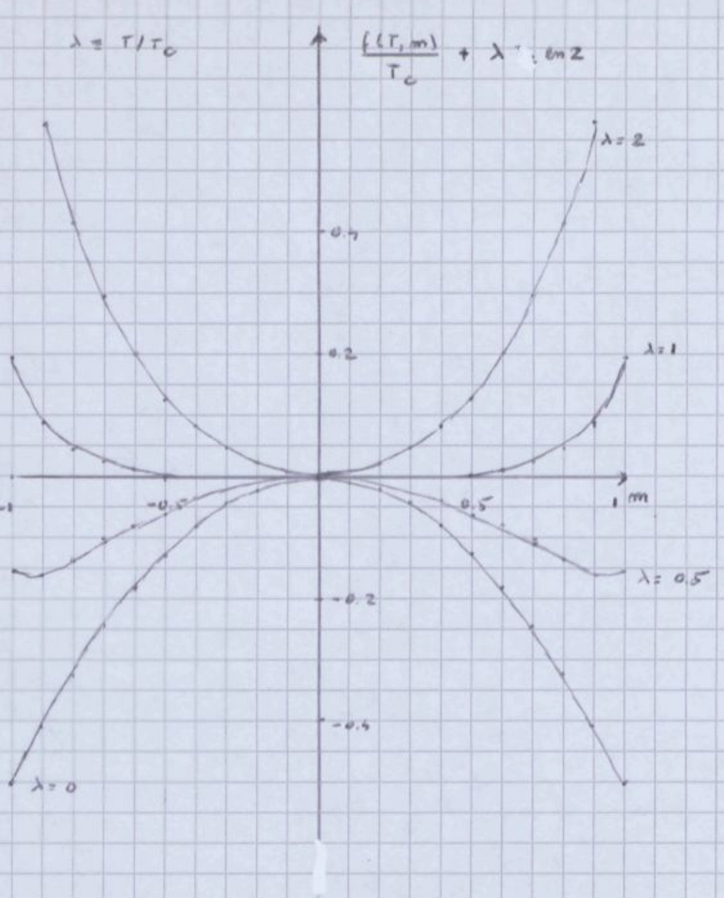
$$\frac{\partial f(T, m)}{\partial m} = -J z\, m + \frac{1}{2} T \ln \frac{1+m}{1-m} \qquad (6)$$

and for small values of m.

$$f(T, m) = -T \ln 2 + \frac{1}{2}(T - T_c)\, m^2 + \frac{1}{12} T m^4 \ldots \qquad T_c \equiv z J \quad , |m| \ll 1 \qquad (7)$$

Equation (5) can be written as

$$f(T, m) = T_c \left\{ -\frac{1}{2} m^2 + \lambda \left[\frac{1}{2}(1+m)\ln(1+m) + \frac{1}{2}(1-m)\ln(1-m) - \ln 2 \right] \right\} \qquad \lambda = \frac{T}{T_c} \qquad (8)$$



In the figure we have plotted

$$\tilde{f}(T, m) = \frac{1}{T_c} f(T,m) + \lambda \ln 2$$

for different values of $\lambda = T/T_c$. For large T, f has a single minimum at $m=0$. Below the critical temperature, T_c, it has two minima at $\pm m$. As $T \to 0$, the two minima occur at values of $|m|$ closer and closer to unity. The equilibrium value of $f(T,m)$ corresponds to the value of m which minimizes $f(T,m)$. Thus, the disappearance of the minimum at $m=0$ and the emergence of lower free energy minima at nonzero m corresponds to a phase transition. As we shall see shortly, the value of m at the new minima grows continuously from zero, so that the transition is second order.

In the vicinity of T_c where m is small we can use eq (3.7) and hence the critical temperature is $T_c \equiv Jz$.

Let us now introduce an external aligning positive magnetic field, then

$$f(T,m,h) = -\frac{1}{2} J z m^2 + \frac{1}{2} T \left[(1+m) \ln (1+m) + (1-m) \ln (1-m) \right] - T \ln 2 - h m \qquad (1)$$

Now $f(T,m,h)$ has a single minimum for $T > T_c$ with $m > 0$. When $T < T_c$ there are two minima. The minimum with $m > 0$ is the absolute minimum and corresponds to the equilibrium state. Thus, the equilibrium state with $m > 0$, $h = 0$ and $T < T_c$ can be reached by first preparing the system in the absolute equilibrium state with $h > 0$ and then allowing $h \to 0$.

From (3.6) the equation of state in an external field is

$$-Jzm + \frac{1}{2} T \ln \frac{1+m}{1-m} = h \qquad (2)$$

i.e.

$$-Jzm + T \tanh^{-1} m = h \qquad (3)$$

Thus the equation of state is

$$m = \tanh\left(\frac{h + T_c m}{T}\right) \tag{1}$$

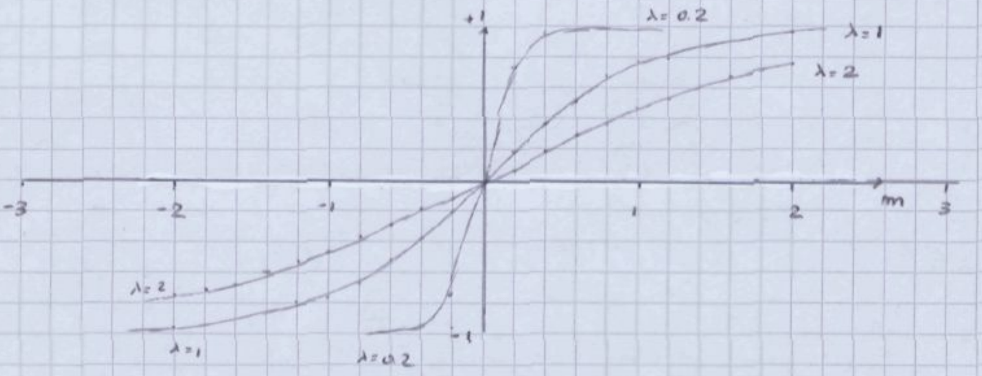
The quantity

$$h_m \equiv h + T_c m \tag{2}$$

is the average local or molecular field at a given side. It arises both from the external field and from the exchange field produced by the neighboring spins with average spin m.

Let us consider the equation of state for $h = 0$

$$m = \tanh(m/\lambda) \qquad \lambda \equiv T/T_c \tag{3}$$



The slope T_c/T of $\tanh(T_c m/T)$ at $m=0$ is less than one for $T/T_c > 1$ and greater than one for $T/T_c < 1$. Thus for $T > T_c$, the only solution of (3) with $h=0$ is $m=0$. For $T < T_c$ there are three solutions $\pm m(T)$ and zero. The tanh function lies between -1 and $+1$ so that $|m| \leq 1$. As $T \to 0$, $\tanh(T_c m/T)$ saturates at its maximum value of one at smaller and smaller m, and $|m(T)| \to 1$ as $T \to 0$ indicating the full ferromagnetic order as expected in the fully aligned ground state of the Ising model.

Near $T = 0$

$$m = \tanh(T_c m/T) \sim 1 - 2e^{-2T_c/T} \tag{4}$$

so that m tends to unity exponentially with temperature

As $T_c \to T_c^-$, the solution of (3) can be obtained expanding $\tanh x$ in powers of x

$$\tanh x = x - \frac{1}{3}x^3 + \frac{2}{15}x^5 + \cdots \tag{5}$$

$$m \simeq \frac{T_c}{T} m - \frac{1}{3}\left(\frac{T_c}{T}\right)^3 m^3 \sim \frac{T_c}{T} m - \frac{1}{3} m^3$$

$$m = \pm \left[\frac{3(T_c - T)}{T}\right]^{1/2} \qquad (1)$$

Thus m tends continously to zero as $(T_c - T)^{1/2}$. This behavior is a general feature of second order mean-field phase transitions

Landau Theory

Landau theory is remarkable in that, under the simple assumptions that the order parameter is small and uniform near T_c it yields a wealth of information about phase transitions. Equilibrium thermodynamics is completely determined by the function $F[T, \langle\phi_i(\vec{x})\rangle]$, where $\langle\phi_i(x)\rangle$ is the local order parameter. F is a function that must be invariant under the symmetry group $\mathcal{G}$ of the disordered phase. This means that it can only be a funcion of those combinations of the order parameter $\langle\phi_i(\vec{x})\rangle$ that do not change (i.e. are scalars) under all operations of $\mathcal{G}$. For example, the Ising Hamiltonian (2.1) is invariant under spin inversion, $\sigma \to -\sigma$, and $F(T, m)$ is a function of m^2 as it is in the Bragg-Williams theory just discussed. $F[T, \langle\phi_i(\vec{x})\rangle]$ is, in general, a very complicated functional of $\langle\phi_i(\vec{x})\rangle$. However, since $\langle\phi_i(\vec{x})\rangle$ is zero for $T > T_c$ it is reasonable, following the example of Braggs-Williams theory, to expand F in a power series of $\langle\phi(\vec{x})\rangle$, at most in the vicinity of the critical point. Furthermore, it is possible in essentially all cases to definy the order parameter so that it is spatially uniform in equilibrium in the ordered phase. This suggest that F be expressed in terms of a local free energy density $f(T, \langle\phi(\vec{x})\rangle)$ that is a function of the field $\langle\phi(\vec{x})\rangle$ at the point $\vec{x}$ only and a part that produces an energy cost for deviations from spatial uniformity. The simplest form that F can take is

$$F = \int d^D x \; f(T, \langle\phi(x)\rangle) + \int d^D x \; \frac{1}{2} c \left[\vec{\nabla}\langle\phi(\vec{x})\rangle\right]^2 \qquad (2)$$

where c is a phenomenological coefficient with units of energy × $(\text{length})^{2-D}$ if $\phi(\vec{x})$ is unitless. f is then expanded in a power series in $\langle\phi(\vec{x})\rangle$. Above T_c, $\langle\phi\rangle$ must be zero when its conjugate field h is zero. Since $\langle\phi\rangle$ and h are related by the equation of state, $\partial f/\partial\langle\phi\rangle = h$, this requires that the linear term in the expansion of f be absent, so that

$$f(T,\phi) = \frac{1}{2} r \phi^2 - w \phi^3 + u \phi^4 + \dots \qquad (1)$$

Each of the terms in the above expansion must be invariant under the operations of $\mathcal{G}$. Thus, as we shall see shortly, odd order terms may often be absent, and on occasion there will be several terms of different symmetry of the same order in ϕ. All the coefficients r, w and u can, in principle, depend on temperature. If f is truncated at a given power of $\langle\phi\rangle$, then the highest term should be even with a positive coefficient to ensure that the equilibrium state will have a bounded value of $\langle\phi(\vec{x})\rangle$.

If the odd order terms in (1) are removed, f has exactly the same form as the free energy per site (3.7) of the Bragg-Williams theory with $r \propto (T - T_c)$. This is one of the motivations for expanding $f(T,\phi)$ in an analytic power series in ϕ. In the continuum limit, when spatial variations of the order parameter are slow on a scale of the lattice spacing, the dominant contribution to F arising from the nonuniformity of the order parameter is proportional to the square of the gradient of the order parameter, as in eq(6.2). It should be emphasized that the neglect of higher gradients on $\langle\phi(\vec{x})\rangle$ is only valid when spatial variations are slow on a microscopic length scale a determined by the range of interactions (the lattice spacing in the Ising model), i.e. when the wave number q of spatial variations in $\phi(\vec{x})$ is less than a <u>cutoff</u>

$$\Lambda \simeq \frac{2\pi}{a} \qquad (2)$$

Thus, it is understood that any phenomenological model such as (6.2) carries with it an upper wave number cutoff Λ. The predictions of mean-field theory generally do not depend on Λ. Corrections to mean-field theory do, however.

Eqs (6.2) and (1) are the essence of Landau mean-field theory and we are going to analyze this theories for some simple models

The Ising and N-vector Models

The order parameter for the Ising ferromagnet is the scalar magnetization $\langle\phi\rangle = m_z$.

The free energy must be invariant under time reversal. Since $\langle\phi\rangle$ changes sign under time reversal, f must be invariant under $\langle\phi\rangle \to -\langle\phi\rangle$, i.e. only even powers of $\langle\phi\rangle$ are permitted in the expansion of f (7.1). Thus we have, keeping terms up to fourth order,

$$f(T, \langle\phi\rangle) = \frac{1}{2} r \langle\phi\rangle^2 + u \langle\phi\rangle^4 \qquad (1)$$

in agreement with (3.7). In order for the partition function to be well defined f must be positive definite at large values of $\langle\phi\rangle$, implying that u must be positive. The value of $\langle\phi\rangle$ is determined by the equation of state

$$\frac{\partial f}{\partial\langle\phi\rangle} = h \quad \Leftrightarrow \quad r\langle\phi\rangle + 4u\langle\phi\rangle^3 = h \qquad (2)$$

where h is the external magnetic field. At high temperature $\langle\phi\rangle$ must be zero when the external magnetic field h is zero. This means that f must have a minimum at $\langle\phi\rangle=0$ for large T. At low temperatures, we expect a ferromagnetic state and f to have at least one minimum with nonzero $\langle\phi\rangle$. From (2) with $h=0$ has always a solution $\langle\phi\rangle=0$ and another one $\langle\phi\rangle=\pm(-r/4u)^{1/2}$ if $r<0$. We can assume u independent of T and

$$r = a(T - T_c) \qquad , a>0 \qquad (3)$$

Then for $h=0$ we have

$$\langle\phi\rangle = \begin{cases} 0 & \text{if } T > T_c \\ \pm\sqrt{-r/4u} & \text{if } T < T_c \end{cases} \qquad (4)$$

Thus, mean-field theory predicts a second-order phase transition with

$$\langle\phi\rangle \sim (T_c - T)^\beta \qquad , \beta = 1/2 \qquad (5)$$

β is called a critical exponent, and it controls the temperature dependence of the order parameter in the vicinity of T_c. When critical fluctuations are important the value of β is less than its mean-field value, typically of order 1/3 in three-dimensional systems. Eq (4) says there are two possible values for $\langle\phi\rangle$ for $T<T_c$ and $h=0$ corresponding to the two possible directions for the bulk magnetization. The sign can be fixed by allowing h to go to zero from positive

or negative values. Both solution for $\langle\phi\rangle$ have the same free energy so that the up and down phases coexist along the line $h=0$ and $T<T_c$, as shown in Fig (b) pag II.23

The susceptibility can be obtained differentiating (8.2) with respect h (II.25.1)

$$\left(r + 12u\langle\phi\rangle^2\right)\frac{\partial\langle\phi\rangle}{\partial h} = 1 \qquad (1)$$

or

$$\chi \equiv \frac{\partial\langle\phi\rangle}{\partial h} = \begin{cases} 1/r & \text{if } T>T_c \\ 1/2|r| & \text{if } T<T_c \end{cases} \qquad (2)$$

which implies, using (8.3), that

$$\chi \sim |T-T_c|^{-\gamma} \quad , \quad \gamma = 1 \qquad (3)$$

γ is called the susceptibility exponent and is generally of order 4/3 in three-dimensional systems where critical fluctuations are important. Finally the dependence of $\langle\phi\rangle$ on h at $T=T_c$ follows from eq (8.2)

$$\langle\phi\rangle = (h/4u)^{1/3} \sim h^{1/\delta} \qquad T=T_c \qquad (4)$$

where $\delta = 3$ is yet another critical exponent. From (8.8) and (8.4) we get

$$f = \begin{cases} 0 & \text{if } T>T_c \\ -r^2/16u & \text{if } T<T_c \end{cases} \qquad (5)$$

Thus the mean-field specific heat is

$$C_V = -T\frac{\partial^2 f}{\partial T^2} = \begin{cases} 0 & T>T_c \\ Ta^2/8u & T<T_c \end{cases} \qquad (6)$$

This equation gives the specific heat associated with the establishment of order. The total specific heat includes a part analytic in temperature arising from degrees of freedom not associated with ordering. Thus a smoothly varying background must be added to (6) to obtain the total specific heat, which will have a jump discontinuity at the transition

Let us now consider the calculation of the correlation function $\chi(\vec{x}, \vec{x}')$. This is most easely done using (II.-26.7) and (6.2)

$$\chi^{-1}(\vec{x}, \vec{x}') = \frac{\delta^2 F}{\delta \langle \phi(\vec{x}) \rangle \, \delta \langle \phi(\vec{x}') \rangle} = \left\{ r + 12 u \langle \phi \rangle^2 - c \vec{\nabla}^2 \right\} \delta(\vec{x} - \vec{x}') \equiv \chi^{-1}(\vec{x} - \vec{x}') \qquad (1)$$

then

$$\chi^{-1}(\vec{q}) = \frac{1}{(2\pi)^{D/2}} \int d^3x \; e^{-i \vec{q} \cdot \vec{x}} \, \chi^{-1}(\vec{x})$$

or

$$\chi(\vec{q}) = (2\pi)^{D/2} \frac{1}{r + 12 u \langle \phi \rangle^2 + c \vec{q}^{\,2}} \qquad (2)$$

which can be rewritten as

$$\chi(\vec{q}) = \chi(0) \frac{1}{1 + \chi(0) (2\pi)^{-D/2} c q^2} = \frac{(2\pi)^{D/2}}{c} \frac{\xi^2}{1 + (q \xi)^2} \qquad (3)$$

where

$$\xi = c^{1/2} \left\{ r + 12 u \langle \phi \rangle^2 \right\}^{-1/2} \qquad (4)$$

Notice

$$\xi = \begin{cases} (c/r)^{1/2} & T > T_c \\ (c/-2r)^{1/2} & T < T_c \end{cases} \qquad (5)$$

i.e.

$$\xi \sim |T - T_c|^{-\nu} \qquad (6)$$

is the <u>correlation length</u> and ν is the correlation length exponent that is 1/2 in mean field theory and of order 2/3 in most three-dimensional critical systems.

The existence of the correlation length ξ follows from a simple dimensional analysis of the model free energy (6.2) with f given by (8.1). If $\langle \phi(\vec{x}) \rangle$ is unit less

$$[\phi(\vec{x})] = 1 \quad , \quad [r] = E L^{-D} \qquad E = \text{energy} \quad L = \text{length} \qquad (7)$$

$$[c] = E L^{-D+2} \quad , \quad [c/r]' = L^2$$

and ξ must have units of length. These arguments allow us to introduce a temperature-independent bare correlation length (8.3)

$$\xi_0 = \left(\frac{c}{r(T=0)} \right)^{1/2} = \left(\frac{c}{a T_c} \right)^{1/2} \qquad (8)$$

that defines a microscopic length scale. The correlation length

$$\xi \sim \xi_0 \, | (T - T_c) / T_c |^{-\nu} \qquad (9)$$

can be arbitrarily larger than ξ_0 near T_c. Dimensional analysis such as this is usually the simplest way to determine what important lengths there are in a given problem and how they scale with controllable parameters.

Eq (10.3) was first proposed for correlations of an order parameter in the vicinity of a critical point by Ornstein and Zernicke in their discussion of the light scattering from a fluid in the vicinity of the liquid-gas transition The Fourier transform

$$\chi(\vec{x}) = \frac{1}{(2\pi)^{D/2}} \int d^D q \, e^{+i\vec{q}\cdot\vec{x}} \chi(\vec{q}) = \frac{1}{c} \int d^D q \, e^{i\vec{q}\cdot\vec{x}} \frac{\xi^2}{1 + (q\xi)^2} \Rightarrow$$

$$\chi(\vec{x}) = \frac{1}{c} \xi^2 \int dq \, q^{D-1} d\Omega_D \, e^{+iqx\cos\theta} \frac{1}{1 + q^2\xi^2}$$

$$= \frac{1}{c} |\vec{x}|^{-(D-2)} \int_0^\infty dz \, z^{D-1} \int d\Omega_D \frac{e^{iz\cos\theta}}{z^2 + \eta^2} \qquad (1)$$

where

$$\eta \equiv |\vec{x}| / \xi \qquad (2)$$

Then

$$\chi(\vec{x}) = c^{-1} |\vec{x}|^{-(D-2)} \, y(|\vec{x}|/\xi) \qquad (3)$$

$$y(\eta) = \int_0^\infty dz \frac{z^{D-1}}{z^2 + \eta^2} \int d\Omega_D \, e^{iz\cos\theta}$$

If $D = 3$

$$y(\eta) = \int_0^\infty dz \frac{z^{D-1}}{z^2 + \eta^2} \, 2\pi \int_{-1}^{+1} d\mu \, e^{iz\mu} = \frac{2\pi}{i} \int_0^\infty dz \frac{z}{z^2 + \eta^2} (e^{iz} - e^{-iz})$$

$$= \frac{2\pi}{i} \int_{-\infty}^{+\infty} dz \frac{z}{z^2 + \eta^2} e^{iz} = \frac{2\pi}{i} \, 2\pi i \, \frac{i\eta}{2i\eta} e^{-\eta} = 2\pi^2 e^{-\eta}$$

$$y(\eta) = 2\pi^2 e^{-\eta} \qquad D = 3 \qquad (4)$$

Thus at $T = T_c$, $\chi(\vec{x})$ is proportional to $|\vec{x}|^{-(D-2)}$, because $\xi \to \infty$. For $T \neq T_c$, $\chi(\vec{x})$ decays exponentially to zero at a rate determination by the correlation length.

Let us now consider the N-vector model where we consider $\phi_i(\bar{x})$ and assume that for hight enough temperatures there is a symmetry $O(N)$, then f can be only function of the only scalar

$$\langle \phi \rangle^2 \equiv \sum_{i=1}^{N} \langle \phi_i \rangle^2 \tag{1}$$

and therefore the Landau free energy for this model is identical to that of the Ising model with the above interpretation of $\langle \phi \rangle^2$. In the presence of an external field with components h_i $(i=1,2,\ldots N)$, the equation of state for $\langle \phi_i \rangle$ is

$$\frac{\partial f}{\partial \langle \phi_i \rangle} = [\, r + 4u \langle \phi^2 \rangle \,] \langle \phi_i \rangle = h_i \qquad i = 1, 2, \ldots, N \tag{2}$$

When $h_i = 0$ $(i=1,2,\ldots N)$ we have as before

$$\langle \phi_i \rangle = \begin{cases} 0 & T > T_c \\ (-r/4u)^{1/2}\, e_i & T < T_c \end{cases} \tag{3}$$

where $\hat{e}$ is the unit vector in the N-dimensional space. Thus, again there is a second-order transition with the same critical exponents β, γ, δ and ν introduced in (8.5), (9.3), (9.4) and (10.6), respectively

Correlation functions for $T < T_c$ in the $SO(N)$ model require some further comment. Since a direction a direction has been explicitly picked out, i.e. the symmetry of the high temperature phase has been broken, the correlation function

$$G_{ij}(\bar{x}, \bar{x}') = \langle \phi_i(\bar{x})\, \phi_j(\bar{x}') \rangle - \langle \phi_i(\bar{x}) \rangle \langle \phi_j(\bar{x}') \rangle \tag{4}$$

can be broken up into two distinct parts describing correlations parallel and perpendicular to the direction of order

$$G_{ij}(\bar{x}, \bar{x}') = G_{\parallel}(\bar{x}, \bar{x}')\, e_i e_j + G_{\perp}(\bar{x}, \bar{x}')\, (\delta_{ij} - e_i e_j) \tag{5}$$

With $\hat{e}$ parallel to the 1-axis, this means

$$G_{\parallel}(\bar{x}, \bar{x}') = \langle \phi_1(\bar{x})\, \phi_1(\bar{x}') \rangle - \langle \phi_1(\bar{x}) \rangle \langle \phi_1(\bar{x}') \rangle \tag{6}$$

$$G_{\perp}(\bar{x}, x') = \langle \phi_i(\bar{x})\, \phi_i(\bar{x}') \rangle - \langle \phi_i(\bar{x}) \rangle \langle \phi_i(\bar{x}') \rangle \qquad i = 2, \ldots, N$$

Differentiating the free energy with respect to $\phi_i(\bar{x})$ and $\phi_j(\bar{x}')$ ((II-25.2) (II-26.7))

$$\chi_{ij}^{-1}(\bar{x},\bar{x}') = T\,G_{ij}^{-1}(x,x') = \frac{\delta^2 F}{\delta\langle\phi_i(\bar{x})\rangle\,\delta\langle\phi_j(\bar{x}')\rangle} =$$

$$= \left\{ r\,\delta_{ij} + 4\,\delta_{ij}\,u\,\langle\phi\rangle^2 + 8\,u\,\langle\phi_i\rangle\langle\phi_j\rangle - c\,\delta_{ij}\,\vec{\nabla}^2 \right\} \delta(\bar{x}-\bar{x}') \equiv \chi_{ij}^{-1}(\bar{x}-\bar{x}') \qquad (1)$$

and hence

$$\chi_{ij}^{-1}(\bar{q}) = T\,G_{ij}^{-1}(\bar{q}) = \frac{1}{(2\pi)^{D/2}} \left\{ [\,r + 4u\langle\phi\rangle^2 + cq^2\,]\,\delta_{ij} + 8u\langle\phi_i\rangle\langle\phi_j\rangle \right\} \qquad (2)$$

or

$$\chi_{\parallel}^{-1}(\bar{q}) = \frac{1}{(2\pi)^{D/2}}\,[\,r + 12u\langle\phi\rangle^2 + cq^2\,] \qquad (3)$$

$$\chi_{\perp}^{-1}(\bar{q}) = \frac{1}{(2\pi)^{D/2}}\,[\,r + 4u\langle\phi\rangle^2 + cq^2\,] \qquad (4)$$

The parallel part is the same as (10.2). For the other

$$\chi_{\perp}^{-1}(\bar{q}) = \frac{1}{(2\pi)^{D/2}} \times \begin{cases} r + cq^2 & T > T_c \\ cq^2 & T < T_c \end{cases} \qquad (5)$$

Thus $G_{\parallel}(\bar{q}) = T\chi_{\parallel}(\bar{q})$ has the same form as $G(\bar{q})$ for the Ising model (10.3). $G_{\perp}(\bar{q}) = T\chi_{\perp}(\bar{q})$, on the other hand, has pure power law form for $T < T_c$

$$G_{\perp}(\bar{q}) = \frac{T}{cq^2}\,(2\pi)^{D/2} \qquad (6)$$

and this implies a power-law rather that exponential decay in real space with

$$G_{\perp}(\bar{x}) \sim |\bar{x}|^{-(D-2)} \qquad (7)$$

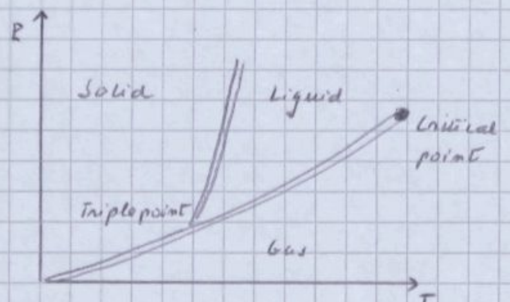
This behavior, as we shall see, is a direct consequence of breaking of a continuous symmetry (rotational in this case)

There are a number of systems whose phase transition are quantitatively described by the mean-field theory considered above. Here we will consider a few of these. In next chapter, we will see why fluctuations that in general modify mean-field result are not important in these systems

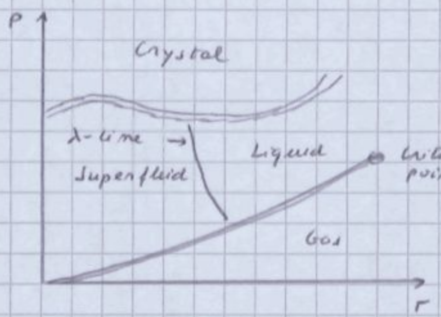
The transition from a normal metal to a superconductor is indisputably one of the transition that is best described by mean-field theory. Here the order parameter follows exactly the $(T-T_c)^{1/2}$ law.

The Liquid - Gas Transition

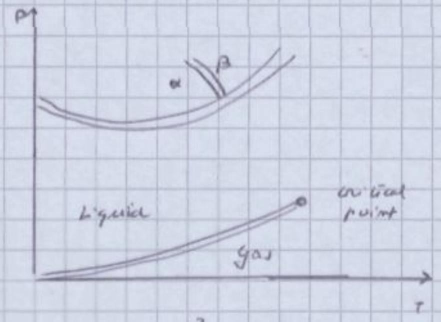
As we have said before, there is no symmetry difference between the liquid and gas phases. The two phases can only be distinguished when they coexist in the same container and are separated by a meniscus. In a closed container with a fixed number of particles and a fixed volume, the meniscus is like a partition, on one side of which is the denser liquid phase and on the other side of which is the less dense gas phase. Particles and energy pass freely through the partition. In addition, the position of the meniscus is free to move to minimize the free energy. This implies that the temperature, chemical potential, and pressure are the same in the coexisting liquid and gas phases even though their respective densities n_ℓ and n_g, are different. Phase diagrams for classical and quantum fluids are shown in this figures. Double lines represent first order transitions and single lines represent continuous or second order transitions. The liquid and gas (or vapor) phases coexist along the liquid-gas coexistence curve (or vapor pressure curve) terminating at a critical point with pressure $P = P_c$ and temperature $T = T_c$. The critical density n_c is determined from P_c and T_c by the equation of state. The phase diagram can also be represented in the chemical potential temperature plane, as shown in the vicinity of the critical point (μ_c, T_c). The critical point can be approached along the coexistence curve, where there are two stable phases, or along various paths, along which there is only a single stable phase. A path of particular interest is the critical isochore, along which the density is equal to the critical density. Approach to the critical point along the critical isochore is easily implemented experimentally by preparing the fluid in a closed volume at the critical density. The average density is then fixed. Other paths to the critical point include the critical isobare, along which $P = P_c$ and the critical isotherm, along which $T = T_c$



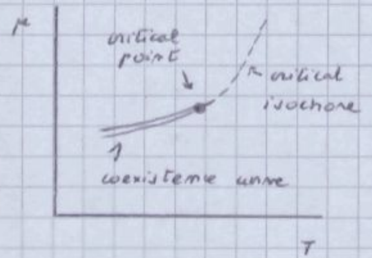
Classical fluid, as liquid argon



He^4



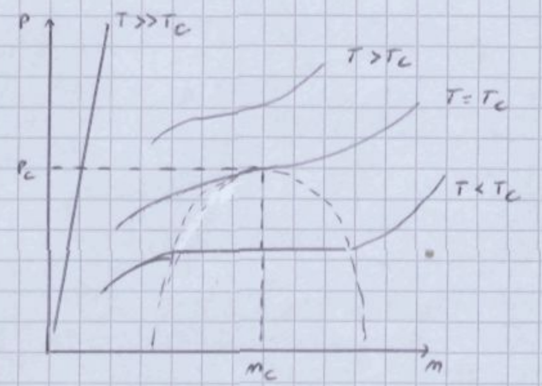
He^3



Three conditions are needed to specify the three parameters μ_c, T_c and m_c, which characterize the critical point. The first is the equation of state

$$\frac{\partial w(\mu, T, m)}{\partial m} = \frac{\partial f(T, m)}{\partial m} - \mu = 0 \qquad (1)$$

where $w(\mu, T, m) \equiv f(T, m) - \mu m$ (eq. II - 11.1) and (II - 10.6) have been used. This equation is always satisfied in equilibrium for all μ and T. It provides a relation between μ and T along the critical isochore when m is set to its critical value m_c. The second condition determining the critical point is that the compressibility must be infinite or the inverse compressibility zero, as it is clear from pressure - density phase diagram shown in the figure (Remember $k_T = \frac{1}{V} (\partial V/\partial P)_{T,N}$ (II. 10.3)). Therefore



$$\left.\frac{\partial^2 w(T_c, \mu_c, m)}{\partial m^2}\right|_{m=m_c} = \left.\frac{\partial^2 f(T_c, m)}{\partial m^2}\right|_{m=m_c} = 0 \qquad (2)$$

(remember II - 10.3 and II - 10.6). The third condition is more subtle. The critical point terminates a line of coexistence. It must, therefore, be a point at which the two solutions of eq (1) corresponding to the liquid and gas densities m_e and m_g merge into a single solution with density $m = m_c$. In a theory in which w is treated as an analytical function of m, this condition is reached by requiring the third derivative of w to be zero at the critical point

$$\left.\frac{\partial^3 w(T_c, \mu_c, m)}{\partial m^3}\right|_{m=m_c} = \left.\frac{\partial^3 f(T_c, m)}{\partial m^3}\right|_{m=m_c} = 0 \qquad (3)$$

Equations (1), (2) and (3) determine T_c, μ_c and m_c. The critical pressure is then (II - 11.2)

$$P_c = - w(T_c, \mu_c, m_c) \qquad (4)$$

To study properties in the vicinity of the critical point, we expand $w(T, \mu, m)$ in powers of the order parameter

$$\phi \equiv m - m_c \qquad (5)$$

i.e.

$$w(T, \mu, m) = w(T, \mu, m_c) + \frac{1}{2} r \phi^2 - v \phi^3 + u \phi^4 - h \phi \qquad (6)$$

where

$$h = \mu - \left.\frac{\partial f(T,m)}{\partial m}\right|_{m=m_c} \quad , \quad r(T) = \left.\frac{\partial^2 f(T,m)}{\partial m^2}\right|_{m=m_c}$$

$$v(T) = -\frac{1}{3!}\left.\frac{\partial^3 f(T,m)}{\partial m}\right|_{m=m_c} \quad , \quad u(T) = \frac{1}{4!}\left.\frac{\partial^4 f(T,m)}{\partial m^4}\right|_{m=m_c} \tag{1}$$

At the critical point $h(\mu_c, T_c)$, $r(T_c)$ and $v(T_c)$ are zero because of equations (15.1) (15.2) and (15.3). They can be expanded in power series of

$$\Delta\mu \equiv \mu - \mu_c \quad , \quad \Delta T \equiv T - T_c \tag{2}$$

The linear coefficient μ depends on both μ and T, whereas r, v and u depend only on T. Therefore

$$h = \Delta\mu - b\Delta T + O((\Delta T)^2) \quad , \quad r = a\Delta T + O((\Delta T)^2)$$

$$v = g\,\Delta T + O((\Delta T)^2) \tag{3}$$

where

$$b = \left.\frac{\partial^2 f(T,m_c)}{\partial m\,\partial T}\right|_{T_c,m_c} \quad , \quad a = \left.\frac{\partial^3 f(T,m)}{\partial m^2\,\partial T}\right|_{T_c,m_c} \quad , \quad g = \frac{1}{3!}\left.\frac{\partial^4 f(T,m)}{\partial m^3\,\partial T}\right|_{T_c,m_c} \tag{4}$$

To the order of our analysis, we can ignore the temperature dependence of $u(T)$ and set it equal to $u(T_c)$

Eq (15.6) is a Landau free energy similar to those studied in the previous pages It has both even and odd terms, but since all three potentials h, r and v are zero at the critical point, its form at the critical point is identical to that of the Ising model.

We can now determine the equation for the critical isochore in the vicinity of the critical point in the $\mu-T$ and $P-T$ planes. Along the critical isochore $m = m_c$, $\phi = 0$ and from (15.1) and (1) $h(\mu, T) = 0$ or from (3)

$$\Delta\mu = b\,\Delta T + O((\Delta T)^2) \tag{5}$$

In order to determine the critical isochore in the $P-T$ plane, we recall (10.4)

$$P = -w(T, \mu, m) \qquad P_c = -w(T_c, \mu_c, m_c) \tag{6}$$

Expanding $w(T, \mu, m_c)$ on ΔT and $\Delta\mu$ we obtain

$$w(T, \mu, m_c) = -P_c - \Delta\mu\, m_c + e\,\Delta T + O((\Delta T)^2) \qquad (1)$$

whee

$$e = \left.\frac{\partial f(m_c T)}{\partial T}\right|_{T=T_c} \qquad (2)$$

Then using (16.5)

$$P - P_c = (b m_c - e)\,\Delta T + O((\Delta T)^2) \qquad (4)$$

Eqs (16.5) and (4) show that the critical isochore in general has both finite slope and curvature at the critical point.

The equation of state

$$\frac{\partial w}{\partial \phi} = r\phi - 3v\phi^2 + 4u\phi^3 - h = 0 \qquad (5)$$

determines $\phi(\mu, T)$ away from the isochore. The inverse compressibility k_T^{-1} goes to zero as the critical point is approached along the critical isochore:

$$\frac{\partial \mu}{\partial m} = \frac{\partial^2 w}{\partial m^2} = m_c^{-2}\, k_T^{-1} = r \qquad (6)$$

Then, like the susceptibility in the Ising model in zero external field, k_T diverges along the critical isochore as

$$k_T \sim (\Delta T)^{-\gamma} \qquad \gamma = 1 \qquad (7)$$

Spatial correlations can be calculated by adding a gradient term to the free energy as was done in the treatment of the Ising model in the preceding section. This leads to the expression

$$S_{mm}(\vec{q}) = (2\pi)^{D/2} \frac{T}{r + cq^2} = (2\pi)^{D/2} m^2 k_T \frac{T}{1 + (q\xi)^2} \qquad (8)$$

for the density correlation function, implying that there is a correlation length

$$\xi = (c/r)^{-1/2} \qquad (9)$$

that diverges with the critical exponent $\nu = 1/2$, as in the Ising model. As we saw before, the intensity of light scattered at $\vec{q}$ is proportional to $S_{mm}(\vec{q})$. Eq. (8) then says that the intensity of scattering light increases dramatically as the critical point is approached along the critical isochore. This is the phenomenon of critical opalescence ($S_{mm} \propto 1/r^2$)

The coexistence curve is determined by the condition that the pressure, chemical potential, and temperature of the liquid and gas phases be equal. The densities m_ℓ and m_g of the liquid and gas phases will differ from the critical density according to

$$m_\ell = m_c + \phi_\ell \quad , \quad m_g = m_c + \phi_g \tag{1}$$

The pressures in the two phases are then

$$P_\ell = -w\,(T, \mu, m_\ell) \quad , \quad P_g = -w\,(T, \mu, m_g) \tag{2}$$

For a general function $w\,(T, \mu, m)$ the determination of the coexistence curve would be quite tedious. For the simple phenomenological model we are using, however, there is a fairly straightforward strategy for its determination. The idea is to break ϕ up into two parts

$$\phi = \phi_0 + \Delta\phi \tag{3}$$

and to choose ϕ_0 and μ as a function of T so that there are no odd order terms in an expansion of $w\,(T, \mu, m)$ in powers of $\Delta\phi$. The expansion of w in powers of $\Delta\phi$ is

$$w\,(T, \mu, m) = -P_c - h\,(\phi_0)\,\Delta\phi + \frac{1}{2}\,r\,(\phi_0)(\Delta\phi)^2 - v\,(\phi_0)\,(\Delta\phi)^3 + u\,(\Delta\phi)^4 \tag{4}$$

$$\begin{aligned} h\,(\phi_0) &= h - r\phi_0 + 3v\phi_0^2 - 4u\phi_0^3 \\ r\,(\phi_0) &= r - 6v\phi_0 + 12u\phi_0^2 \\ v\,(\phi_0) &= v - 4u\phi_0 \end{aligned} \tag{5}$$

The third order term in the expansion of w is eliminated by choosing

$$\phi_0 = \frac{v}{4u} = \frac{g\,\Delta T}{4u} + O((\Delta T)^2) \tag{6}$$

The first-order term is eliminated by choosing $\Delta\mu$ as a function of ΔT so that $h\,(\phi_0) = 0$. This yields

$$h = \frac{ag}{4u}\,(\Delta T)^2 + O((\Delta T)^3) \tag{7}$$

Thus, along the line determined by eqs (18.5) and (18.6)

$$w(T,\mu,m) = w(T,\mu,m_c) + \frac{1}{2} r(\phi_0)(\Delta\phi)^2 + u(\Delta\phi)^4 \qquad (1)$$

with

$$r(\phi_0) = a\,\Delta T + O((\Delta T)^2) \qquad (2)$$

Eq (1) has exactly the same form as the Ising free energy. In that case, there will be two values of $\Delta\phi$ which minimize the free energy, and

$$m_g = m_c + \phi_0 - \Delta\phi \quad , \quad m_\ell = m_c + \phi_0 + \Delta\phi \qquad (3)$$

$$\Delta\phi = [-r(\phi_0)/4u]^{1/2} = [-a\,\Delta T/4u]^{1/2} + O((\Delta T)^{3/2})$$

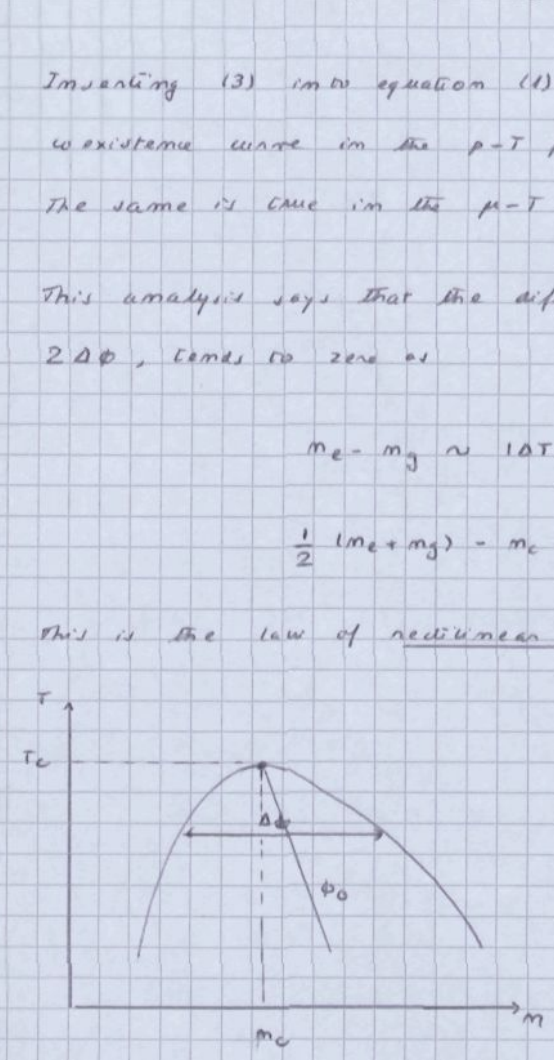
Inserting (3) into equation (1), one finds that the critical isochore and the coexistence curve in the $p-T$ plane have the same slope but different curvatures. The same is true in the $\mu-T$ plane.

This analysis says that the difference in density of the liquid and gas phases, $2\Delta\phi$, tends to zero as

$$m_\ell - m_g \sim |\Delta T|^\beta \qquad \beta = 1/2 \qquad (4)$$

$$\frac{1}{2}(m_\ell + m_g) - m_c \sim |\Delta T|^{1-\alpha} \qquad \alpha = 0 \qquad (5)$$

This is the law of <u>rectilinear diameters</u>. This is represented in the figure $m-T$. The experimental situation is in a very good agreement with (4) but with $\beta = 1/3$, rather that the mean-field value $\beta = 1/2$



IV - FIELD THEORIES, CRITICAL PHENOMENA, AND THE RENORMALIZATION GROUP

Mean-field theory correctly describes the qualitative features of most phase transitions and, in some cases, the quantitative features since mean-field theory replaces the actual configurations of the local variables by their average values, it neglects the effects of fluctuation about this mean. These fluctuations may or may not be important. The more spins (local variable) that interact with a particular test spin, the more the test spin sees an effective average field or mean field. If the test spin interacts with two neighbors, the averaging is minimal and the fluctuations are large and important. The number of spins producing the effective field increases with the range of the interaction and with the dimension. Thus we will find that mean-field theory is a good approximation in high dimensions but fails to provide a quantitatively correct description of second-order critical points in low dimensions.

Breakdown of Mean-Field Theory

A quantitive measure of the importance of fluctuations of the order parameter can be obtained by considering the average over a coherence volume $V_\xi \sim \xi^D$ of the deviation $\delta\phi(\bar{x}) = \phi(\bar{x}) - \langle\phi\rangle$, of the local order parameter from its equilibrium value

$$\delta\phi_{coh} = V_\xi^{-1} \int_{V_\xi} d^D\bar{x}\ \delta\phi(\bar{x}) \tag{1}$$

Fluctuations are negligible if, in the ordered phase $\langle(\delta\phi_{coh})^2\rangle$ is much less than $\langle\phi^2\rangle$, i.e. if

$$V_\xi^{-2} \int_{V_\xi} d^D\bar{x}\, d^D x'\ \langle\delta\phi(\bar{x})\,\delta\phi(\bar{x}')\rangle = V_\xi^{-1} \int_{V_\xi} d^D x\ G(\bar{x},0) < \langle\phi\rangle^2 \tag{2}$$

where $G(\bar{x},\bar{x}')$, which depends only on $\bar{x}-\bar{x}'$ is the order parameter correlation function. Remarkably, mean-field theory itself provides a prediction for $G(\bar{x},\bar{x}') = T\chi(\bar{x},\bar{x}')$, where $\chi(\bar{x},\bar{x}')$ is the susceptibility relating $d\langle\phi(\bar{x})\rangle$ to a conjugate external field at $\bar{x}'$. Thus, mean-field theory gives rise to its own internal consistency criterion. If eq (2) is satisfied by the mean-field values of $G(\bar{x},0)$ and $\langle\phi\rangle$, then mean-field theory is internally consistent and a good approximation. If not, fluctuations are important, and an alternative theory must be found.

The left hand side of (1.2) can be obtained for ϕ^4 theories in mean-field theory using eq. (III-11.3) for $\chi(\vec{x})$ and (III-8.2) for $\langle\phi\rangle$

$$\langle(\delta\phi_{con})^2\rangle = V_\xi^{-1}\, T\, c^{-1} \int_{V_\xi} d^D x\, |x|^{-(D-2)}\, Y(|\vec{x}|/\xi)$$

$$= A_D\, T\, \xi^{-(D-2)}/c < |r|/4u \qquad (1)$$

where $\xi = (c/|r|)^{1/2}$ is the correlation length and A_D is a constant for fixed dimension D. This equation can be expressed in a unitless form

$$\left(\frac{\xi}{\xi_0}\right)^{D-4} = \left(\frac{T - T_c}{T_c}\right)^{(4-D)/2} \geq \frac{A_D}{2\,(\Delta c_v)\,\xi_0^D} \qquad (2)$$

where $\xi_0 = (c/a T_c)^{1/2}$ is the bare coherence length and $\Delta c_v = T_c a^2/8u$ is the mean-field specific heat jump per unit volume. Though this equation was derived by consideration of fluctuation in the ordered phase (i.e. $T > T_c$), it also applies in the disordered phase

For $D > 4$, ξ^{D-4} diverges at $T \to T_c$, and eq (2) is always satisfied near a critical point. For $D < 4$, ξ^{D-4} tends to zero as $T \to T_c$, and eq (2) is never satisfied near a critical point. Thus, mean-field theory provide an internal consistent description of the second-order phase transition of ϕ^4 and related models for all $D > 4$. It does not provide an adequate description for $D < 4$. The dimension D_c below which mean-field theory breaks down is called upper critical dimension. For phase transitions described by ϕ^4 and related theories, $D_c = 4$. Other transitions can have other values of D_c

For $D < D_c$, mean-field theory is valid for temperatures sufficiently far from T_c that (2) is satisfied. As T approaches to T_c (either from above or below) fluctuations become important, and inequality (2) is eventually violated. A temperature T_G at which fluctuations become important is called the Ginzburg temperature and is determined by equality in (3)

$$t_G \equiv \frac{|T_G - T_c|}{T_c} = \left(\frac{A_D}{2\,(\Delta c_v)\,\xi_0^D}\right)^{2/(4-D)} \qquad (3)$$

Here and in what follows, we will use upper case T to denote temperature and lower case $t = (T - T_c)/T_c$ to denote reduce temperature. Thus t_G is the reduced

Ginzburg temperature. Alternatively, a Ginzburg length, ξ_G, can be defined via (2.2)

$$\xi_G^{4-D} \sim (\Delta c_v)\, \xi_0^4 = c^2/(8 u T_c) \qquad (1)$$

or

$$\xi_G \sim \xi_0 \left[(\Delta c_v)\, \xi_0^D\right]^{1/(4-D)} \qquad (2)$$

Mean-field theory is valid when $\xi < \xi_G$ and invalid when $\xi > \xi_G$. Note that $|T_G - T_c| \to 0$ as $\xi_0 \to \infty$ for $D < 4$. Thus, mean-field theory will be valid even very close to a critical point for $D < D_c$ if the bare coherence length ξ_0 is large. This is the case for systems with long-range forces, or, as we shall see, for superconductors. When $|T_G - T_c|$ is not small, one can expect a crossover from mean-field behavior to critical behavior when the reduced temperature t becomes of order t_G.

In three dimensions, a more careful evaluation of A_D yields

$$t_G = \frac{k_B^2}{32\pi^2 (\Delta c_v)^2 \xi_0^6} \qquad (3)$$

where Δc_v is measured in units erg cm^{-3} K^{-1} and $k_B = 1.38 \times 10^{-16}$ erg K^{-1}. This is the form for t_G that is usually used in $D = 3$.

Let us see what is the situation with superconductors. The specific heat jump in Aluminium is of order 2×10^4 erg mole^{-1} K. The lattice spacing in Al is 4 Å, whereas the coherence length is $\xi_0 \simeq 1.6 \times 10^4$ Å. Thus $\Delta c_v = (2 \times 10^4 / 4^3)$ erg cm^{-3} K^{-1} and $t_G \simeq 10^{-17}$. Since $T_c = 1.19$ K so access to the critical region is virtually impossible. The reason for the very small value of t_G is the enormous coherence length relative to the lattice space. This is a common feature to most non high T_c superconductors.

Construction of a Field Theory

The partition function discussed before involves a trace over all possible states of the system. To facilitate discussion of the appearance of order and properties of the ordered phases, we would like a formulation of the partition function that emphasizes the role of the order parameter. One way to do this is to divide the system up into many cells with dimensions large compared to any microscopic length such as the interparticle spacing or range of the interparticle potential. Each cell contains a large number of particles. The order parameter field, $\phi(\vec{x})$, like the Hamiltonian, is a quantum mechanical operator or a function of the classical dynamical variables (e.g. the magnetization). Its average over the particles in a cell centered at position $\vec{x}$ is $\tilde{\phi}(\vec{x})$. Since there are many particles in each cell, $\tilde{\phi}(\vec{x})$ can be regarded as a continuous classical variable, which can vary from cell to cell. This process of averaging over many particles in some volume of space is called coarse graining. In essence, we take the Landau form for the free energy and treat it as the energy for a particular local configuration of the order parameter. Then instead of considering the minimum energy we allow for excitations according to their statistical weight. The states of the system can now be specified by the field $\tilde{\phi}(\vec{x})$ and have an effective energy $\tilde{H}[\tilde{\phi}(x)]$. The partition function is thus an integral, or more properly a functional integral, over all possible values of $\tilde{\phi}(x)$ at all positions $\vec{x}$:

$$Z = \int \mathcal{D}\tilde{\phi}(x)\, e^{-\left(\tilde{H}[\tilde{\phi}(x)] - \int d^D x\, h(\vec{x})\, \tilde{\phi}(\vec{x})\right)/T} \qquad (1)$$

The integral over $\tilde{\phi}(x)$ is often called a path integral. In purely classical systems, one can arrive to eq. (1) by introducing a delta function and setting the field $\phi(\vec{x})$ equal to $\tilde{\phi}(\vec{x})$ into the expression for the partition function

$$Z = \int \mathcal{D}\tilde{\phi}(x)\, \mathrm{Tr}\left\{ \prod_{\vec{x}} \delta[\phi(\vec{x}) - \tilde{\phi}(\vec{x})]\, e^{-[H - \int d^D x\, h(\vec{x})\, \phi(\vec{x})]/T} \right\} \qquad (2)$$

This yields (1) with

$$e^{-\tilde{H}/T} = \mathrm{Tr} \prod_{\vec{x}} \delta[\phi(\vec{x}) - \tilde{\phi}(\vec{x})]\, e^{-H/T} \qquad (3)$$

For our present purposes, the distinction between the operator field $\phi(\vec{x})$ and its coarse-grained local average $\tilde{\phi}(\vec{x})$ is irrelevant, and we will denote both fields by $\phi(\vec{x})$

The effective energy $\tilde{H}$ is usually called a Hamiltonian in the statistical mechanical and critical phenomena literature, even though it is not a function of variables for which commutation or Poisson bracket relations have been defined. It is closely related to the action of quantum field theories and is, therefore, referred to as the action in some literature. Since we will usually not consider in detail the original microscopic Hamiltonian, we will use the symbol H rather than $\tilde{H}$

$$Z = \int \mathcal{D}\phi(x) \exp\left\{ -\beta \left(H[\phi(x)] - \int d^D x \, h(\vec{x}) \, \phi(\vec{x}) \right) \right\} \qquad (1)$$

A phenomomological form for H can be derived in much the same way as the Landau form for the mean-field free energy F. There should be a local part of H depending only on the order parameter at a single position in space and a part favoring a spatially uniform order parameter. We therefore write

$$H[\phi(\vec{x})] = \int d^D x \, f[\phi(\vec{x})] + \frac{1}{2} \int d^D x \, c \, [\vec{\nabla} \phi(\vec{x})]^2 \qquad (2)$$

where $f[\phi(\vec{x})]$ is a local function of $\phi(\vec{x})$, which can be expanded in a power series in combinations which are invariant under the symmetry group of the disordered phase. The Hamiltonian (2) provides a description of the energy associated with long-wavelength, slow spatial variations of $\phi(\vec{x})$. It does not provide a realistic description of short-wavelength distorsions. However, most phenomena in the vicinity of critical points are controlled by long-wavelengths fluctuations, and (2) is adequate provided short-wavelength fluctuations are supressed. This can be accomplished by the so-called <u>hard cutoff</u> procedure whereby excitations with wave number greater than a <u>cutoff</u> $\Lambda \sim 2\pi/a$, where a is a length of order the range of interparticle interactions, are simply not permitted in the partition trace.

The definition of the functional integral in (4.1) is a little vague. We will now refine this definition by considering the continuum limit of a theory with fields $\phi_{\vec{\ell}}$ defined on N sites $\vec{\ell}$ of a D-dimensional lattice. The partition function for such a lattice model can be written

$$Z = \int \prod_{\vec{\ell}} d\phi_{\vec{\ell}} \; e^{-\beta H_L[\phi_{\vec{\ell}}]} \qquad (3)$$

$$H_L[\phi_{\vec{\ell}}] = \sum_{\vec{\ell}} f_L(\phi_{\vec{\ell}}) + \frac{1}{2} \sum_{\vec{\ell}, \vec{\ell}'} c_{\vec{\ell}, \vec{\ell}'} (\phi_{\vec{\ell}} - \phi_{\vec{\ell}'})^2$$

where $f_L(\phi_{\vec{\ell}})$ has a power series expansion about $\phi_{\vec{\ell}} = 0$ and $c_{\vec{\ell}, \vec{\ell}'}$ has a finite range, typically of lattice spacing. Each $\phi_{\vec{\ell}}$ can take on any value between $-\infty$ and $+\infty$.

The continuum limit of the lattice model defined in (5.1) is obtained by allowing the volume per lattice site v_0 to tend to zero, $\vec{R}_{\vec{\ell}}$ to become a continuous variable $\vec{x}$, and $\phi_{\vec{\ell}}$ to become $\phi(\vec{x})$, while keeping the total volume $V = N v_0$ fixed. In this limit

$$v_0 \sum_{\vec{\ell}} \longrightarrow \int d^D x$$

$$\sum_{\vec{\ell}} f_L(\phi_{\vec{\ell}}) \longrightarrow \int d^D x \, f[\phi(\vec{x})] \quad , \quad f = \frac{1}{v_0} f_L \tag{1}$$

$$\frac{1}{2} \sum_{\vec{\ell},\vec{\ell}'} C_{\vec{\ell},\vec{\ell}'} (\phi_{\vec{\ell}} - \phi_{\vec{\ell}'})^2 \longrightarrow \frac{1}{2} \int d^D x \, C \, (\vec{\nabla}\phi)^2$$

Let us consider the last expression. In the left hand side we keep only the lowest term in the gradient expansion

$$\frac{1}{2} \sum_{\vec{\ell},\vec{\ell}'} C_{\vec{\ell},\vec{\ell}'} (\phi_{\vec{\ell}} - \phi_{\vec{\ell}'})^2 \simeq \frac{1}{2} \sum_{\vec{\ell},\vec{\ell}'} C_{\vec{\ell},\vec{\ell}'} (\nabla_i \phi_{\vec{\ell}}) (\nabla_j \phi_{\ell}) (\vec{R}_{\vec{\ell}'} - \vec{R}_{\vec{\ell}})_i (\vec{R}_{\vec{\ell}'} - \vec{R}_{\vec{\ell}})_j =$$

$$= \frac{1}{2} \sum_{\vec{\ell}} (\nabla_i \phi_{\vec{\ell}}) (\nabla_j \phi_{\vec{\ell}}) \sum_{\vec{\ell}'} C_{\vec{\ell},\vec{\ell}'} (\vec{R}_{\vec{\ell}'} - \vec{R}_{\vec{\ell}})_i (\vec{R}_{\vec{\ell}'} - \vec{R}_{\vec{\ell}})_j =$$

$$= \frac{1}{2} \sum_{\vec{\ell}} (\nabla_i \phi_{\vec{\ell}}) (\nabla_j \phi_{\vec{\ell}}) \frac{1}{D} \delta_{ij} \sum_{\vec{\ell}'} C_{0,\vec{\ell}'} (\vec{R}_{\vec{\ell}'})^2 \tag{2}$$

and therefore this implies (1) if

$$C = \frac{1}{D v_0} \sum_{\vec{\ell}} C_{0,\vec{\ell}} \vec{R}^2_{\vec{\ell}} \tag{3}$$

When the Hamiltonian is harmonic in $\phi(\vec{x})$, then the weight function becomes Gaussian, and (4.1) can be evaluated exactly. In order to carry out this calculation we need

$$\int \prod_{i=1}^{N} d^D x_i \; \exp\left\{ - \sum_{i,j=1}^{N} A_{ij} \, \vec{x}_i \cdot \vec{x}_j + \sum_{i=1}^{N} \vec{\beta}_i \cdot \vec{x}_i \right\} =$$

$$= \pi^{DN/2} [\det A]^{-D/2} \exp\left\{ \frac{1}{4} \sum_{i,j=1}^{N} (A^{-1})_{ij} \, \vec{\beta}_i \cdot \vec{\beta}_j \right\} \tag{4}$$

where A is a definite positive matrix and $AA^{-1} = A^{-1}A = I$. A similar formula is

Let us try to derive this expression. The starting point for the evaluation of Gaussian functional integrals is the identity

$$\int_{-\infty}^{+\infty} dy\, e^{-\frac{1}{2} c y^2 + \lambda y} = \left(\frac{2\pi}{c}\right)^{1/2} e^{\lambda^2/2c} \quad , \quad c>0 \qquad (1)$$

We will now derive the generalization of this result to multidimensional integrals. Let $\underline{C}$ be an $N \times N$ positive matrix with components $C_{ij} = \langle i|\underline{C}|j\rangle$. If $\underline{C}$ is real and symmetric, then it can be diagonalized with real orthogonal eigenfunctions $\langle i|p\rangle$ such that $\langle p|\underline{C}|p'\rangle = \delta_{p,p'} C_p$, where C_p is an eigenvalue that is necessarily real. We can therefore write

$$\int \left(\prod_{i=1}^{N} dy_i\right) e^{-\frac{1}{2} y_i C_{ij} y_j + \lambda_i y_i} = \prod_{p=1}^{N} \int dy_p\, e^{-C_p y_p^2/2 + \lambda_p y_p}$$

$$= \prod_{p=1}^{N} \left(\frac{2\pi}{C_p}\right)^{1/2} e^{\lambda_p^2/2C_p} .$$

$$= (2\pi)^{N/2} [\det \underline{C}]^{-1/2} \exp\left\{ \frac{1}{2} \lambda_i (C^{-1})_{ij} \lambda_j \right\}$$

$$= \exp\left\{ -\frac{1}{2} \mathrm{Tr} \ln (\underline{C}/2\pi) + \frac{1}{2} \lambda_i (C^{-1})_{ij} \lambda_j \right\} \qquad (2)$$

where the summation convention on repeated indices is understood and where

$$y_p = \sum_i \langle p|i\rangle y_i \quad , \quad \lambda_p = \sum_i \langle p|i\rangle \lambda_i \qquad (3)$$

The Jacobian of the transformation from the variable y_i to y_p is the determinant of the matrix $\underline{M}$ with components $\langle p|i\rangle$. It is one because

$$|\det \underline{M}| = |\det \underline{M}^2|^{1/2} \qquad (4)$$

and

$$\langle p|M^2|p'\rangle = \sum_i \langle p|i\rangle \langle i|p'\rangle = \delta_{pp'} \qquad (5)$$

The eigenfunctions $\langle p|i\rangle$ can always be chosen to be real for a real symmetric matrix. It is often convenient, however, to choose them to be complex (e.g. plane waves $\exp(i\vec{q}\cdot\vec{R}_\ell)$ with periodic boundary conditions). Since the complex functions can always be expressed as linear combinations of real eigenfunctions the result (2) remains unchanged.

Now we can apply this to the evaluation of the partition function of an harmonic lattice model

$$Z = \int \prod_{\vec{e}} d\phi_{\vec{e}} \; e^{-\beta \left(H_L^0 [\phi_{\vec{e}}] + H_{ext} [\phi_{\vec{e}}] \right)} \qquad (1)$$

$$H_L^0 = \frac{1}{2} \sum_{\vec{e},\vec{e}'} r_{\vec{e},\vec{e}'} \, \phi_{\vec{e}} \, \phi_{\vec{e}'} \qquad (2)$$

$$H_{ext} = - \sum_{\vec{e}} h_{\vec{e}} \, \phi_{\vec{e}} \qquad (3)$$

Notice that $r_{\vec{e},\vec{e}'}$ are the components of a matrix $\underline{r}$. From (A-8.4) and (A-8.5) we can introduce the orthogonal eigenfunctions

$$\langle \vec{e} \,|\, \vec{q} \rangle = \frac{1}{N^{1/2}} \, e^{i \vec{q} \cdot \vec{R}_{\vec{e}}} \qquad (4)$$

Then

$$\langle \vec{q}' | \underline{r} | \vec{q} \rangle = \sum_{\vec{e},\vec{e}'} \langle \vec{q}' | \vec{e}' \rangle \, r_{\vec{e}',\vec{e}} \, \langle \vec{e} | \vec{q} \rangle = \frac{1}{N} \sum_{\vec{e},\vec{e}''} e^{i \vec{q} \cdot \vec{R}_e} \, e^{-i \vec{q}' \cdot \vec{R}_{\vec{e}'}} \, r_{\vec{e}',e}$$

$$= \frac{1}{N} \sum_{\vec{e},\vec{e}''} e^{i \vec{q} \cdot \vec{R}_e} \, e^{-i \vec{q}' \cdot (R_{\vec{e}} + R_{\vec{e}''})} \, r_{\vec{e}+\vec{e}'',\vec{e}} =$$

$$= \frac{1}{N} \sum_{\vec{e}''} e^{-i \vec{q}' \cdot \vec{R}_{e''}} \, r_{\vec{e}'',0} \sum_{e} e^{i(\vec{q} - q') \cdot \vec{R}_e} = \delta_{\vec{q},\vec{q}'} \sum_{\vec{e}} e^{-i \vec{q} \cdot R_{\vec{e}}} \, r_{\vec{e},0} \qquad (5)$$

and therefore in this new basis the matrix $\underline{r}$ is diagonal. We can write

$$\langle \vec{q}' | \underline{r} | \vec{q} \rangle = \delta_{\vec{q},\vec{q}'} \, v_0 \, r(\vec{q}) \qquad , \qquad r(\vec{q}) = \frac{1}{v_0} \sum_{\vec{e}} e^{-i \vec{q} \cdot \vec{R}_e} \, r_{\vec{e},0} \qquad (6)$$

Notice

$$\phi_{\vec{q}} = \frac{1}{\sqrt{N}} \sum_{\vec{e}} e^{-i \vec{q} \cdot \vec{R}_{\vec{e}}} \, \phi_{\vec{e}} \qquad , \qquad \phi_{\vec{e}} = \frac{1}{\sqrt{N}} \sum_{\vec{q}} e^{i \vec{q} \cdot \vec{R}_{\vec{e}}} \, \phi_{\vec{q}} \qquad (7)$$

Now we would like to calculate

$$\mathcal{A}[T, h_e] \equiv - T \ln Z[T, h_e] = - T \ln \left(\int \prod_{e} d\phi_{\vec{e}} \; e^{\beta (H_L^0 + H_{ext})} \right)$$

and therefore using (7.2)

$$\mathcal{A}[T, h_{\vec{\ell}}] = \frac{1}{2} T \sum_{\vec{q}} \ln[\beta \nu_0 r(\vec{q})/2\pi] - \frac{1}{2} T \sum_{\vec{\ell},\vec{\ell}'} \beta h_{\vec{\ell}} \frac{1}{\beta} \langle \vec{\ell} | \underline{r}^{-1} | \vec{\ell}' \rangle \beta h_{\vec{\ell}'} \qquad (1)$$

Notice

$$\langle \vec{\ell} | \underline{r}^{-1} | \vec{\ell}' \rangle = \sum_{\vec{q},\vec{q}'} \langle \vec{\ell} | \vec{q} \rangle \langle \vec{q} | \underline{r}^{-1} | \vec{q}' \rangle \langle \vec{q}' | \vec{\ell}' \rangle = \sum_{\vec{q}} \langle \vec{\ell} | \vec{q} \rangle \frac{1}{\nu_0 r(\vec{q})} \langle \vec{q} | \ell' \rangle$$

$$= \frac{1}{V} \sum_{\vec{q}} e^{i\vec{q}\cdot(\vec{R}_{\vec{\ell}} - \vec{R}_{\vec{\ell}'})} \frac{T}{r(\vec{q})} \qquad (2)$$

and we can write

$$\mathcal{A}[T, h_{\vec{\ell}}] = \frac{1}{2} T \sum_{\vec{q}} \ln[\beta r(\vec{q}) \nu_0/2\pi] - \frac{1}{2} \sum_{\vec{\ell},\vec{\ell}'} h_{\vec{\ell}} \beta G^0_{\vec{\ell},\vec{\ell}'} h_{\vec{\ell}'} \qquad (3)$$

with

$$G^0_{\vec{\ell},\vec{\ell}'} = \frac{1}{V} \sum_{\vec{q}} e^{i\vec{q}\cdot(\vec{R}_{\vec{\ell}} - \vec{R}_{\vec{\ell}'})} \frac{T}{r(\vec{q})} = \langle \phi_{\vec{\ell}} \phi_{\vec{\ell}'} \rangle \qquad (4)$$

In the continuum model we have

$$H_0 = \frac{1}{2} \int d^D x \, d^D x' \, \phi(\vec{x}) \, r(\vec{x}, \vec{x}') \, \phi(\vec{x}') \qquad (5)$$

$$H_{ext} = - \int d^D x \, h(\vec{x}) \, \phi(\vec{x}) \qquad (6)$$

$$\mathcal{A}[T, h(\vec{x})] = \frac{1}{2} T V \int \frac{d^D q}{(2\pi)^D} \ln[\beta r(\vec{q}) \nu_0/2\pi]$$

$$- \frac{1}{2} \int d^D x \, d^D x' \, h(\vec{x}) \, \beta \, G_0(\vec{x}, \vec{x}') \, h(\vec{x}') \qquad (7)$$

with

$$G_0(\vec{x}, \vec{x}') = \int \frac{d^D q}{(2\pi)^D} e^{i\vec{q}\cdot(\vec{x}-\vec{x}')} \frac{T}{r(\vec{q})} = \langle \phi(\vec{x}) \phi(\vec{x}') \rangle \qquad (8)$$

Note that the free energy in the above equation is formally infinite in the limit $\nu_0 \to 0$ (assuming $r(\vec{q})$ remains finite in this limit as it must). This infinite has no physical significance and can be removed merely by redefining the continuum trace operation.

Notice that the number of wave vectors $\vec{q}$ must be equal to the number of lattice points in a discrete theory ((A-8.8))

$$\sum_{\vec{q}} 1 = N = V \int \frac{d^D q}{(2\pi)^D} \qquad (1)$$

Thus, if there is a hard spherical cutoff restricting $|\vec{q}|$ to be less than Λ, then

$$v_0 = \frac{V}{N} = \left\{ \int_{|\vec{q}|<\Lambda} \frac{d^D q}{(2\pi)^D} \right\}^{-1} = \left\{ \frac{\Omega_D}{(2\pi)^D} \int_0^\Lambda dq \, q^{D-1} \right\}^{-1} \Rightarrow$$

Hence

$$v_0 = D \, \frac{\Lambda^{-D}}{K_D} \qquad K_D \equiv \Omega_D / (2\pi)^D \qquad (2)$$

where Ω_D is the solid angle subtended by a D-dimensional sphere. In the continuum model, N has no meaning, but Λ does, and by the above relation, we can assign a meaning to v_0.

Eqs (5.1) and (5.2) define a field theory from which the thermodynamic potential $A[T, \phi(x)]$ and its conjugate potential $F[\langle \phi(\vec{x}) \rangle]$ can be calculated All possible configurations in functional space contribute to Z. Some of these configurations contribute to Z more than others. The configuration contributing the most to Z is the one minimizing $\beta[H - \int d^D x \, h(x) \phi(x)]$, i.e. the functional integral is dominated by the saddle point path along with $\phi(\vec{x}) = \phi_{sad}(\vec{x})$ determined by

$$\left. \frac{\delta H}{\delta \phi(\vec{x})} \right|_{\phi(\vec{x}) = \phi_{sad}(\vec{x})} = h(\vec{x}) \qquad (3)$$

Mean-field theory consists of approximating Z by its contribution from the saddle point path only. Thus the mean-field approximation for the partition function is

$$Z_{MF} = \exp \left\{ -\beta \left[H[\phi_{sad}(\vec{x})] - \int d^D x \, h(\vec{x}) \, \phi_{sad}(\vec{x}) \right] \right\} \equiv$$

$$\equiv \exp \left\{ -\beta \left[F_{MF}[\langle \phi(x) \rangle] - \int d^D x \, h(\vec{x}) \langle \phi(\vec{x}) \rangle \right] \right\} \qquad (4)$$

where F_{MF} is the mean-field free energy. It is clear from (3) and (4), that in mean-field theory

$$\langle \phi(\vec{x}) \rangle = \phi_{sad}(\vec{x}) \qquad , \qquad F_{MF} = H\,[\,\phi_{sad}(\vec{x})\,] \tag{1}$$

Corrections to mean-field theory can now be studied by expanding H in powers of

$$\delta\phi(\vec{x}) = \phi(\vec{x}) - \langle \phi(\vec{x}) \rangle \tag{2}$$

By definition

$$\langle \delta\phi(\vec{x}) \rangle = 0 \tag{3}$$

In general, fluctuations will cause $\langle \phi(\vec{x}) \rangle$ to differ from $\phi_{sad}(\vec{x})$. There are well controlled ways of calculating $\langle \phi(\vec{x}) \rangle$ which are beyond the scope of these notes. We are going to consider only Gaussian fluctuations about the saddle point. Expanding H up to second order in $\delta\phi(\vec{x})$ we have

$$H - \int d^D x \; h(x)\,\phi(x) = H(\langle \phi(x) \rangle) - \int d^D x \; h(x) \langle \phi(x) \rangle + H'$$

$$\beta H' = \frac{1}{2} \int d^D x \, d^D x' \; \delta\phi(\vec{x}) \left[\frac{\delta^2 \beta H}{\delta\phi(\vec{x})\,\delta\phi(\vec{x}')} \right]_{\phi(\vec{x}) = \langle \phi(\vec{x}) \rangle} \delta\phi(\vec{x}') \equiv$$

$$\equiv \frac{1}{2} \int d^D x \, d^D x' \; \delta\phi(\vec{x}) \; G_0^{-1}(\vec{x},\vec{x}') \; \delta\phi(\vec{x}') \tag{4}$$

where $G_0^{-1}(\vec{x},\vec{x}')$ is the inverse of the mean-field correlation function. In a ϕ^4-theory

$$G_0^{-1}(\vec{x},\vec{x}') = \beta \left\{ r + 12u \langle \phi(\vec{x}) \rangle^2 - c\,\vec{\nabla}^2 \right\} \delta(\vec{x}-\vec{x}') \tag{5}$$

Thus, harmonic fluctuations about the mean-field or saddle point solution are controlled by the mean-field order parameter correlation function. The lowest order fluctuation corrections to the mean-field free energy are obtained by evaluating the gaussian integral over $\delta\phi(\vec{x})$

$$F - F_{MF} = -T \ln \left\{ \int \mathcal{D}\,\delta\phi(\vec{x}) \; \exp\left[\frac{1}{2} \int d^D x \, d^D x' \; \delta\phi(\vec{x}) \, G_0^{-1}(\vec{x},\vec{x}') \, \delta\phi(\vec{x}') \right] \right\} \tag{6}$$

and this can be calculated as before

$$F - F_{MF} = \frac{1}{2} T V \int \frac{d^D q}{(2\pi)^D} \ln \left[G_0^{-1}(\bar{q}) v_0 / 2\pi \right] \tag{1}$$

Eq (1) is often called the one loop approximation for the free energy. It depends on $\langle \phi(\bar{x}) \rangle$ via the dependence of G_0 on $\langle \phi(\bar{x}) \rangle$, and can be expanded in a power series in $\langle \phi(\bar{x}) \rangle$. The second-order term in this expansion gives the one-loop correction to the inverse correlation function, $G^{-1}(\bar{x}, \bar{x}')$, which in the disordered phase with $\langle \phi(\bar{x}) \rangle = 0$ is

$$G^{-1}(\bar{x}, \bar{x}') = \frac{\partial^2 \beta F}{\partial \langle \phi(\bar{x}) \rangle \, \partial \langle \phi(\bar{x}') \rangle} =$$

$$= G_0^{-1}(\bar{x}, \bar{x}') + \frac{1}{2} \mathrm{Tr} \left\{ G_0 \frac{\partial G_0^{-1}}{\partial \langle \phi(\bar{x}) \rangle \, \partial \langle \phi(\bar{x}') \rangle} \right\} =$$

$$= G_0^{-1}(\bar{x}, \bar{x}') + \frac{1}{2} \int d^D x_1 \, d^D x_2 \; G_0(\bar{x}_1, \bar{x}_2) \frac{\partial G_0^{-1}(\bar{x}_2, \bar{x}_1)}{\partial \langle \phi(\bar{x}) \rangle \, \partial \langle \phi(\bar{x}') \rangle} \tag{2}$$

where the second two forms apply only to the disordered phase. For a ϕ^4-theory, this reduces to

$$G^{-1}(\bar{x}, \bar{x}') = G_0^{-1}(\bar{x}, \bar{x}') + 12 u \, \delta(\bar{x} - \bar{x}') \, G_0(\bar{x}, \bar{x}) \tag{3}$$

which in the disordered phase when $\langle \phi(\bar{x}) \rangle = 0$ is

$$T \, G^{-1}(\bar{q}, r) = r + c q^2 + 12 u \int \frac{d^D q}{(2\pi)^D} \frac{T}{r + c q^2} \tag{4}$$

One loop corrections to fourth- and higher order terms of the expansion of F in powers of $\langle \phi(x) \rangle$ can be calculated in a similar way.

We have just shown how fluctuations can lead to a breakdown of mean-field theory. We have just seen that the replacement of Z by its contribution from the most probable path with a spatially uniform order parameter is equivalent to mean-field theory. We will now show that the criterion for the breakdown of this approximation is exactly the same as the Ginzburg criterion discussed before.

When $h(\bar{x})$ is spatially uniform, the saddle point path yielding mean-field theory is one with a spatially uniform $\langle \phi(\bar{x}) \rangle$. This is a good approximation so long as the contribution of spatially non-uniform paths to Z is unimportant. This is the case when the energy,

$$H_{n.u} = \frac{1}{2} c \int d^D x \, (\nabla \phi(\vec{x}))^2 \qquad (1)$$

associated with non-uniform paths is large compared to T. We can estimate the magnitude of $H_{n.u}$ by noting that $\langle \phi \rangle^2 = |r|/4u$ at the saddle point and that spatial correlations only extend up to a distance of order $\xi = (c/|r|)^{-1/2}$.
We can, therefore, estimate

$$H_{n.u} = \frac{1}{2} c \int d^D x \, (\nabla \phi(\vec{x}))^2 \sim \frac{1}{2} c \, \xi^{D-2} \langle \phi \rangle^2 = \frac{c^2}{8u} \xi^{D-4} \qquad (2)$$

In order that the mean field theory to be valid $H_{n.u.} > T$ which reproduces the Ginzburg criterium.

The Ginzburg temperature also indicates when perturbation theory will break down. Consider the one-loop expression for

$$\frac{d\,(T G^{-1}(\vec{q}, r))}{dr} = 1 - 12 u T \int \frac{d^D q}{(2\pi)^D} \frac{1}{(r + c q^2)^2} \qquad (3)$$

derived from (12.4). The perturbation term in this expression proportional to u diverges as $(uT/c^2)\,\xi^{4-D}$ for $D<4$ and becomes comparable to unity at the Ginzburg temperature. Thus, for $T > T_G$, a perturbation expansion in u (or the number of loops) present no problems. For $T < T_G$, low-order terms in perturbation theory become divergent, and simple perturbation theory will not work

The Self-consistent Field Approximation

We have just seen that mean-field theory breaks down below an upper critical dimension $D_c = 4$. One can see explicitly how this happens in a simple treatment of the ϕ^4-field theory. This approximation is variously called the self-consistent field, Hartree or random phase approximation (RPA) It becomes exact (as will be shown at the end of this section) for N-component fields in the limit $N \to \infty$. It consists of replacing one factor of ϕ^2 in ϕ^4 term in f_{SL} by its average, $\langle \phi^2 \rangle$, to be determined self-consistently.

There are six ways of choosing the two factors of ϕ to be paired in $\langle \phi^2 \rangle$ from the four factors of ϕ in ϕ^4, and in the free energy of RPA becomes $r\phi^2/2 + 6u\langle\phi^2\rangle\phi^2$ (see III - 7.1). In an N - component theory, the factor of 6 becomes $2(n+2)$. The correlation function $G(\vec{q})$ can be evaluated using the equipartition theorem as before (A. 8), (II.5)

$$T\,G^{-1}(\vec{q}) = r + cq^2 + 12u\langle\phi^2\rangle \tag{1}$$

where as before $r = a(T - T^*)$. For T greater than the as yet to be determined transition temperature T_c,

$$\langle\phi^2\rangle = G(\vec{x},\vec{x}) = \int \frac{d^Dq}{(2\pi)^D}\, G(\vec{q}) = \int \frac{d^Dq}{(2\pi)^D}\, \frac{T}{r + cq^2 + 12u\langle\phi^2\rangle} \tag{2}$$

Eq (2) provides a self-consistent equation for $\langle\phi^2\rangle$

Before evaluating the integral in (2), we recall that the expansion of $G(\vec{q})$ to first order in q^2 is only valid for small q (long wavelength). For larger q, higher powers in the expansion are needed. Alternatively, one can say that the q^2 form is valid up to some cutoff Λ of order the inverse bare correlation length, $\xi_0 = (c/aT_c)^{1/2}$. In this case, the integral in (2) is restricted to a sphere of radius Λ. Using (1) and (2), we can now calculate the temperature dependence of $\chi^{-1} = T\,G^{-1}(\vec{q}=0)$:

$$\chi^{-1} \equiv \tau = r + 12uT \int_0^\Lambda \frac{d^Dq}{(2\pi)^D}\, \frac{1}{\tau + cq^2} =$$

$$= r + 12uT K_D \int_0^\Lambda dq\, \frac{q^{D-1}}{\tau + cq^2} \quad , \quad K_D \equiv \frac{\Omega_D}{(2\pi)^D} \tag{3}$$

At the actual transition temperature T_c, the susceptibility diverges : $\chi^{-1} = \tau = 0$. This allows us to determine the critical temperature for $D \geq 2$ via

$$r_c \equiv a(T_c - T^*) = -\frac{12uT_c}{c} \int_0^\Lambda \frac{d^Dq}{q^2} = -\frac{12uT_c}{c}\, \frac{K_D\Lambda^{D-2}}{D-2} \tag{4}$$

This gives

$$T_c = \left\{ 1 + \frac{12uK_D\Lambda^{D-2}}{(D-2)\,ca} \right\}^{-1} T^* \tag{5}$$

The transition temperature is depressed below the mean - field limit of metastability. Note also that $T_c \to 0$ as $D \to 2$. This is the <u>lower critical dimension D_L</u>

at which critical fluctuations become so violent that no phase transition at nonzero temperature is possible. For all $D < D_L$, there is no transition at all.

Let us continue the analysis of $\chi^{-1} \equiv \tau$. We will introduce $r = a(T - T^*)$ and $r - r_c = a(T - T_c)$. Remember

$$0 = r_c + 12 u T_c K_D \int_0^\Lambda dq \, \frac{q^{D-1}}{c q^2} \qquad (1)$$

Then

$$\chi^{-1} \equiv \tau = r - r_c + 12 u K_D \int_0^\Lambda dq \, q^{D-1} \left(\frac{T}{\tau + c q^2} - \frac{T_c}{c q^2} \right) =$$

$$= r - r_c + 12 u K_D (T - T_c) \int_0^\Lambda dq \, \frac{q^{D-1}}{\tau + c q^2} - \frac{12 u K_D T_c}{c} \tau I_D(\tau) \qquad (2)$$

where

$$I_D(\tau) \equiv \int_0^\Lambda dq \, \frac{q^{D-1}}{q^2 (\tau + c q^2)} \qquad (3)$$

Hence

$$\chi^{-1} = r - r_c - \frac{12 u K_D T_c}{c} \tau I_D(\tau) + 12 u K_D (T - T_c) \left\{ \frac{1}{c} \int_0^\Lambda dq \, q^{D-3} - \frac{\tau}{c} I_D(\tau) \right\}$$

$$= r - r_c + \frac{12 u K_D (T - T_c) \Lambda^{D-2}}{c (D-2)} - \frac{12 u K_D T_c}{c} \tau I_D(\tau) - \frac{12 u K_D (T - T_c)}{c} \tau I_D(\tau)$$

Neglecting the last term we obtain

$$\chi^{-1} = \tau = \left\{ 1 + \frac{12 u K_D \Lambda^{D-2}}{a c (D-2)} \right\} (r - r_c) - \frac{12 u K_D T_c}{c} \tau I_D(\tau) \qquad (4)$$

For $D > 4$, $I_D(\tau)$ is analytic and tends to $I_D(0) = \Lambda^{D-4} / [c(D-4)]$ as $\tau \to 0$, and τ is a linear function of small $r - r_c$. Solving for τ in terms of $r - r_c$ for small $T - T_c$ we obtain

$$\tau + \frac{12 u K_D T_c}{c} I_D(0) \tau = \left\{ 1 + \frac{12 u K_D \Lambda^{D-2}}{a c (D-2)} \right\} a (T - T_c) \Rightarrow$$

$$\chi = \frac{1 + (12 u K_D T_c / c) I_D(0)}{1 + (12 u K_D \Lambda^{D-2} / a c (D-2))} \, \frac{1}{T - T_c} \sim (T - T_c)^{-1} \qquad (5)$$

The critical exponent $\gamma = 1$ is thus the same as in mean-field theory. The only modification in χ for $D > D_c = 4$ is in the value of T_c and in the prefactor of $(T-T_c)^{-1}$

For $D<4$, $I_D(\tau)$ is divergent at $\tau = 0$

$$I_D(\tau) = \int_0^\Lambda dq \, \frac{q^{D-3}}{\tau + c q^2} = \left| q = \sqrt{\frac{\tau}{c}}\, y \right| = c^{-(D-2)/2} \, \tau^{(D-4)/2} \int_0^{\Lambda\sqrt{c/\tau}} dy \, \frac{y^{D-3}}{1+y^2}$$

and for $\tau \to 0$

$$I_D(\tau) \xrightarrow[\tau \to 0]{} c^{-(D-2)/2} \, \tau^{-\epsilon/2} \, B_D \tag{1}$$

$$\epsilon \equiv 4 - D \quad , \quad B_D \equiv \frac{1}{2} \, \Gamma\left(\frac{D-2}{2}\right) \Gamma\left(\frac{D-4}{2}\right)$$

Hence, if $\tau^{-\epsilon/2}$ is small, the term involving $I_d(\tau)$ in eq (15.4) can be neglected and $\tau \sim (r - r_c)$. This implies a mean-field form for χ for $T > T_G$.

$$a\,(T_G - T_c) = \frac{12\, u\, K_D\, T_c}{c} \, a\,(T_G - T_c)\, c^{-(D-2)/2} \, [a\,(T_G - T_c)]^{-(4-D)/2} \, B_D \Rightarrow$$

$$T_G = T_c + \frac{1}{a} \left\{ 12\, B_D\, K_D\, u\, T_c\, c^{-D/2} \right\}^{2/(4-D)} \tag{2}$$

in agreement with the Ginzburg temperature calculated previously. For $T < T_G$, $\tau I_D(\tau)$ dominates in (15.4), and we have

$$r - r_c = 12\, u\, (K_d / c)\, T_c\, c^{-(D-2)/2} \, B_D \, \tau^{(D-2)/2} \tag{3}$$

$$\chi = \tau^{-1} \sim \frac{1}{(r - r_c)^\gamma} \qquad \gamma = \frac{2}{D-2}$$

Note that the susceptibility exponent $\gamma \to 1$ as $D \to 4$ as required.

In this approximation, there are no q-dependent corrections to the mean-field $\chi(\vec{q})$. Therefore

$$\chi(\vec{q}) = (\tau + c q^2)^{-1} = \chi\, [1 + (q\,\xi)^2]^{-1} \tag{4}$$

where

$$\xi^2 = c/\tau \sim |T - T_c|^{-2\nu} \tag{5}$$

Thus, the correlation length exponent ν

$$\nu = \frac{1}{2}\gamma = \frac{1}{D-2} \tag{6}$$

which again reduces to its mean field value 1/2 for D = 4

The crossover of the correlation length from its mean-field value

$$\xi_{MF}^2 = \frac{c}{a\,|T - T_c|} \qquad (1)$$

to its critical value is of some interest. From eq (16.4), (15.4), (16.3) and (3.2) we find

$$\xi^2 = \xi_{MF}^2 \left\{ 1 + g\,(\xi/\xi_G)^6 \right\} \qquad (2)$$

where $g = 12 k_B B_D$ and ξ_G is the Ginzburg length. This implies

$$\xi \sim \begin{cases} \xi_{MF} & \text{if} \quad \xi \ll \xi_G \\ \xi_{MF}^{2/(D-2)} \; \xi_G^{-(4-D)/(D-2)} & \text{if} \quad \xi \gg \xi_G \end{cases} \qquad (3)$$

Note that when $\xi_{MF} \sim \xi_G$, $\xi \sim \xi_G$.

This simple approximation shows the major effects of fluctuations corrections to mean-field theory. First, fluctuations in general reduce the transition temperature below its mean-field value. Secondly, they lead to critical exponents that differ from those of mean-field theory for physical dimensions less that the upper critical dimension D_c. For $D < D_c$, there is a crossover from mean-field to critical behavior for reduced temperature t less that t_G.

The self-consistent field solution just presented becomes exact in the $N \to \infty$ limit of the N-vector model. To see this consider the N-vector Hamiltonian

$$H = \frac{1}{2}\int d^Dx\; r\,\vec{\phi}\cdot\vec{\phi} + \frac{1}{2}\int d^Dx\; c\,[\vec{\nabla}\vec{\phi}\,]^2 + \frac{1}{N}\,u\int d^Dx\,(\vec{\phi}\cdot\vec{\phi})^2 \qquad (4)$$

where $\vec{\phi} = (\phi_1, \phi_2, \ldots \phi_N)$ is an N-component vector field and where the quartic term is explicitly proportional to $1/N$ to produce a meaningful $N \to \infty$ limit. The exponential of the quartic term in (4) can be expressed as the exponential of a quadratic term with a fluctuating coefficient with the aid of the Gaussian identity (7.2)

$$\exp\left\{ -\beta u\,(\vec{\phi}\cdot\vec{\phi})^2/N \right\} = C \int_{-i\infty}^{+i\infty} \mathcal{D}\psi(\vec{x})\, \exp\left\{ \frac{1}{16u} N \beta\, \psi^2(\vec{x}) - \frac{1}{2}\beta\,\psi(\vec{x})\,(\vec{\phi}\cdot\vec{\phi}) \right\} \qquad (5)$$

where C is an unimportant constant. In this expression, the integration contour is along the imaginary rather than the real axis because of the negative sign in the argument of the exponential in the right hand side. The partition function is

$$Z = \int \prod_{i=1}^{N} \mathcal{D}\phi_i(\vec{x})\, \mathcal{D}\psi(\vec{x})\, \exp\left\{ N \frac{\beta}{16u} \int d^Dx\, \psi^2(\vec{x}) \right\} \cdot \exp\left\{ -\frac{\beta}{2} \int d^Dx\, [(r+\psi(\vec{x}))\vec{\phi}\cdot\vec{\phi} + c(\vec{\nabla}\vec{\phi})^2] \right\}$$

$$= \int \mathcal{D}\psi(x)\, \exp\left\{ N \frac{\beta}{16u} \int d^Dx\, \psi^2 - N\, \Phi[\psi(\vec{x})] \right\} \qquad (1)$$

where

$$e^{-N\Phi[\psi(\vec{x})]} = \left(\int d\phi(\vec{x})\, \exp\left\{ -\frac{\beta}{2} \int d^Dx\, [(r+\psi(\vec{x}))\phi^2(\vec{x}) + c(\nabla\phi)^2] \right\} \right)^N \qquad (2)$$

The integral in (2) can be evaluated formally using (7.2) leading to

$$\Phi[\psi(\vec{x})] = \frac{1}{2} \operatorname{Tr} \ln [\beta G^{-1}(\vec{x},\vec{x}')/2\pi] \qquad (3)$$

$$G^{-1}(\vec{x},\vec{x}') = [r + \psi(\vec{x})]\,\delta(\vec{x}-\vec{x}') - c\vec{\nabla}^2 \delta(\vec{x}-\vec{x}')$$

The saddle point approximation to the partition function in eq (1) is exact in the limit $n \to \infty$ and yields

$$\psi = 4u \int \frac{d^Dq}{(2\pi)^D} \frac{T}{r+\psi+cq^2} \qquad (4)$$

and

$$T G^{-1}(\vec{q}) = r + \psi + cq^2 \qquad (5)$$

Apart from the difference in prefactors of u, these two equations are identical to (15.2) and (15.1)

Critical Exponents, Universality, and Scaling

Critical exponents for most experimental second-order transitions differ from those predicted by mean-field theory. The next page table reviews the definitions of critical exponents and critical amplitudes defining the strenght of leading singularities ($t \equiv (T-T_c)/T$). A representative sample of transitions and associated exponents are also given in the next page. It is remarkable that there is very little variation in the critical exponents between systems of fixed spatial dimension D. In $D=3$, $\beta \sim 1/3$, $\gamma \sim 4/3$, $\nu \sim 2/3$, $\alpha \sim 0$. There is, however,

a substantial difference between exponents in two- or three-dimensional systems. The renormalization group introduced by Kenneth Wilson in the early 1970s provided a method for calculating exponents and established that they should depend on the spatial dimension, the symmetry of the order parameter, and the symmetry and range of interactions, but not on the detailed form and magnitude of interactions. Thus, there are <u>universality classes</u>, and all transitions in the same universality class have the same critical exponents.

Another remarkable feature of second-order phase transitions is that not all of the critical exponents are independent. For example $\gamma \simeq 2\nu$, $\alpha + 2\beta + \gamma \simeq 2$. These relations are a result of the homogeneity or scaling properties of correlation functions and thermodynamic properties near $T = T_c$ that can be derived using renormalization group equations. This homogeneity is already present in the mean-field correlation function (III-11.1)

$$G(\vec{x}, 0) \equiv G(|\vec{x}|) = |\vec{x}|^{-(D-2)} Y(|\vec{x}|/\xi) \qquad (1)$$

The only length that appears in this function is ξ. The microscopic length is not important. At $T = T_c$, $\xi = \infty$ and $G \sim |\vec{x}|^{-(D-2)}$ is a homogeneous function of $|\vec{x}|$ and

$$G(|\vec{x}|) = b^{-(D-2)} G(b^{-1}|\vec{x}|) \qquad (2)$$

The susceptibility is

$$\chi = T^{-1} \int d^D x \; G(|\vec{x}|) = T^{-1} \xi^2 \int d^D y \; y^{-(D-2)} Y(y) \sim \xi^2 \sim (T - T_c)^{-\gamma} \qquad (3)$$

From this we see that the divergence of χ is due to the increasing spatial range of correlations in the order parameter field. Eq (3) also says

$$\gamma = 2\nu = 1 \qquad (4)$$

In this context, we see that γ is completely determined by ν and the way G falls off with $|\vec{x}|$ at $T = T_c$.

In critical systems, the behavior of $G(|\vec{x}|)$ at $T = T_c$ is characterized by an exponent η defined via

$$G(|\vec x|) \sim |\vec x|^{-(D-2+\eta)} \tag{1}$$

This sujest a generalization of (20.1) to

$$G(|\vec x|) = |\vec x|^{-(D-2+\eta)}\, Y(|\vec x|/\xi) \tag{2}$$

In this form $G(|\vec x|, t)$ ($t \equiv (T-T_c)/T$) satisfies the generalized homogeneity relation

$$G(|x|, t) = b^{-(D-2+\eta)}\, G(b^{-1}|\vec x|, b^{1/\nu} t) \tag{3}$$

(remember $\xi \sim t^{-\nu}$) and $\chi(\vec q, t) = T^{-1} G(\vec q, t)$ satisfies

$$\chi(\vec q, t) = b^{2-\eta}\, \chi(b\vec q, b^{1/\nu} t) \qquad \forall b \tag{4}$$

When $t=0$ we can choose $b = |\vec q|^{-1} \equiv q^{-1}$ to obtain

$$\chi(\vec q, t=0) \sim q^{-(2-\eta)} \tag{5}$$

since rotational invariance implies that χ should depend only on q. Alternatively we can choose $b \equiv |t|^{-\nu}$, then

$$\chi(\vec q, t) = |t|^{-\gamma}\, \chi(\vec q\, |t|^{-\nu}, t/|t|) \qquad \gamma = (2-\eta)\nu \tag{6}$$

Note that $\chi(\vec q, t)$ depends on $\vec q\,|t|^{-\nu}$ and on $t/|t| = \pm 1$. Thus the scaling function can be different for $t>0$ and $t<0$

$$\chi(\vec q, t) = |t|^{-\gamma}\, X_2(q|t|^{-\nu}) \tag{7}$$

where $X_2(u) = \chi(\vec q u/q, \pm 1)$. When $q\xi = 0$, X_2 depends only on the sign of t. In commonly accepted notation, coefficients for $t<0$ are denoted with primes and those for $t>0$ without primes so that $X_2(0) = \Gamma$ for $t>0$ and $X_2(0) = \Gamma'$ for $t<0$. More generally, as already noted, $X_2(u) = X_2^+(u)$ for $t>0$ and $X_2(u) = X_2^-(u)$ for $t<0$. At $t=0$, $\chi(\vec q, t)$ is independent of t and this is compatible with (7) only if $X_2(u) \sim u^{-\gamma/\nu}$ as $u \to \infty$. Thus

$$X_2(u) = \begin{cases} \Gamma & \text{as } u \to 0,\ t>0 \\ D_\infty u^{-\gamma/\nu} & \text{as } u \to \infty \\ \Gamma' & \text{as } u \to 0,\ t<0 \end{cases} \tag{8}$$

summarizes the limiting forms of $X_2(u)$.

The scaling equation for $G(\vec x, t)$ given in (3) can be used to determine the order parameter exponent β in term of ν and η. Since $\bar{G}(|\bar{x}|) = \langle \phi(\bar{x}) \phi(0) \rangle$ and $\bar{G}(|\bar{x}|) = G(|\bar{x}|) + \langle \phi(\bar{x}) \rangle \langle \phi(0) \rangle$ are identical for $T > T_c$, we expect $\bar{G}$ to obey the same scaling law as G. For $T < T_c$, $\langle \phi(\bar{x}) \rangle$ is non zero, and from this

$$\lim_{|\bar{x}| \to \infty} \bar{G}(|\bar{x}|) \to \langle \phi \rangle^2 \sim |T - T_c|^{2\beta} \tag{1}$$

The choice $b = |t|^{-\nu}$ in (21. 3) leads to

$$\lim_{|\bar{x}| \to \infty} G(|\bar{x}|, t) \to |t|^{(D-2+\eta)\nu} \tag{2}$$

which is independent of $\bar{x}$. Thus comparing (1) and (2)

$$\beta = \frac{1}{2} (D - 2 + \eta)\nu \tag{3}$$

This relation involves D, and relation involving D are called <u>hyperscaling relation</u>. Note that mean-field exponents satisfy this relation only at the upper critical dimension $D_c = 4$. Combining (21. 6) $[\gamma = (2-\eta)\nu]$ and (3) we obtain

$$\gamma + 2\beta = D\nu \tag{4}$$

Again this equation is satisfied by the mean field exponents at $D = D_c = 4$

The existence of a single length scale allows the specific heat exponent α to be determined. Remember C_V is the second derivative of the free energy density f with respect to temperature and diverges as $|t|^{-\alpha}$ as indicated on pag 19. The free energy density has units of energy divided by volume. An energy scale is provided by T_C and a volume by ξ^D. Thus

$$f \sim T_C\, \xi^{-D} \sim T_C\, \xi_0^{-D}\, t^{D\nu} \tag{5}$$

and

$$C_V = -T \frac{\partial^2 f}{\partial T^2} \sim |T - T_c|^{D\nu - 2} \tag{6}$$

and hence

$$\alpha = 2 - D\nu \tag{7}$$

Combining all that

$$\gamma + 2\beta + \alpha = 2 \tag{8}$$

Hyperscaling applies quite generally to transitions that are fluctuation dominated. When it applies, there are only two independent critical exponents, say η and ν, and the critical point is said to obey <u>two scale factor universality</u>

The correlation function $G(|\vec{x}|, t)$ obeys a generalized homogeneity relation in which both $|\vec{x}|$ and t are rescaled

$$G(|\vec{x}|, t) = b^{-(D-2+\eta)} G(b^{-1}|\vec{x}|, b^{1/\nu} t) \tag{1}$$

It is predicted by the renormalization group and found experimentally that any thermodynamic function obeys a homogeneity relation in which t and external fields, such as h, rescale by different factors. The free energy density as a function of external fields satisfies

$$f(t, h) = b^{-D} f(b^{1/\nu} t, b^{\lambda} h) \tag{2}$$

When $h = 0$ this implies $f \sim \xi^{-D}$ as previously predicted (eq 22.5). This equation allows us to calculate the order parameter and the susceptibility

$$\langle \phi \rangle = \frac{\partial f}{\partial h} = b^{-D+\lambda} f'(b^{1/\nu} t, b^{\lambda} h) \tag{3}$$

$$\chi = \frac{\partial^2 f}{\partial h^2} = b^{-D+2\lambda} f''(b^{1/\nu} t, b^{\lambda} h) \tag{4}$$

With $b = t^{-\nu}$ this leads to

$$\langle \phi \rangle = t^{\nu D - \nu\lambda} f'(1, t^{-\nu\lambda} h) \quad , \quad \chi = t^{\nu D - 2\lambda\nu} f''(1, t^{-\nu\lambda} h) \tag{5}$$

and hence

$$\beta = \nu D - \Delta \quad , \quad \gamma = -\nu D + 2\Delta \tag{6}$$

$$\Delta \equiv \lambda\nu = \beta + \nu \qquad (\underline{\text{gap exponent}}) \tag{7}$$

With the choice $b = |t|^{-\nu}$, eqs (2), (3) and (4) can be reexpressed as

$$f(t, h) = |t|^{2-\alpha} \Xi_0(h/|t|^{\Delta}) \quad , \quad \langle \phi \rangle = |t|^{\beta} \Xi_1(h/|t|^{\Delta}) \quad , \quad \chi = |t|^{-\gamma} \Xi_2(h/|t|^{\Delta}) \tag{8}$$

where each Ξ_i is a scaling function whose form depends in general on the sign of t. (see pag 21). This scaling relation for the equation of state has been verified for some systems in great detail.

The Kadanoff Construction

We have seen that thermodynamic functions near second-order critical points exhibit scaling with universal exponents determined by the symmetry of the order parameter. There remains, however, to develop a theoretical understanding of the origin of scaling and universality. We will present here a theory due to Kadanoff that provides a heuristic explanation for the origin of scaling. It also provides a starting point from which to build the Wilson renormalization group, which, as we shall see, permits the actual calculation of critical exponents and scaling functions

To be concrete, let us consider an Ising model with spins $s(\vec{y})$ at sites $\vec{y}$ on a D-dimensional lattice of N sites with lattice constant a. At the critical point, the correlation length ξ is infinite, and the spins at different spatial positions are strongly correlated. Thus, the average spin

$$S_{av}(\vec{x}) = b^{-D} \sum_{y \in C(\vec{x})} s(\vec{y}) \qquad (1)$$

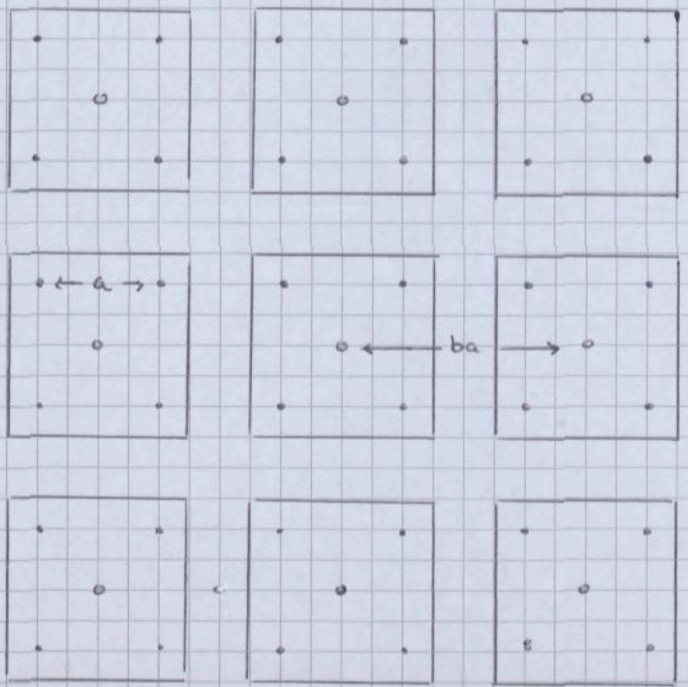
in a cell $C(\vec{x})$ containing b^D sites centered at $\vec{x}$ behaves at the critical point like the spin $s(\vec{y})$. In particular, the correlation function of the average spin dies off with distance with the same power law as the correlation function of the original spins:

$$b^{-2D} \sum_{y_1 \in C(\vec{x}_1)} \sum_{y_2 \in C(x_2)} \langle s(\vec{y}_1)\, s(\vec{y}_2) \rangle = \langle S_{av}(\vec{x}_1)\, S_{av}(\vec{x}_2) \rangle \sim |\vec{x}_1 - \vec{x}_2|^{-2\omega} \qquad (2)$$

where

$$\omega = \frac{1}{2}(D - 2 + \eta) = \beta/\nu \qquad (3)$$

as follows from (21.1) and (22.3)



In the Kadanoff construction, the original lattice is divided into $N' = b^{-D} N$ cells centered on a new lattice with lattice constant $a' = ba$. Each cell centered at $\vec{x}$ in the original lattice contains b^D sites of the original lattice and corresponds to a site in the new lattice. Distances in the new lattice are measured in terms of the new lattice constant a' so that the position of a site in the lattice corresponding to a cell centered at $\vec{x}$ in the original lattice is $\vec{x}' = \vec{x}/b$. At each site $\vec{x}/b$ of the new lattice is a block spin variable

$$S'(\vec{x}') = S'(\vec{x}/b) = b^{\omega_s} S_{av}(\vec{x}) \qquad (1)$$

proportional to the average spin in the cell centered at that site. Since correlation functions of $S_{av}(\vec{x})$ and $S(\vec{y})$ for $\vec{y}$ in a cell centered at $\vec{x}$ scale in the same way at the critical point, it is not really necessary to distinguish between $S_{av}(\vec{x})$ and $S(\vec{x})$ and we can express (1) as

$$S'(\vec{x}/b) = b^{\omega_s} S(\vec{x}) \qquad (2)$$

The exponent ω_s in the b-dependent proportionality constant in the above two equations will be determined shortly. Kadanoff argued that there is a Hamiltonian that is a function of the block spin variables on the new lattice. At the critical point, the new Hamiltonian is in some sense identical to the original Hamiltonian expressed in terms of $S(\vec{y})$ on the original lattice. In particular, the correlation function of the block spin variable as a function of distances measured in the new lattice should be identical to the correlation function of the original spin as a function of distance in the original lattice:

$$\langle S'(\vec{x}_1/b)\, S'(\vec{x}_2/b)\rangle = b^{2\omega_s} \langle S_{av}(\vec{x}_1)\, S_{av}(\vec{x}_2)\rangle \sim \left| \vec{x}_1/b - \vec{x}_2/b \right|^{-2\omega} \qquad (3)$$

Comparing (3) with (24.2) we conclude that

$$\omega_s = \omega \qquad (4)$$

The exponent ω, therefore, determines the relation between original and block spin variables.

The scaling of the external field $h(\vec{y})$ conjugate to the order parameter $s(\vec{y})$ under the above block spin transformation can be determined by requiring that the free energy associated with the external field does not change. If $h(\vec{x})$ varies so slowly in space that it can be considered constant within any cell, then the Hamiltonian describing the interaction of spins with the external field can be expressed either in terms of the original spins on the original lattice or in terms of the block spin on the new lattice.

$$H_{ext} = -\sum_{\vec{y}} h(\vec{y})\, S(\vec{y}) = -\sum_{\vec{x}'} h'(\vec{x}')\, S'(\vec{x}') \qquad (5)$$

since $h(\bar y)$ is slowly varying and can be assumed to have the same value $h(\bar x)$ for each $\bar y \in C(\bar x)$, we can write, using (25.1),

$$H_{ext} = -\sum_{\bar y} h(\bar y)\, s(\bar y) = -\sum_{\bar x} h(x)\, b^{D} \left(b^{-D} \sum_{\bar y \in C(\bar x)} s(\bar y) \right) = -\sum_{\bar x} h(\bar x)\, b^{D-\omega}\, s'(\bar x') \tag{1}$$

and comparing this with (25.5)

$$h'(\bar x') = h'(\bar x / b) = b^{D-\omega}\, h(\bar x) \tag{2}$$

It is easy to verify from the scaling relations presented in the last section that

$$\lambda = D - \omega = (\beta + \gamma)/\nu \tag{3}$$

The exponent λ associated with the external field h is precisely the same exponent that appears in the phenomenological scaling relations of the preceding section (eq (23.2))

Block variables can be defined for any function of the spin operators. For example, the local energy density for a ferromagnetic Ising model is

$$\varepsilon(\bar y) = -\frac{1}{2} J \sum_{\vec\delta} s(\bar y)\, s(\bar y + \bar\delta) \tag{4}$$

where $\vec\delta$ is a nearest neighbor vector. It rescales according to

$$\epsilon'(\bar x / b) = b^{\omega_\epsilon}\, \epsilon_{av}(\bar x) \tag{5}$$

The reduced Hamiltonian $\bar H = H/T$ near the critical point can be expanded in the reduced temperature $t \equiv (T - T_c)/T_c$ as

$$\bar H = \bar H_c + \frac{1}{2} (tJ/T_c) \sum_{\bar y, \bar\delta} s(\bar y)\, s(\bar y + \bar\delta) + O(t^2) =$$

$$= \bar H_c - (t/T_c) \sum_{\bar y} \epsilon(\bar y) \tag{6}$$

where $\bar H_c$ is the reduced Hamiltonian at the critical point. Thus the field conjugated to the energy density is proportional to the reduced temperature, and we can conclude, following the argument leading to eq (2), that

$$t' = b^{D - \omega_\epsilon} t \equiv b^{\lambda_t} t \tag{7}$$

We saw before that the scaling exponent associated with t is the inverse of the correlation length exponent. Thus

$$\lambda_t = \frac{1}{\nu} = d - w_E \tag{1}$$

More generally, there are a wide variety of additional local fields, $\phi_\alpha(\bar{y})$, involving for example multi-spin interactions or anysotropies, that can be constructed from the original spin variables $s(\bar{y})$. External field h_α coupling linearly to $\phi_\alpha(\bar{y})$ can be introduced into $\bar{H}$ by the addition of term

$$\bar{H}_\alpha = - h_\alpha \sum_y \phi_\alpha(y) \tag{2}$$

to the reduced Hamiltonian. Under Kadanoff transformation, the field $\phi_\alpha(\bar{x})$ will transform with a dominant exponent w_α according

$$\phi'_\alpha(\bar{x}/b) = b^{w_\alpha} \phi_\alpha(\bar{x}) \tag{3}$$

Its conjugate field h_α, will then transform as

$$h'_\alpha = b^{\lambda_\alpha} h_\alpha \tag{4}$$

with

$$\lambda_\alpha = D - w_\alpha \tag{5}$$

Note that λ_α can be positive, as it is if ϕ_α is the order parameter or the energy density, or it can be negative. If λ_α is positive, h_α grows with successive rescalings associated with the transformations from the original block spin variables and is a *relevant field*; if λ_α is negative, h_α approaches zero with successive rescalings and is an *irrelevant field*. The field ϕ_α is also classified as relevant or irrelevant if its associated exponent w_α is, respectively, less than or greater than D.

The Hamiltonian can be expressed either in terms of the original variables on a lattice on N sites or in terms of the block variables on a lattice of $N' = b^{-D} N$ sites. The free energy F calculated with either set of variables is the same. This implies a simple relation between the original free energy $f(t, h, h_\alpha) = F/N$ and the block free energy $f'(t', h', h'_\alpha) = F/N'$:

$$N f(t, h, h_\alpha) = b^{-D} N f(t', h', h'_\alpha) \tag{6}$$

or

$$f(t, h, h_\alpha) = b^{-D} f(b^{1/\nu} t, b^{\lambda} h, b^{\lambda_\alpha} h_\alpha) \tag{7}$$

This is precisely the scaling form of the free energy introduced in Eq (23.2). The arbitrary rescaling factor b can be eliminated choosing $b = t^{-\nu}$. In this case

$$f(t, h, h_\alpha) = |t|^{d\nu}\, \mathbb{X}(h|t|^{-\Delta}, h_\alpha |t|^{-\Delta_\alpha}) \qquad (1)$$

depends only on the fields h_α and h in the combinations $h_\alpha / |t|^{\Delta_\alpha}$ and $h/|t|^{\Delta}$, where

$$\Delta_\alpha = \lambda_\alpha \nu \qquad (2)$$

and

$$\Delta = \lambda\nu = \gamma + \beta \qquad (3)$$

If $\lambda_\alpha < 0$, $h_\alpha |t|^{-\Delta_\alpha} = h_\alpha |t|^{|\Delta_\alpha|}$ tends to zero as $t \to 0$, and the field h_α does not affect the leading order singularities in f at the critical point. This is why such fields are called irrelevant. Note that if one is interested in the leading singularities of f, one could have set all irrelevant fields equal to zero initially. This fact, as we shall see, is the essence what is responsible for universality. If two Hamiltonians differ only by irrelevant fields, they will have the same leading critical exponents and thus be in the same universality class.

Though the irrelevant variables do not affect the leading singularities near the critical point, they do give rise to nonzero corrections to leading singularities that are called <u>corrections to scaling</u>. Consider, for example, a system with a single irrelevant variable h_1 with $\lambda_1 \nu = \Delta_1 < 0$. The susceptibility will satisfy a scaling relation

$$\chi = |t|^{-\gamma}\, \mathbb{X}_2(h_1 |t|^{\Delta_1}) \qquad (4)$$

As $t \to 0$, $h_1 |t|^{\Delta_1} \to 0$ for any h_1, and we expand $\mathbb{X}_2$ as a power series to obtain

$$\chi = \Gamma |t|^{-\gamma} + E h_1 |t|^{-\gamma + \Delta_1} + \ldots \qquad (5)$$

where $E = \mathbb{X}_2'(0)$. Thus the irrelevant term leads to subdominant singularities in χ, which may even diverge if $\Delta_1 < \gamma$. The existence of such corrections to scaling considerably complicates the determination of critical exponents from experimental data.

The introduction of block spins that interact via the same Hamiltonian as do the original spins leads naturally to scaling of the free energy. The Kadanoff construction, however, assumes but not demonstrates this, and it does not provide an algorithm for actually calculating any critical exponent. All that is done by Wilson renormalization group.

The One-dimensional Ising model

We are going to introduce the renormalization group through the one-dimensional Ising model.

We will start considering the exact solution. In one-dimensional Ising model, there is a spin variable $\sigma_i = \pm 1$ $i = 1, 2, \ldots, N$ on a one-dimensional lattice. The reduced Hamiltonian is

$$-\bar{H} = -H/T = K \sum_i \sigma_i \sigma_{i+1} + L \sum_i \sigma_i + \sum_i C =$$

$$= K \sum_i \sigma_i \sigma_{i+1} + \frac{1}{2} L \sum_i (\sigma_i + \sigma_{i+1}) + \sum_i C$$

$$= \sum_i \bar{K}(\sigma_i, \sigma_{i+1}) \tag{1}$$

Where $K = J/T$, $L = h/T$ being J the exchange integral and h the external magnetic field. C is a constant that defines the zero of the free energy. It is introduced to facilitate discussion of the renormalization group. The partition function for this model can be calculated exactly using transfer matrices. The exponential of $\bar{K}(\sigma, \sigma')$ is a two by two matrix in the variable σ and σ' with entries

$$e^{\bar{K}(\sigma, \sigma')} = e^{C} \begin{vmatrix} e^{K+L} & e^{-K} \\ e^{-K} & e^{K-L} \end{vmatrix} \equiv \underline{M}(K, L, C) \tag{2}$$

When $h = 0$ and $C = 0$, $\underline{M}(K, L, C)$ takes on a simple form

$$\underline{M}(K, 0, 0) = \cosh K \,(1 + \sigma\sigma' \tanh K) \tag{3}$$

Bulk properties in the thermodynamic limit are insensitive to boundary conditions. Calculations are most easily carried out in a model with periodic boundary conditions in which σ_{N+1} is identical to σ_1 or equivalently in a model in which lattice sites lie on a circle with sites 1 and N connected. In this case there are N bonds connecting N spins and the partition function can be expressed as a trace of a product of transfer matrices

$$Z_N = \sum_{\sigma_1, \sigma_2, \ldots \sigma_N} e^{-\bar{H}} = \sum_{\sigma_1, \sigma_2, \ldots \sigma_N} e^{\bar{K}(\sigma_1, \sigma_2)} e^{\bar{K}(\sigma_2, \sigma_3)} \ldots e^{\bar{K}(\sigma_{N-1}, \sigma_N)} e^{\bar{K}(\sigma_N, \sigma_1)}$$

$$= \mathrm{Tr}\,\{ \underline{M}^N \} = e^{NC} (\lambda_+^N + \lambda_-^N) \tag{5}$$

Where λ_+ and λ_- are the eigenvalues of $\underline{M}(K, L, 0)$:

$$\lambda_\pm = e^{K}\cosh L \pm \left(e^{2K}\sinh^2 L + e^{-2K}\right)^{1/2} \tag{1}$$

If $h = 0$ then

$$\lambda_+ = 2\cosh K \quad , \quad \lambda_- = 2\sinh K \qquad h=0 \tag{2}$$

In the limit $N\to\infty$ the free energy per spin becomes

$$\frac{f}{T} = \lim_{N\to\infty}\frac{1}{N}\left[-\ln Z_N\right] = \lim_{N\to\infty}\frac{1}{N}\left\{-NC - N\ln\lambda_+ - \ln\left(1+(\lambda_-/\lambda_+)^N\right)\right\} \Rightarrow$$

$$\frac{f}{T} = -C - \ln\left\{ e^{K}\cosh L + \left(e^{2K}\sinh^2 L + e^{-2K}\right)^{1/2}\right\} \tag{3}$$

In the low T $(K\to\infty)$, low h $(L\to 0,\ Le^{2K}\ll 1)$ limit

$$f = T\left\{-C - K - \ln\left[\cosh L + e^{-2K}\left(1+\sinh^2 L\, e^{4K}\right)^{1/2}\right]\right\}$$

$$\longrightarrow T\left\{-C-K-\ln\left[1+e^{-2K}+\frac{1}{2}L^2e^{2K}\right]\right\}$$

$$\longrightarrow T\left\{-C-K-e^{-2K}-\frac{1}{2}L^2e^{2K}\right\}$$

$$f - f_0 \longrightarrow -Te^{-2K} - \frac{1}{2}e^{2K}\frac{h^2}{T} \qquad f_0 \equiv -J - TC \tag{4}$$

This shows, as expected, that the ground state energy per spin is J (when $C=0$) and that there is a gap in the excitation spectrum leading to an exponential approach with temperature to the ground state. The susceptibility is

$$\chi = -\frac{\partial^2 f}{\partial h^2} \to \frac{1}{T}e^{2K} \tag{5}$$

Thus, χ diverges as $T\to 0$, indicating that there is a critical point at $T=0$ in the 1D Ising model. In the high temperature limit, $e^K \to 1 + K + K^2/2$. Then

$$f \longrightarrow -T\ln 2 - \frac{1}{2}\frac{h^2}{T} \tag{6}$$

when $C=0$. This implies that

$$\chi = T^{-1} \tag{7}$$

is the familiar Curie spin susceptibility

Correlation functions are also easily calculated in the 1D Ising model. In particular

$$G(m) = \frac{1}{Z_N} \sum_{\sigma_1,\dots,\sigma_N} e^{-\bar{H}} \sigma_1 \sigma_{m+1}$$

$$= \frac{1}{Z_N} \sum_{\sigma_1 \dots \sigma_N} \sigma_1 \, e^{\bar{K}(\sigma_1, \sigma_2)} \dots e^{\bar{K}(\sigma_m, \sigma_{m+1})} \sigma_{m+1} \, e^{\bar{K}(\sigma_{m+1}, \sigma_{m+2})} \dots e^{\bar{K}(\sigma_N, \sigma_1)} =$$

$$= \frac{1}{Z_N} \sum_{\sigma_1, \sigma_{m+1}} \sigma_1 \, e^{m \bar{K}(\sigma_1, \sigma_{m+1})} \sigma_{m+1} \, e^{(N-m) \bar{K}(\sigma_{m+1}, \sigma_1)} \qquad (1)$$

when h and C are zero, we can calculate ((29.3))

$$e^{m \bar{K}(\sigma, \sigma')} = 2^{m-1} (\cosh K)^m (1 + \sigma\sigma' \tanh^m K) \qquad (2)$$

and

$$G(m) = \frac{1}{Z_N} 2^{N-2} (\cosh K)^N \sum_{\sigma_1, \sigma_{m+1}} \sigma_1 (1 + \sigma_1 \sigma_{m+1} \tanh^m K) \sigma_{m+1} (1 + \sigma_{m+1} \sigma_1 \tanh^{N-m} K)$$

$$= \frac{1}{Z_N} (2 \cosh K)^N \tanh^m K (1 + \tanh^{N-2m} K) \qquad (3)$$

When $N \to \infty$ at fixed m, this reduces to

$$G(m) = \tanh^m K \equiv e^{-m/\xi} \qquad (4)$$

where

$$\xi = - [\ln (\tanh K)]^{-1} \xrightarrow[T \to 0]{} \frac{1}{2} e^{2K} \qquad (5)$$

is the correlation length that diverges as the $T=0$ critical point is approached.

We can see now that there is scaling in the vicinity of $T=0$ if functions are expressed in terms of the correlation length. The susceptibility is the sum over m of $T^{-1} G(m)$

$$T\chi = \sum_m G(m) = \sum_m (\tanh K)^m = (1 - \tanh K)^{-1} \longrightarrow \frac{1}{2} e^{2K} = \xi \qquad (6)$$

The scaling relations predict $\chi \sim \xi^{\gamma/\nu}$, and therefore

$$\gamma / \nu = 1 \qquad (7)$$

Near $T=0$, the free energy (30.4) can be expressed as scaling function of L and ξ

$$T^{-1} (f + J) \sim e^{-2K} (1 + \tfrac{1}{2} L^2 e^{2K}) = \xi^{-1} f_a (L\xi) \qquad (8)$$

This is to be identified with the scaling form for the free energy (23.8) expressed in terms of $\xi = |t|^{-\nu}$ rather than reduced temperature.

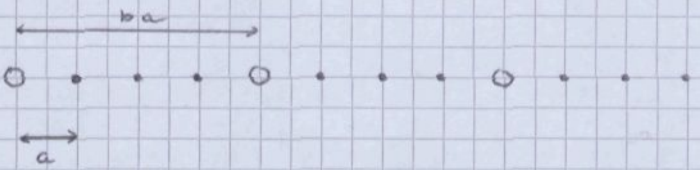
$$f \sim \xi^{-(2-\alpha)/\nu} \mathcal{Y}_0 (L \xi^{\Delta/\nu}) \tag{1}$$

Then

$$\frac{2-\alpha}{\nu} = 1 \qquad \frac{\Delta}{\nu} = \frac{\gamma+\beta}{\nu} = 1 \tag{2}$$

Since $\gamma/\nu = 1$ this leads to $\beta = 0$. In summary, the exact solution of the one dimensional Ising model shows that there is a critical point at $T=0$ at which the correlation length and susceptibility diverge. The free energy and related functions satisfy the standard scaling relations with exponents

$$\frac{\gamma}{\nu} = \frac{2-\alpha}{\nu} = 1 \quad , \quad \eta = 1 \quad , \quad \beta = 0 \tag{3}$$



A new lattice with block spin variables can be obtained in the 1D Ising model merely by tracing (decimating) over blocks of b-1 spins leaving a spin at every bth site. The partition function of the new lattice is identical to that of the original lattice and can be expressed as

$$Z_N(K, L, C) = \mathrm{Tr}\,[\underline{M}^N] = \mathrm{Tr}\,[\underline{M}^b]^{N'} = Z_{N'}(K', L', C') \tag{4}$$

where $N' = N/b$ is the number of site in the lattice. The potentials of the decimated lattice are determined by

$$\underline{M}(K', L', C') = \underline{M}^b (K, L, C) \tag{5}$$

When $L=0$, this leads, with the help of eq. (29.3)

$$\tanh K' = (\tanh K)^b \tag{6}$$

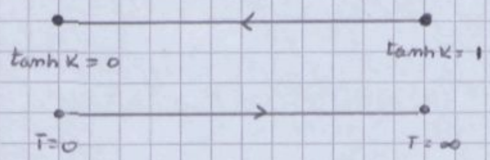
or equivalently

$$K' = \tanh^{-1} [(\tanh K)^b] \tag{7}$$

This is the relation K' and K that is independent of C. This is a renormalization group recursion relation, that can be iterated an arbitrary number of times. After an infinite number of iterations, K reaches a fixed point value K^* determined by $K' = K = K^*$ in eq (6). There are only two fixed point solutions to this equation

$$\tanh K = 0 \quad (T=\infty) \qquad , \qquad \tanh K = 1 \quad (T=0) \tag{8}$$

The function tanh K lies between zero and one. Thus, unless $K=\infty$, tanh K will diminish upon iteration of the recursion relation approaching the fixed point of tanh $K=0$ as the number of iterations tends to infinity. If $K=\infty$, tanh K will remain equal to the unity after any number of iterations of the recursion relation. Since all values of K other than $K=\infty$ flow towards $K=0$, the fixed point tanh $K=0$ $(T=\infty)$ is said to be stable. The set of values of K flowing to $K=0$ is called the basin of attraction of the $K=0$ fixed point. The fixed point at $K=\infty$ is unstable and its basin of attraction consist of a single point $K=\infty$



The stable fixed point describes all finite temperature behavior. It is associated with the paramagnetic phase. The unstable fixed point describes the Ising critical point at $T=0$. The recursion relation can be expressed in terms of the correlation length (31.5)

$$\xi' = \xi / b \tag{1}$$

This is merely the statement that the correlation length measured in term of the lattice constant of the new lattice is b^{-1} times that measured in term of the lattice constant of the original lattice. This is a general property of all renormalization group transformations. The correlation length decreases when the lattice is rescaled. There are only two fixed points to this recursion relation: $\xi=0$ and $\xi=\infty$. The first corresponding to the non-critical high temperature fixed point, and the second corresponds to the critical point.

Let us consider the general case of (32.5) for $b=2$. Let us introduce

$$x = e^{-4K}, \quad y = e^{-2L}, \quad w = e^{-4C} \tag{2}$$

then from (29.3) and (32.5)

$$\begin{aligned} e^{C'-L'} &= e^{2C+L} + e^{2C-L} \\ e^{C'+K'+L'} &= e^{2C+2K+2L} + e^{2C-2K} \\ e^{C'+K'-L'} &= e^{2C-2K} + e^{2C+2K-2L} \end{aligned} \tag{3}$$

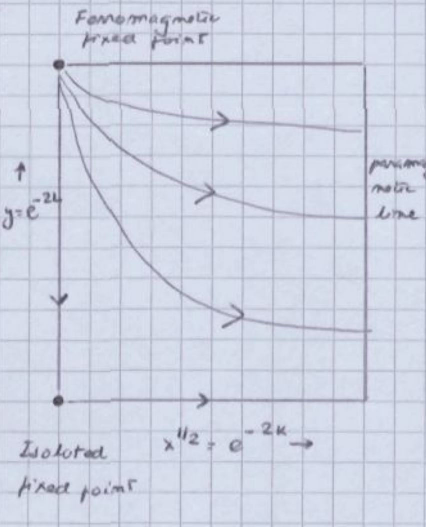
and hence

$$x' = \frac{x(1+y)^2}{(x+y)(1+xy)} \quad , \quad y' = \frac{y(x+y)}{(1+xy)} \tag{1}$$

$$w' = \frac{w^2 x y^2}{(1+y)^2 (x+y)(1+xy)}$$

The equations for x and y do not depend on w and have three fixed points. They are

$$\begin{aligned} &1) \quad x^* = y^* = 0 \\ &2) \quad x^* = 1 \quad , \quad y = \text{arbitrary} \\ &3) \quad x^* = 0 \quad , \quad y^* = 1 \end{aligned} \tag{2}$$



The first fixed point $(x^* = y^* = 0)$ is an isolated fixed point corresponding to a frozen spin configuration (aligned spin at all temperatures as a result of an infinite external field). The second fixed point describes the high temperature paramagnetic phase. The third fixed point describes the $T=0$ critical point that is our primary concern. The recursion relation can be linearized in the vicinity of the third fixed point

$$\begin{aligned} \Delta y' &= (-2L') = 2\Delta y = 2(-2L) \\ \Delta x' &= 4\Delta x \end{aligned} \tag{3}$$

where $\Delta y = y - y^*$ and $\Delta x = x - x^*$. These equations imply that the singular part of the free energy satisfies the scaling law derived from the exact solution of the Ising model. The free energy per spin is

$$f(K,L,C) = -\frac{1}{N} \ln Z_N(K,L,C) = -\frac{1}{bN'} \ln Z_{N'}(K',L',C') \tag{4}$$

where (32.4) has been used. The partition function depends on C only via the prefactor e^{NC} and the free energy per spin can be written as

$$f(K,L,C) = C + f_{\text{sing}}(K,L) \tag{5}$$

Thus, apart from terms involving the nonsingular C, eq (4) and (3) imply

$$f_{\text{sing}}(\Delta x', \Delta y') = \frac{1}{b'} f_{\text{sing}}(b^2 \Delta x, b\Delta y) \tag{6}$$

for rescaling parameter $b = 2$. With $\Delta y = -2L$ and $\Delta x = e^{-4K}$, we then have

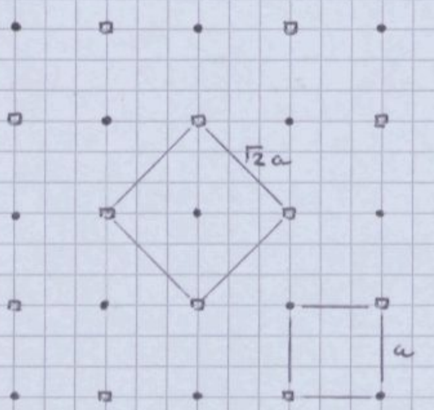
$$f_{sing}(e^{-K}, L) = e^{-2K} f_{sing}(Le^{2K}) \tag{1}$$

in agreement with the exact result (32.1)

The Migdal - Kadanoff Procedure

We are going to study a simple approximate renormalization procedure due to Migdal and Kadanoff that yields nontrivial critical points in dimensions greater than one. We will first apply this procedure to the Ising model.

The 1D Ising model suggests an obvious approach to models in two or more dimensions: decimate spins on a subset of lattice points leaving spins on a new larger lattice-constant lattice interacting via a new Hamiltonian determined by the decimation procedure. Consider, for example, spins σ on a square lattice with lattice constant a and N sites interacting via a reduced Hamiltonian $\bar{H}_N(\sigma, a)$. The square lattice can be decomposed into two sublattices (marked with squares and circles) with lattice constant $ba = \sqrt{2}a$. The trace over spins σ_1 on the sublattice marked with circles yields a new reduced Hamiltonian $\bar{H}_{N'}(\sigma', ba)$ $(N' = b^{-2}N)$ describing interactions among spins σ' on the 'square' sublattice defined via

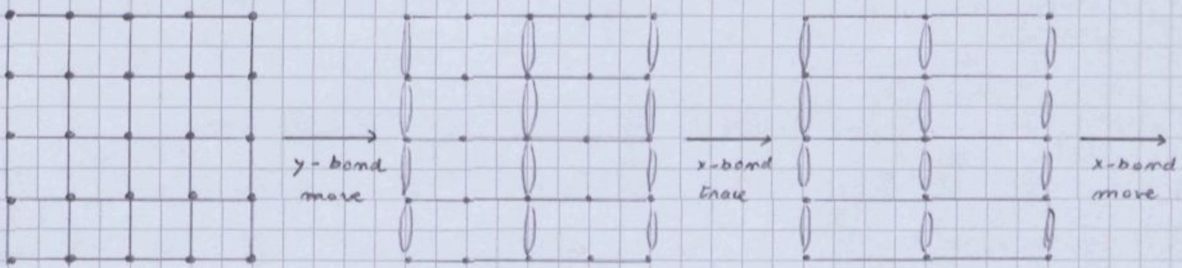


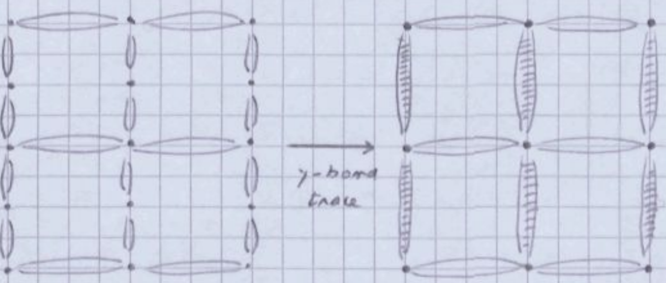
$$e^{-\bar{H}_{N'}(\sigma', ba)} = \mathrm{Tr}_{\sigma_1} e^{-\bar{H}_N(\sigma, a)} \tag{2}$$

Clearly, the partition functions associated with the two Hamiltonians $\bar{H}_N$ and $\bar{H}_{N'}$ are equal since

$$Z_{N'} = \mathrm{Tr}_{\sigma'}[e^{-\bar{H}_{N'}}] = \mathrm{Tr}_{\sigma'}[\mathrm{Tr}_{\sigma_1}[e^{-\bar{H}_N}]] = Z_N \tag{3}$$

Unfortunately, this procedure leads after several iterations to hopelessly complicated Hamiltonians. For example, if H_N is a nearest neighbor Ising Hamiltonian, then $H_{N'}$ will have not only nearest neighbor but also next nearest neighbor and four-spin interactions of the form $H_4 = \sum \sigma_1\sigma_2\sigma_3\sigma_4$, where the sum is over all four-spin plaquettes of the figure. A second decimation applied to $H_{N'}$ produces a new Hamiltonian $H_{b^{-2}N'}$ with further neighbor and more multi-spin interactions. Clearly, some method of truncating the range and complexity of interactions is needed. Various truncation methods, none of which is fully controlled, have been proposed. The simplest, and in many ways the most successful, is the bond-moving scheme introduced by Migdal and elaborated by Kadanoff. The Migdal-Kadanoff procedure is a two step process illustrated for the





square lattice in the figure. First, bonds of nearest neighbor interaction strength K_y on $b-1$ lines parallel to the y-axis are broken and moved to create bonds of strength bK_y at every bth line. The sites originally connected by the broken bonds are no longer connected to their neighbors along the y-axis. Thus spins at these sites can be removed by the one-dimensional decimation procedure discussed in the previous section. The recursion relations of the Migdal-Kadanoff procedure are, therefore

$$K_y' = b\,K_y \qquad\qquad K_x' = R^b(K_x) \tag{1}$$

where R^b is the operator defined by the 1D decimation. In the Ising model

$$R^b(K) = \tanh^{-1}\left[(\tanh K)^b\right] \tag{2}$$

as can be seen from (32.6). The recursion relations (1) have the undesirable property that K_y and K_x are treated unsymmetrically. To restore symmetry at least partially, the same process can be repeated with the lattice rotated by 90° so that the bonds parallel to the x-axis are moved and decimation is along the y-axis.

The extension of the Migdal-Kadanoff approach to arbitrary dimension is straightforward. There are nearest neighbor interactions K_ρ ($\rho = 1, 2, \dots, D$) for bonds parallel to the D axes of a D-dimensional hypercubic lattice. Bond moving and decimation are alternated to produce

$$K_p' = b^{D-p} R^b (b^{p-1} K_p) \tag{1}$$

These equations again do not preserve the equality of coupling constants in different directions. At least partial symmetry can be restored by performing the same series of operations for all equivalent orientations of the lattice. To illustrate how these equations describe a non-trivial critical point at finite temperature, it is more instructive, however, to consider them in the limit where $b \to 1$. Though it is impossible to remove a non-integral number of bonds in the procedure used to obtain (1), this equation has a well defined analytic continuation to all b. Setting

$$b = e^{\delta \ell} \simeq 1 + \delta \ell \tag{2}$$

then

$$R^b [b^{p-1} K_p] = R^{1+\delta\ell} [(1+\delta\ell)^{p-1} K] = \tanh^{-1} \left\{ [\tanh ((1+\delta\ell)^{p-1} K)]^{1+\delta\ell} \right\}$$

$$= \tanh^{-1} \left\{ \tanh [(1 + (p-1)\delta\ell) K] , (1 + \delta\ell \ln (\tanh K) \right\} + O[(\delta\ell)^2] \tag{3}$$

This expansion allows us to calculate the rate of change of K resulting from an infinitesimal change in $b = e^{\delta\ell}$

$$\frac{dK}{d\delta\ell} = (D-1) K + \frac{1}{2} [\sinh 2K \ln (\tanh K)] \tag{4}$$

when $D = 1$, this equation is identical with (32.6) in the limit $b \to 1 + \delta\ell$. For small $D-1$, new structure appears at small $T = K^{-1}$. To see this, we expand (4) to second order in T

$$\frac{dT}{d(\delta\ell)} = -\epsilon T + \frac{1}{2} T^2 \qquad \epsilon \equiv (D-1) \tag{5}$$

The fixed points of our equation occur when $dT/d(\delta\ell) = 0$ and are trivially

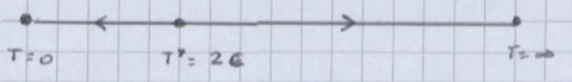
$$T^* = 0 \qquad\qquad T^* = 2\epsilon \tag{6}$$

The fixed point $T = 0$ is stable, whereas the one at $T = 2\epsilon$ is not, as can be seen by the linear stability equation in the vicinity of $T = 2\epsilon$

$$\frac{d\,\delta T}{d\,\delta\ell} = (-\epsilon + T^*)\,\delta T = \epsilon\,\delta T \equiv \lambda_t\,\delta T \tag{7}$$

where $\delta T = T - T^*$. Thus for $T < 2\epsilon$, the flow is towards the fixed point at $T = 0$ describing the ordered phase of the Ising model. For $T > 2\epsilon$, the flow is toward

$T = \infty$, a paramagnetic phase



The Migdal-Kadanoff recursion relations yield a non-trivial fixed point that describes the Ising critical point. To see how the correlation length exponent follows from the above recursion relations, we note that, in the vicinity of $T = T^*$, eq (37.7) can be integrated to yield

$$\delta T(\delta \ell) = e^{\epsilon \delta \ell} \, \delta T(0) \tag{1}$$

But, under the rescaling transformations, the lattice spacing goes from a to $e^{\delta \ell} a$, and the correlation length measured in terms of the new lattice constant is $\xi(\delta \ell) = e^{-\delta \ell} \xi(0)$. On the other hand $\xi(\delta \ell) \propto [\delta T(\delta \ell)]^{-\nu}$. Therefore

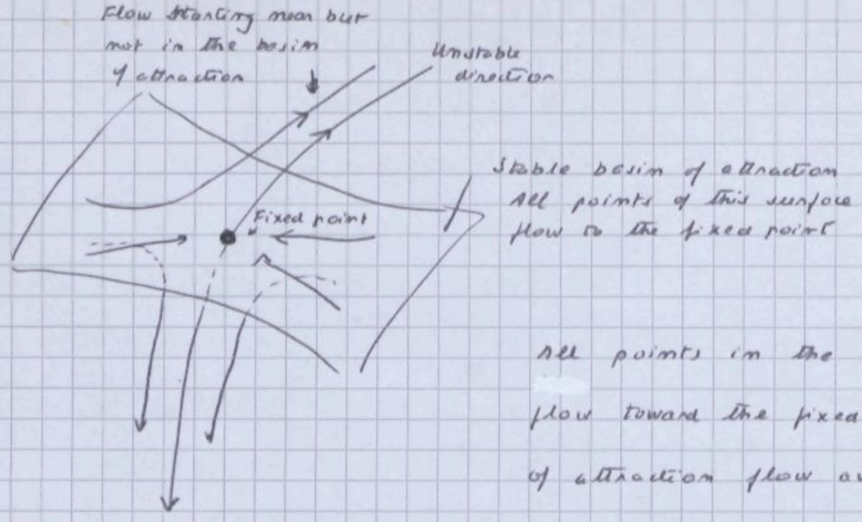
$$\frac{\xi(\delta \ell)}{\xi(0)} = e^{-\delta \ell} = \left(\frac{\delta T(\delta \ell)}{\delta T(0)} \right)^{-\nu} = \left(e^{\lambda_t \delta \ell} \right)^{-\nu} \tag{2}$$

from which we conclude

$$\nu = \frac{1}{\lambda_t} = \frac{1}{\epsilon} \tag{3}$$

Thus stability exponents at fixed points of renormalization group recursion relations are equivalent to critical exponents of the critical point associated with the fixed point

The Migdal-Kadanoff treatment of the Ising model in $1+\epsilon$ dimensions provides a simple illustration of how the renormalization group describes critical points with divergent correlation lengths and how critical exponents can be calculated from the stability exponents of fixed points of recursion relations. This example is, however, artificially simple, and there are a number of features of more complete calculations that are of some interest. In a general renormalization group procedure, there is a Hamiltonian characterized by a set of potentials K_α (e.g. the nearest neighbor, next nearest neighbor, etc interactions in an Ising model). Under rescaling and removal of degrees of freedom, the Hamiltonian changes and is characterized by a new set of potentials K'_α that are functions of the original set (i.e. $K'_\alpha = \Phi_\alpha(K_\alpha)$). The renormalization group equations, therefore, generate flows in a multi-dimensional space, as illustrated schematically in the next page. Fixed points are typically unstable in a few directions in this space and stable in many others. In other words, associated with each fixed point, there is a



local basin of attraction of dimensionality less than or equal to the total dimensionality of the space of potentials

All points in the basin of attraction of a fixed point flow toward the fixed point. Points outside of the basin of attraction flow away. Points outside of the basin of attraction flow away. Flow toward the fixed point is described by negative stability exponents, and flow away from the fixed point is described by positive exponents. Negative exponents are associated with irrelevant potentials (or fields) and positive exponents are associated with relevant potentials. There are two relevant fields: the temperature and the field conjugate to the order parameter, for fixed points describing standard second-order critical points. Higher order critical points, such as tricritical and tetracritical points, have more relevant fields. The positive exponents determine the dominant singularities of the free energy near a critical point. All points near the basin of attraction of a given fixed point flow away from the basin of attraction with rates determined by the positive exponent of the fixed points. Thus, all initial Hamiltonians near the basin of attraction of a fixed point have the same critical properties. This is universality. It follows directly from the renormalization group description of critical points

Momentum Shell Renormalization group

The renormalization group consists of a thinning of degrees of freedom followed by a rescaling of lengths. We have seen in the preceding sections how the thinning procedure can be implemented by tracing over variables on a subset of sites on a lattice. The renormalization group transformations can also be carried out by thinning degrees of freedom in momentum or wave number space rather than in real space. Recall that fields $\phi(\vec{x})$ defined on lattice sites $\vec{x}$ can be expressed in terms of their Fourier transformed fields $\phi(\vec{q})$, where $\vec{q}$ is restricted to the first Brillouin zone (BZ) of the reciprocal lattice. There are exactly N vectors $\vec{q}$ in the first BZ if the direct lattice contains N sites. The volume of the first BZ in a reciprocal lattice associated with a hypercubic direct lattice with lattice constant a is $(2\pi/a)^D$, and the volume per point is $(2\pi/a)^D/N$. In the field theories introduced before, the lattice Brillouin zone is replaced by a spherical zone of the same volume with radius Λ defined via $\Omega_D \Lambda^D/D = (2\pi/a)^D$, where Ω_D is the solid angle of a D-dimensional sphere. The cutoff Λ is proportional to $2\pi/a$. The thinning of degrees of freedom now consists over all fields with wave vector $\vec{q}$ lying in the spherical shell defined by $\Lambda/b < q < \Lambda$. This trace operation defines a new Hamiltonian with $N' = N/b^D$ degrees of freedom and an upper wave number cutoff Λ/b. The reduced cutoff is equivalent to an increased lattice spacing $a' = ba$. The next step is to rescale lengths so that distances are measured in the units natural to the new Hamiltonian. This is done by introducing a rescaled wave vector $\vec{q}' = b\vec{q}$. The cutoff for $\vec{q}'$ is Λ, as it was for $\vec{q}$ in the original system prior to thinning of degrees of freedom. This transformation is equivalent to the transformation $\vec{x}' = \vec{x}/b$ of the real space renormalization procedure. A final step in momentum-space renormalization group procedures is a rescaling of the fields $\phi(\vec{q})$ via $\phi'(\vec{q}'/b) = \zeta \phi'(\vec{q}')$. The choice of the rescaling parameter ζ will be discussed below.

The counting of degrees of freedom is most straightforward if $\phi(\vec{x})$ is defined on a lattice. However, the low wave number Fourier transforms for fields defined on a lattice and those defined at all points in space are the same. Since the operations of the momentum shell renormalization group involve the Fourier transform fields $\phi(\vec{q})$, they can be used for either lattice or continuum models. In what follows, we will adopt the language of the latter approach.

To summarize, there are three steps in momentum-space renormalization group procedures.

1) Thinning of degrees of freedom by tracing over fields $\phi(\vec{q})$ with $\Lambda/b < q < \Lambda$. This leads to a new Brillouin zone with radius (cutoff) Λ/b.
2) Rescaling of lengths via $\vec{q}' = b\vec{q}$. The cutoff associated with $\vec{q}'$ is Λ.
3) Rescaling of fields via $\phi(\vec{q}'/b) = \zeta \phi'(\vec{q}')$.

We now turn to how these renormalization procedures are actually implemented for field theories of the type discussed before. For simplicity, we will restrict our attention for the moment to systems with Ising symmetry and a single scalar field $\phi(\bar{x})$. First, the reduced Hamiltonian $\bar{H}_\Lambda$ with cutoff Λ is expressed as a functional of the fields $\phi(\vec{q})$, which are decomposed into high and low wave number parts

$$\phi(\vec{q}) = \phi^<(\bar{q}) + \phi^>(\bar{q}) \tag{1}$$

where

$$\phi^<(\bar{q}) = \begin{cases} \phi(\bar{q}) & \text{if} \quad 0<q<\Lambda/b \\ 0 & \text{if} \quad \Lambda/b<q<\Lambda \end{cases} \qquad \phi^>(\bar{q}) = \begin{cases} 0 & \text{if} \quad 0<q<\Lambda/b \\ \phi(\bar{q}) & \text{if} \quad \Lambda/b<q<\Lambda \end{cases} \tag{2}$$

Fields $\phi^<(\bar{x})$ and $\phi^>(\bar{x})$ are defined as the Fourier transforms of $\phi^<(\bar{q})$ and $\phi^>(\bar{q})$. Clearly, $\phi(\bar{x}) = \phi^<(\bar{x}) + \phi^>(\bar{x})$. Thinning ~~the~~ degrees of freedom is accomplished by integrating out the fields $\phi^>(\bar{q})$. This leads to a new Hamiltonian

$$\bar{H}_{\Lambda/b}[\phi^<(\bar{q})] \equiv R_b^c\, \bar{H}_\Lambda[\phi(\bar{q})] \tag{3}$$

with cutoff Λ/b defined via

$$e^{-\bar{H}_{\Lambda/b}[\phi^<(q)]} = \int \mathcal{D}\phi^>(\bar{q})\, e^{-\bar{H}_\Lambda[\phi^<(\bar{q})+\phi^>(\bar{q})]} \tag{4}$$

This defines the effect on the Hamiltonian of the operator R_b^c removing degrees of freedom. Next, rescale the momentum via $\vec{q}' = b\bar{q}$ and fields via

$$\phi^<(\vec{q}'/b) = \zeta\, \phi'(\bar{q}') \tag{5}$$

This operation defines a second transformation R_b^s. The combined operation $R_b = R_b^s R_b^c$ is the complete renormalization operation associated with removal of degrees of freedom with wave vectors in the shell $\Lambda/b<q<\Lambda$ and rescaling. The operator R_b applied to $\bar{H}_\Lambda[\phi(\bar{q})]$ leads to a new Hamiltonian with cutoff Λ that is a functional of $\phi'(\bar{q})$:

$$\bar{H}'_\Lambda[\phi'(\bar{q}')] = R_b \bar{H}_\Lambda[\phi(\bar{q})] \tag{6}$$

Equations (1) to (6) provide a formal definition of the momentum space renormalization procedure. We will implement these procedures in some simple situations below.

Before carrying out explicit calculations, however, it is useful to consider how correlation functions can be calculated from $\bar{H}_\Lambda$ or $\bar{H}'_\Lambda$. This will provide us with some guidance as to how the field rescaling factor ζ should be chosen

If $q < \Lambda/b$, then $\phi(\bar{q}) = \phi^{<}(\bar{q}) = \zeta\,\phi'(b\bar{q})$ and we can use either $\bar{H}_\Lambda$ or $\bar{H}_\Lambda'$ to calculate its correlation function. In particular

$$\langle \phi(\bar{q}_1)\,\phi(\bar{q}_2)\rangle = \frac{1}{Z}\int \mathcal{D}\phi(\bar{q})\; e^{-\bar{H}_\Lambda[\phi(\bar{q})]}\;\phi(\bar{q}_1)\,\phi(\bar{q}_2) =$$

$$= \frac{1}{Z'}\int \mathcal{D}\phi'(\bar{q}')\; e^{-\bar{H}'_\Lambda[\phi'(\bar{q}')]}\;\zeta^2\,\phi'(b\bar{q}_1)\,\phi'(b\bar{q}_2) \tag{1}$$

where $\bar{q}' = b\bar{q}$ and

$$Z' = \int \mathcal{D}\phi'(\bar{q}')\; e^{-\bar{H}'_\Lambda[\phi'(\bar{q}')]} \tag{2}$$

The correlation functions are non-zero in translationally invariant systems only if $\bar{q}_1 = -\bar{q}_2$, and they proportional to the Fourier transform $G(\bar{q})$ of the correlation function $\langle\phi(\bar{x})\,\phi(\bar{x}')\rangle$. The first line of (1) is therefore

$$\langle \phi(\bar{q}_1)\,\phi(\bar{q}_2)\rangle = G(\bar{q}_1)\,V\,\delta_{\bar{q}_1,-\bar{q}_2} = G(\bar{q}_1)\,(2\pi)^D\,\delta(\bar{q}_1+\bar{q}_2) \tag{3}$$

Here it is understood that $G(\bar{q}_1)$ depends on the potentials in the original $\bar{H}_\Lambda$. The second line on (1) yields

$$\langle \phi'(b\bar{q}_1)\,\phi'(b\bar{q}_2)\rangle = G'(b\bar{q}_1)\,(2\pi)^D\,\delta(b\bar{q}_1+b\bar{q}_2)\,\zeta^2 \tag{4}$$

where $G'(b\bar{q}_1)$ depends on the potentials in the renormalized Hamiltonian $\bar{H}_\Lambda'$. Then

$$G(\bar{q}) = \zeta^2\, b^{-D}\, G'(b\bar{q}) \tag{5}$$

This equation, when applied at the critical point where both $G(\bar{q})$ and $G'(q)$ are proportional to $q^{-(2-\eta)}$, implies

$$\frac{A}{q^{2-\eta}} = \zeta^2\, b^{-D}\,\frac{A'}{(bq)^{2-\eta}} = \zeta^2\, b^{-(D+2-\eta)}\,\frac{A'}{q^{2-\eta}} \tag{6}$$

where A is the critical point amplitude arising from $\bar{H}_\Lambda$, and A' is that arising from $\bar{H}_\Lambda'$. Thus

$$\zeta^2 = b^{(D+2-\eta)}\,\frac{A}{A'} \tag{7}$$

The ratio A/A' can depend on b. We can, however, use our freedom to choose ζ to fix $A = A'$. In this case

$$\zeta = b^{(D+2-\eta)/2} \tag{8}$$

$$\Rightarrow \quad G(\bar{q}) = A\, q^{-(2-\eta)} \tag{9}$$

when calculated using either $\bar{H}_\Lambda$ or $\bar{H}_\Lambda'$. This is the choice of ζ generally used.

The momentum space renormalization procedure can be carried out exactly for the Gaussian model with reduced Hamiltonian

$$\bar{H}_{0,\Lambda} = \frac{1}{2}\int_{\vec{q}}^{\Lambda} (r + c q^2)\, |\phi(\vec{q})|^2 + V_0 =$$

$$= \frac{1}{2}\int_{\vec{q}}^{<} (r + c q^2)\, |\phi^{<}(\vec{q})|^2 + \frac{1}{2}\int_{\vec{q}}^{>} (r + C q^2)\, |\phi^{>}(\vec{q})|^2 + V_0 =$$

$$= \bar{H}_{0,\Lambda}^{<} + \bar{H}_{0,\Lambda}^{>} + V_0 \tag{1}$$

where V_0 is a constant potential independent of $\phi(\vec{q})$, analogous to the constant C introduced in our discussion of the Ising model, and where

$$\int_{\vec{q}}^{\Lambda} \equiv \int_0^{\Lambda} \frac{d^D q}{(2\pi)^D} \quad , \quad \int_{\vec{q}}^{<} \equiv \int_0^{\Lambda/b} \frac{d^D q}{(2\pi)^D} \quad , \quad \int_{\vec{q}}^{>} \equiv \int_{\Lambda/b}^{\Lambda} \frac{d^D q}{(2\pi)^D} \tag{2}$$

We will use r, c, u as parameters of the reduced Hamiltonian. They differ from the ones used before by a factor $1/T$. The decomposition of $\bar{H}_\Lambda$ into a part depending only on $\phi^<$ and a part depending only on $\phi^>$ makes the evaluation of $\bar{H}_{\Lambda/b}$ trivial:

$$e^{-\bar{H}_{\Lambda/b}[\phi^<(\vec{q})]} = e^{-\bar{H}_{0,\Lambda}^{<}} \int \mathcal{D}\phi^>(\vec{q})\, e^{-\bar{H}_{0,\Lambda}^{>}[\phi^>(\vec{q})]}\, e^{-V_0} = e^{-\bar{H}_{0,\Lambda}^{<} - V_0}\, Z_0^{<} \tag{3}$$

or

$$\bar{H}_{\Lambda/b} = \bar{H}_{0,\Lambda}^{<} + V_0 - \ln Z_0^{>} \tag{4}$$

Then, after rescaling $\phi^<(\vec{q})$ (31.5)

$$\bar{H}'_\Lambda = V_0' + \frac{1}{2}\int_{\vec{q}'}^{\Lambda} (r' + c' q'^2)\, |\phi'(\vec{q}')|^2 \tag{5}$$

where we used $\zeta^2 = b^{D+2}$ since η is trivially zero for this model. The constant part V_0' of $\bar{H}'_\Lambda$ is $V_0 - \ln Z_0^>$ plus an additional term arising from the Jacobian associated with the change of variables $\phi^<(\vec{q}'/b) = \zeta\,\phi'(\vec{q}')$. We will not consider this term further. We note, however, that it is needed in the calculation of the free energy. Furthermore

$$r' = \zeta^2 b^{-D} r = b^2 r \quad , \quad c' = \zeta^2 b^{-(D+2)} c = c \tag{6}$$

The choice of ζ is equivalent to keeping the coefficient c constant. In fact, in the Gaussian model $A = 1/c$. Usually, c is fixed at unity initially, and it remains unity under successive applications of R_b. The correlation length of the rescaled Hamiltonian is

$$\xi' = (c'/r')^{1/2} = b^{-1}(c/r)^{1/2} = b^{-1}\xi \tag{7}$$

This is independent of the choice of ζ.

The recursion relation for r ($r' = b^2 r$) has two fixed points: $r^* = 0$ and $r^* = \infty$. The latter is the high-temperature fixed point describing the disordered phase; the former is the Gaussian fixed point describing the critical point at $T = T_c$. The exponent $\lambda_t = 1/\nu$ controlling the growth of r in the vicinity of the critical fixed point is 2. Thus, the renormalization group predicts

$$\eta = 0 \qquad\qquad \nu = 1/2 \tag{1}$$

The values of η and ν for the Gaussian fixed point are the same as those of the mean-field theory.

As for the Migdal-Kadanoff equations, it is often more elegant to rescale lengths by an infinitesimal amount at each iteration of R_b. This is accomplished by removing an infinitesimal shell of width dl of wave vectors by setting $b = 1 + dl$. A rescaling of lengths by a factor e^l results from repeated rescalings $1 + dl$ as $e^l = \lim_{dl \to 0} (1 + dl)^{1/dl}$. Potentials and correlation length $\xi(l)$ can thus be regarded as continuous functions of l. Recursion relations become differential equations. In particular, from $r' = b^2 r$ with $b = 1 + dl$

$$r(l + dl) = (1 + dl)^2 r(l) \quad \Rightarrow \quad \frac{dr(l)}{dl} = 2 r(l) \quad \Rightarrow$$

$$r(l) = e^{2l} r(0) \tag{2}$$

and

$$e^l = [r(l)/r(0)]^{1/2} \tag{3}$$

Each momentum shell recursion relation can be obtained for the Gaussian model because there is no cross coupling between the high- and low-momentum fields $\phi^>$ and $\phi^<$. The addition of terms to the Gaussian Hamiltonian cubic or higher order in ϕ will lead to such couplings and make the evaluation of $\bar{H}_{\Lambda/b}(\phi^<)$ non-trivial. Before attempting to deal with non-linear terms in $\bar{H}_\Lambda$, let us investigate how potentials scale in the vicinity of the Gaussian fixed point. Consider the Hamiltonian

$$\bar{H}^p_\Lambda = u_p \int d^D x\, \phi^p(x) = u_p \int_{\vec{q}_1, \vec{q}_2, \dots \vec{q}_{p-1}} \phi(\vec{q}_1)\, \phi(\vec{q}_2) \cdots \phi(-\vec{q}_1 - \vec{q}_2 - \cdots - \vec{q}_{p-1}) \tag{4}$$

of order p. We can calculate how u_p scales near the Gaussian fixed point by replacing $\phi(\bar{q})$ by $\phi^<(\bar{q})$ and rescaling $\bar{q}$ according $\bar{q}' = b\bar{q}$ and $\phi^<(\bar{q})$ according to $\phi^<(\bar{q}'/b) = \zeta\,\phi'(\bar{q}')$ with $\zeta = b^{(D+2)/2}$. This leads to

$$u'_p = \zeta^p\, b^{-(p-1)D}\, u_p = b^{[-(p-2)D+2p]/2}\, u_p \equiv b^{\lambda_p} u_p \tag{1}$$

because there are $(p-1)$ $\bar{q}$-integrals in (44.4). The exponent λ_p is $\lambda_1 = (D+2)/2$ for $p=1$ and $\lambda_2 = 2$ for $p=2$. Thus the external field h $(p=1)$ and the temperature r $(p=2)$ are relevant at the gaussian fixed point in all dimensions. For $p > 2$, λ_p is negative, and u_p will flow to zero and is irrelevant at the gaussian fixed point for all dimensions

$$D > D_c(p) = \frac{2p}{p-2} \tag{2}$$

Thus $D_c(3) = 6$, $D_c(4) = 4$ and $D_c(p>4) < 4$

The Hamiltonian $\bar{H}^p_\Lambda$ in eq. (44.4) has a potential of zero range in that it couples fields at a single point in space. Potentials with non-zero range are also permitted by symmetry. For example, $\bar{H}^4_\Lambda$ in (44.4) could be replaced by

$$\bar{H}^4_\Lambda = \int d^Dx_1\, d^Dx_2\, d^Dx_3\, d^Dx_4\; u(\bar{x}_1, \bar{x}_2, \bar{x}_3, \bar{x}_4)\, \phi(\bar{x}_1)\, \phi(\bar{x}_2)\, \phi(\bar{x}_3)\, \phi(\bar{x}_4) \tag{3}$$

$$= \int_{\bar{q}_1 \bar{q}_2 \bar{q}_3 \bar{q}_4} u(\bar{q}_1, \bar{q}_2, \bar{q}_3, \bar{q}_4)\, \phi(\bar{q}_1)\, \phi(\bar{q}_2)\, \phi(\bar{q}_3)\, \phi(\bar{q}_4) \tag{4}$$

where

$$u(\bar{q}_1, \bar{q}_2, \bar{q}_3, \bar{q}_4) = \int d^Dx_1\, d^Dx_2\, d^Dx_3\, d^Dx_4\; e^{-i(\bar{q}_1\bar{x}_1 + \bar{q}_2\cdot\bar{x}_2 + \bar{q}_3\bar{x}_3 + \bar{q}_4\bar{x}_4)}\; u(\bar{x}_1, \bar{x}_2, \bar{x}_3, \bar{x}_4) \tag{5}$$

$$= u(\bar{q}_1, \bar{q}_2, \bar{q}_3)\, (2\pi)^D\, \delta(\bar{q}_1 + \bar{q}_2 + \bar{q}_3 + \bar{q}_4) \tag{6}$$

The local interaction (44.4) is retrieved by setting

$$u(\bar{x}_1\, \bar{x}_2\, \bar{x}_3\, \bar{x}_4) = u\, \delta(\bar{x}_1 - \bar{x}_2)\, \delta(\bar{x}_2 - \bar{x}_3)\, \delta(\bar{x}_3 - \bar{x}_4) \tag{7}$$

Then $u(\bar{q}_1, \bar{q}_2, \bar{q}_3) = u$ is independent of wave number. More generally $u(\bar{q}_1, \bar{q}_2, \bar{q}_3)$ depends on the wave number and, like $r(\bar{q}) = r + cq^2$, can be expanded in powers of wave number

$$u(\bar{q}_1, \bar{q}_2, \bar{q}_3) = u + O(q^2) \tag{8}$$

where q^2 represents any quadratic combination of $\bar{q}_1$, $\bar{q}_2$ and $\bar{q}_3$ permitted by symmetry. Using the scaling procedures of the preceding paragraph, it is straightforward to show that the coefficient of q^2 in $u(\bar{q}_1 \bar{q}_2 \bar{q}_3)$ scales as $\zeta^4 b^{-3D} b^{-2} = b^{2-D}$ and is more irrelevant than $u = u_4$. In general, any potential of any order can be expanded in powers of $\vec{q}$. The lowest power of $\vec{q}$ is always the most relevant.

To simplify our discussion, we will restrict our attention to Ising and O_N models with no external magnetic fields so that no odd order potentials are permitted. In this case, the gaussian fixed point above four dimension is stable with respect to all potentials except the temperature variable r. This means that the gaussian fixed point with its mean-field exponents determines the critical properties of all O_N models above four dimensions. Just below $D=4$, the potential $u_4 = u$ in addition to r is relevant at the gaussian fixed point, and we expect flow away from the gaussian fixed point with $u=0$ to a new fixed point with $u = u^* > 0$, with u^* approaching zero as $D \to 4^-$. Critical exponents at the new fixed point will depend on u^* and will approach mean-field values as $D \to 4^-$. Thus, the momentum shell renormalization group should predict a change from mean-field to non-mean-field critical exponents when D falls below the upper critical dimension $D_c = 4$, in agreement with previous heuristic arguments.

Since u^* is expected to be small near four dimensions, and all other potentials except r are irrelevant, we can restrict our attention to a Hamiltonian parametrized only by r and u, with u small. Other Hamiltonians with more potentials will flow towards this Hamiltonian under successive iterations of the renormalization group. Since u is small, we can calculate the renormalized Hamiltonian $\overline{H}'_\Lambda$ and recursion relations perturbatively in u. Our Hamiltonian is thus

$$\overline{H}_\Lambda = \overline{H}_{0,\Lambda} + \overline{H}^4_\Lambda \qquad (1)$$

where $u_4 = u$. The Hamiltonian $\overline{H}_{\Lambda/b}(\phi^<)$ has the same form as $\overline{H}_\Lambda$:

$$\overline{H}_{\Lambda/b} = \int d^D x \left\{ \frac{1}{2} r^< (\phi^<)^2 + \frac{1}{2} c^< (\vec{\nabla}\phi^<)^2 + u^< (\phi^<)^4 \right\} \qquad (2)$$

It is obtained as before by integrating over $\phi^>$.

$$e^{-[\overline{H}_{\Lambda/b}(\phi^<) - \overline{H}^<_{0,\Lambda}(\phi^<)]} = \int \mathcal{D}\phi^> \, e^{-\overline{H}_{0,\Lambda}(\phi^>)} \, e^{-\overline{H}^4_\Lambda(\phi^< + \phi^>)}$$

$$= Z_0^> \langle e^{-\overline{H}^4_\Lambda} \rangle_> \qquad (3)$$

where

$$Z_0^> = \int \mathcal{D}\phi^> \, e^{-\overline{H}^>_{0,\Lambda}} \qquad (5)$$

and

$$\langle A \rangle_> = \frac{1}{Z_0^>} \int \mathcal{D}\phi^> \, e^{-\bar{H}_{0,\Lambda}} A \tag{1}$$

The exponential in (46.3) can be expanded in powers of $\bar{H}^4_\Lambda$

$$\langle e^{-\bar{H}^4_\Lambda} \rangle_> = 1 - \langle \bar{H}^4_\Lambda \rangle_> + \frac{1}{2} \langle (\bar{H}^4_\Lambda)^2 \rangle_> + \cdots -$$

$$= \exp \left\{ - \langle \bar{H}^4_\Lambda \rangle_> + \frac{1}{2} \left[\langle (\bar{H}^4_\Lambda)^2 \rangle_> - \langle \bar{H}^4_\Lambda \rangle_>^2 \right] + \cdots \right\} \tag{2}$$

The evaluation of $\bar{H}_{\Lambda/b}(\phi^<)$ is thus reduced to the evaluation of averages of powers of $\bar{H}^4_\Lambda$ with respect to $\bar{H}_{0,\Lambda}$.

Consider first $\langle \bar{H}^4_\Lambda \rangle_>$. The binomial expansion of $(\phi^<(\vec{x}) + \phi^>(\vec{x}))^4$ leads to five distinct terms in this quantity, each with a different power of $\phi^>(\vec{x})$. The average with respect to $\bar{H}^>_{0,\Lambda}$ of any odd power of $\phi^>(\vec{x})$ is zero, and hence

$$\langle \bar{H}^4_\Lambda \rangle_> = u \int d^D x \, (\phi^<(\vec{x}))^4 + 6u \int d^D x \, (\phi^<(x))^2 \langle (\phi^>(\vec{x}))^2 \rangle_> + u \int d^D x \, \langle (\phi^>(\vec{x}))^4 \rangle_> \tag{3}$$

This equation and eq. (47.3) for $\bar{H}_{\Lambda/b}$ imply

$$u^< = u \tag{4}$$

$$r^< = r + 12u \int_{\vec{q}}^{>} G_0(\vec{q}) \tag{5}$$

where $G_0(\vec{q}) = (r + q^2)^{-1}$ when $c = 1$ and where $\langle (\phi^>(\vec{x}))^2 \rangle_>$ is expressed as an integral over $\vec{q}$ of $G_0(\vec{q})$. The contribution to $\bar{H}_{\Lambda/b}$ to second order in u can be calculated in much the same way as the first-order contributions after expressing the average of product of $\phi^>(\vec{x})$ in terms of $G_0(\vec{q})$. This calculation can be carried out by perturbation theory. In this way we can calculate $r^<$, $c^<$, $u^<$ and rescale $\phi^<(\vec{q})$ according to $\phi^<(\vec{q}'/b) = \zeta \phi'(\vec{q}')$. This rescaling leads to

$$r' = b^{-D} \zeta^2 r^< \quad , \quad u' = b^{-3D} \zeta^4 u^< \tag{6}$$

The recursion relations for the O_N models are then

$$r' = b^{-D} \zeta^2 \left\{ r + 4(N+2) u \int_{\vec{q}}^{>} G_0(\vec{q}) \right\} \tag{7}$$

$$c' = b^{-(D+2)} \zeta^2 c = 1 \tag{8}$$

$$u' = b^{-3D} \zeta^4 \left\{ u - 4(N+8) u^2 \int_{\vec{q}}^{>} G_0^2(\vec{q}) \right\} \tag{9}$$

Note that we have retained contributions to the recursion relation for u' to second order in u, whereas we have retained only terms linear in u in the equations for r' and c'. This is because as we shall see below, the second-order term in u in the equation for u' is essential if u is to have a non-trivial fixed point. The fixed point value for u is then of order $\epsilon = 4-D$. Thus u^2 terms in r' and c' equations are of order ϵ^2 and do not contribute to order ϵ. There are no terms in the equation for c' that are linear in u. Thus, to keep $c=1$, we choose $\zeta^2 = b^{D+2}$ as in the Gaussian case. Taking the continuum limit $b \to 1+\delta l$ we obtain

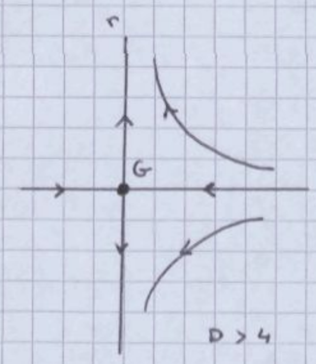
$$\frac{dr(l)}{dl} = 2r(l) + 4K_D(N+2)\frac{u(l)}{1+r(l)} \tag{1}$$

$$\frac{du(l)}{dl} = \epsilon u(l) - 4K_D(N+8)\frac{u^2(l)}{[1+r(l)]^2} \tag{2}$$

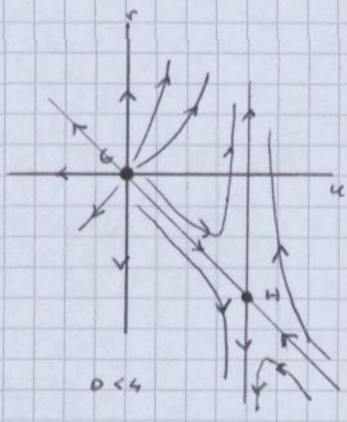
where $\epsilon \equiv 4-D$. For $D \geq 4$ the Gaussian fixed point is stable with respect to u. For $D<4$ there are two fixed points to these equations: the Gaussian fixed point G with $r=u=0$ and a new Heisenberg fixed point with

$$u^* = \frac{\epsilon}{4(N+8)K_D} + O(\epsilon^2) \tag{3}$$

$$r^* = -\frac{1}{2}\frac{N+2}{N+8}\epsilon + O(\epsilon^2)$$



D > 4



D < 4

The Gaussian fixed point is unstable with respect to u and r. The Heisenberg fixed point, on the other hand, is stable with respect to u and unstable with respect to r. Linearizing the recursion relations (1) and (2)

$$\begin{pmatrix} d\delta r/dl \\ d\delta u/dl \end{pmatrix} = \begin{pmatrix} 2-(N+2)\epsilon/(N+8) & 4(N+2)K_D/1+r^* \\ 0 & -\epsilon \end{pmatrix}\begin{pmatrix} \delta r \\ \delta u \end{pmatrix} \tag{4}$$

where $\delta r = r - r^*$ and $\delta u = u - u^*$. The eigenvalues of the matrix above are

$$\lambda_t = \frac{1}{\nu} = 2 - \frac{N+2}{N+8}\epsilon \qquad \lambda_u = -\epsilon \tag{5}$$

The flow is shown in the figure.

V - DYNAMICS : CORRELATION AND RESPONSE

Dynamic Correlation and Response Functions

The time dependence of both classical and quantum systems is governed by equations of motion determined by a Hamiltonian H. A quantum mechanical operator (or field) $\phi_i(\bar{x},t)$ evolves in time in the Heisenberg representation according to

$$\phi_i(\bar{x},t) = e^{iHt/\hbar}\,\phi_i(\bar{x},0)\,e^{-iHt/\hbar} \tag{1}$$

We will often be interested in the frequency rather than time dependence of operators

$$\phi_i(\bar{x},t) = \int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\,e^{-i\omega t}\,\phi_i(\bar{x},\omega) \quad , \quad \phi_i(\bar{x},\omega) = \int_{-\infty}^{+\infty} dt\; e^{i\omega t}\,\phi(\bar{x},t) \tag{2}$$

Time-dependent correlation function can be introduced

$$C_{\phi_i\phi_j}(\bar{x},\bar{x}',t,t') = \langle \phi_i(\bar{x},t)\,\phi_j(\bar{x}',t')\rangle \tag{3}$$

$$\begin{aligned} S_{\phi_i\phi_j}(\bar{x},\bar{x}';t,t') &\equiv \langle (\phi_i(\bar{x}t) - \langle\phi_i(\bar{x}t)\rangle)(\phi_j(\bar{x}'t') - \langle\phi_j(\bar{x}'t')\rangle)\rangle \\ &= C_{\phi_i\phi_j}(\bar{x},\bar{x}',t,t') - \langle\phi_i(\bar{x}t)\rangle\langle\phi_j(\bar{x}'t')\rangle \end{aligned} \tag{4}$$

where $\langle\;\rangle$ signifies an average with respect to an equilibrium ensemble. Unless otherwise specified, we will consider only Hamiltonians that are independent of time so that all thermodynamic averages are invariant under time translations. This implies that $\langle\phi_i(\bar{x},t)\rangle \equiv \langle\phi_i(\bar{x})\rangle$ is independent of time and the correlation functions (3) and (4) depend only of $t-t'$. Then we can write

$$\langle\phi_i(\bar{x},\omega)\,\phi_j(\bar{x}',\omega')\rangle = C_{\phi_i\phi_j}(\bar{x},\bar{x}',\omega)\;2\pi\,\delta(\omega+\omega') \tag{5}$$

where

$$C_{\phi_i\phi_j}(\bar{x},\bar{x}',\omega) \equiv \int_{-\infty}^{+\infty} d(t-t')\,e^{i\omega(t-t')}\,C_{\phi_i\phi_j}(\bar{x},\bar{x}',t-t') \tag{6}$$

The correlation function $C_{\phi_i\phi_j}(\bar{x},\bar{x}',\omega)$ is often called the <u>power spectrum</u> of $\phi_i(\bar{x}t)$. Eq (5) and (6) are generalizations of the <u>Wiener-Khintchine theorem</u> relating a power spectrum to the Fourier transform of a time-dependent correlation function. Similarly we define

$$S_{\phi_i\phi_j}(\bar{x},\bar{x}',\omega) = \int_{-\infty}^{+\infty} d(t-t')\,e^{i\omega(t-t')}\,S_{\phi_i\phi_j}(\bar{x},\bar{x}',t-t') \tag{7}$$

Hence

$$C_{\phi_i\phi_j}(\bar{x},\bar{x}',\omega) = S_{\phi_i\phi_j}(\bar{x},\bar{x}',\omega) + \langle\phi_i(\bar{x})\rangle\langle\phi_j(\bar{x}')\rangle\, 2\pi\,\delta(\omega) \qquad (1)$$

indicating that the $\langle\phi_i(\bar{x})\rangle\langle\phi_j(\bar{x}')\rangle$ term contributes only to the zero-frequency or static part of $C_{\phi_i\phi_j}(\bar{x},\bar{x}',\omega)$.

The dynamic response function $\tilde{\chi}_{\phi_i\phi_j}(\bar{x},\bar{x}',t,t')$ relates changes $\delta\langle\phi_i(\bar{x}t)\rangle$ in averages of time-dependent fields to time-dependent changes $\delta h_j(\bar{x}'t')$ in external fields:

$$\delta\langle\phi_i(\bar{x}t)\rangle = \int d^D x'\, dt'\, \tilde{\chi}_{\phi_i\phi_j}(\bar{x},\bar{x}',t,t')\,\delta h_j(\bar{x}'t') \qquad (2)$$

Disturbances at $\bar{x}'$ can lead to changes in $\langle\phi_i(\bar{x},t)\rangle$ at all points $\bar{x}$. Disturbances at time t' can lead to changes in $\langle\phi_i(\bar{x}t)\rangle$ only for $t > t'$, i.e. the response of $\langle\phi_i(\bar{x},t)\rangle$ to $h_j(\bar{x}'t')$ is <u>causal</u>. This means that $\tilde{\chi}_{\phi_i\phi_j}(\bar{x},\bar{x}',t,t')$ can be nonzero only for $t>t'$. It is useful to write

$$\tilde{\chi}_{\phi_i\phi_j}(\bar{x},\bar{x}',t,t') = 2i\,\theta(t-t')\,\tilde{\chi}''_{\phi_i\phi_j}(\bar{x},\bar{x}',t,t') \qquad (3)$$

We will discuss now some analytic properties of the response function and its Fourier transform with respect to time. In order to keep notation compact, we will consider the response of a single position independent field $\phi(t)$ to its conjugate external field $h(t)$. In this case

$$\langle\delta\phi(t)\rangle = \int_{-\infty}^{+\infty} dt'\, \tilde{\chi}(t-t')\,\delta h(t') \qquad (4)$$

where

$$\tilde{\chi}(t) = 2i\,\theta(t)\,\tilde{\chi}''(t) \qquad (5)$$

Both $\langle\phi(t)\rangle$ and $h(t)$ are real so that $\tilde{\chi}''(t)$ is pure imaginary. We will be interested in response as a function of frequency rather than time. We therefore need to calculate the temporal Fourier transform of $\tilde{\chi}(t)$. Because of the causal step-function prefactor in $\tilde{\chi}(t)$, it is useful to introduce the Laplace transform as a function of complex frequency z:

$$\chi(z) = \int_{-\infty}^{+\infty} dt\, e^{izt}\,\tilde{\chi}(t) = \int_{0}^{\infty} dt\, e^{izt}\,\tilde{\chi}(t) \qquad (6)$$

The function $\tilde{\chi}''(t)$ is bounded as $t\to\infty$ because a disturbance at time $t=0$ will only produce a finite change in $\phi(t)$ at later times. Thus, because t is positive in the above integral, $\chi(z)$ is <u>analytic function in the upper half z-plane</u> ($\mathrm{Im}\, z > 0$)

The function $\tilde{\chi}''(t,t') = \tilde{\chi}''(t-t')$ is bounded, and we can define its Fourier transform with respect to a real frequency variable

$$\tilde{\chi}''(t) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi}\, e^{-i\omega t}\, \chi''(\omega) \quad , \quad \chi''(\omega) = \int_{-\infty}^{+\infty} dt\, e^{+i\omega t}\, \tilde{\chi}''(t) \tag{1}$$

If $\tilde{\chi}''(t)$ approaches a constant as $t \to \infty$, then $\chi''(\omega)$ will have delta-function parts. Quite general arguments discussed below show that $\tilde{\chi}''(t) = -\tilde{\chi}''(-t)$. This, along with the fact that $\tilde{\chi}''(t)$ is pure imaginary, implies that <u>$\chi''(\omega)$ is real and odd in ω</u>. Eqs (2.5), (2.6) and (1) imply

$$\chi(z) = 2i \int_{0}^{\infty} dt\, e^{izt}\, \tilde{\chi}''(t) = 2i \frac{1}{2\pi} \int_{0}^{\infty} dt\, e^{izt} \int_{-\infty}^{+\infty} d\omega\, e^{-i\omega t}\, \chi''(\omega) =$$

$$= \int_{-\infty}^{+\infty} \frac{d\omega}{\pi}\, \frac{\chi''(\omega)}{\omega - z} \qquad \operatorname{Im} z > 0 \tag{2}$$

This representation of $\chi(z)$ shows clearly that it only has singularities on the real axis and is, therefore, analytic in the upper half-plane. The time-dependent function $\tilde{\chi}(t)$ is the inverse Laplace transform of $\chi(z)$

$$\tilde{\chi}(t) = \int_{-\infty+ic}^{+\infty+ic} dz\, e^{-izt}\, \chi(z) \tag{3}$$

where c is a real number. If $t>0$, the contour $[-\infty+ic, +\infty+ic]$ can be closed in the lower half plane, and there is a contribution to the integral at $z=\omega$. If $t<0$, the contour can be closed in the upper half plane where $\chi(z)$ is zero. Thus $\tilde{\chi}(t)$ is zero for $t<0$ and $2i\tilde{\chi}''(t)$ for $t>0$.

The response function $\chi(\omega)$ relating $\langle d\phi(\omega)\rangle$ to $dh(\omega)$ can be obtained by using

$$\theta(t) = \lim_{\epsilon\to 0} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi i}\, e^{i\omega t}\, \frac{1}{\omega - i\epsilon} \qquad \epsilon > 0 \tag{4}$$

From this

$$\langle d\phi(\omega)\rangle = \int_{-\infty}^{+\infty} dt\, e^{i\omega t} \int_{-\infty}^{+\infty} dt'\, 2i\,\theta(t-t')\,\tilde{\chi}''(t-t')\, dh(t') = \chi(\omega)\, dh(\omega) \tag{5}$$

with

$$\chi(\omega) \equiv \lim_{\epsilon\to 0} \chi(\omega + i\epsilon) \qquad \epsilon > 0 \tag{6}$$

where $\chi(\omega+i\epsilon)$ is given by (2) with $z = \omega + i\epsilon$. Thus the response function $\chi(\omega)$ is the limit as z approaches the real axis of the function $\chi(z)$, which is analytic for $\operatorname{Im} z > 0$

When the frequency of the external perturbation tends to zero, $\chi(\omega)$ must reduce to the static susceptibility

$$\lim_{\omega\to 0} \chi(\omega) = \int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \frac{\chi''(\omega')}{\omega'} = \frac{\partial\langle\phi\rangle}{\partial h} = \chi \qquad (1)$$

This is a sum rule relating an integral over $\chi''(\omega)$ to a static quantity. Because the static quantity is a thermodynamic derivative, this is often called the thermodynamic sum rule.

The function $\chi(\omega)$, unlike its static limit, has a real part and an imaginary part, as can be seen using

$$\frac{1}{\omega'-\omega-i\epsilon} = P\frac{1}{\omega'-\omega} + i\pi\,\delta(\omega-\omega') \qquad \epsilon\downarrow 0 \qquad (2)$$

in (3.2) and (3.5)

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega) \qquad (3)$$

where

$$\chi'(\omega) = P\int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \frac{\chi''(\omega')}{\omega'-\omega} \qquad (4)$$

and χ' and χ'' are the real and imaginary parts of the response function. Eq (4) is a Kramers-Kronig relation between real and imaginary parts of $\chi(\omega)$. There is also a complementary relation relating $\chi''(\omega)$ to $\chi'(\omega)$. This is most easily derived by using the Cauchy representation

$$\chi(z) = \oint_{\Gamma} \frac{d\xi}{2\pi i} \frac{\chi(\xi)}{\xi - z} \qquad (5)$$

where Γ is a semicircle in the upper half-plane. If $\chi(z)$ tends to zero faster than $1/z$, as $z\to\infty$ as in most cases of interest, the integral in (5) reduces to the integral $-\infty+i\epsilon'$ to $+\infty+i\epsilon'$, $\epsilon'\downarrow 0$. Then, setting $z=\omega+i\epsilon$, $\epsilon'\ll\epsilon$, we obtain

$$\chi(\omega+i\epsilon) = P\int \frac{d\omega'}{2\pi i} \frac{\chi(\omega'+i\epsilon')}{\omega'-\omega} + \frac{1}{2}\chi(\omega+i\epsilon) \qquad (6)$$

and using (3) and (4)

$$\chi''(\omega) = -P\int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \frac{\chi'(\omega')}{\omega'-\omega} \qquad (7)$$

The above analysis of the response function can be applied in general. Thus the Laplace transform of $\tilde{\chi}_{\phi_i\phi_j}(\vec{x},\vec{x}',t,t')$ satisfies

$$\chi_{\phi_i\phi_j}(\bar{x},\bar{x}',z) = \int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\,\frac{\chi''_{\phi_i\phi_j}(\bar{x},\bar{x}',\omega)}{\omega - z} \tag{1}$$

Following (3.6) and (4.3)

$$\chi_{\phi_i\phi_j}(\bar{x},\bar{x}',\omega) = \chi'_{\phi_i\phi_j}(\bar{x},\bar{x}',\omega) + i\,\chi''_{\phi_i\phi_j}(\bar{x},\bar{x}',\omega) \tag{2}$$

where $\chi'_{\phi_i\phi_j}(\bar{x},\bar{x}',\omega)$ is related to $\chi''_{\phi_i\phi_j}(\bar{x},\bar{x}',\omega)$ by a Kramers-Kronig relation. Later on we will see that χ' and χ'' are the real and imaginary parts of χ if the system is invariant under time reversal. The zero-frequency limit of (2) leads to the thermodynamic sum rule

$$\chi_{\phi_i\phi_j}(\bar{x},\bar{x}') = \frac{\partial\langle\phi_i(\bar{x})\rangle}{\partial h_j(\bar{x}')} = \int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\,\frac{\chi''_{\phi_i\phi_j}(\bar{x},\bar{x}',\omega)}{\omega} \tag{3}$$

The Harmonic Oscillator

The dynamical properties of condensed matter systems are very often dominated by harmonic oscillator-like models. The Hamiltonian of an undamped oscillator of mass m and spring constant k is

$$H = \frac{1}{2m}p^2 + \frac{1}{2}kx^2 \tag{4}$$

The equations of motion are

$$\begin{aligned}\dot{x} &= v = \{H, x\} = \left(\frac{\partial H}{\partial p}\frac{\partial x}{\partial x} - \frac{\partial H}{\partial x}\frac{\partial x}{\partial p}\right) = \frac{1}{m}p\\ \dot{p} &= \{H, p\} = -\frac{\partial H}{\partial x} = -kx\end{aligned} \tag{5}$$

The mode structure implied by these equations is obtained by assuming that both $x(t)$ and $p(t)$ are proportional to $e^{-i\omega t}$ and solving the resulting characteristic equation

$$\det\begin{vmatrix} -i\omega & -1/m \\ k & -i\omega \end{vmatrix} = -\omega^2 + m/k = 0 \tag{6}$$

There are two solutions to this equation

$$\omega = \pm\,\omega_0 = \pm\sqrt{k/m} \tag{5}$$

Each of these solutions corresponds to a <u>mode</u> of the harmonic oscillator. Note that there is a mode per degree of freedom (x and p). The time dependence of each degree of freedom is governed by a <u>first-order</u> differential equation in time. Thus, there is one mode per first-order differential equation in the equations of motion. This property is quite general. The variables x(t) and p(t) have opposite signs under the operation of time reversal. The Hamiltonian and its associated equations of motion are invariant under time reversal. The equations of motion relate the time derivative of a variable with one sign under time reversal to the variable with the opposite sign. These relations lead to the off-diagonal terms in the characteristic equation and to *real* and *non-zero solutions* to the characteristic equations. This property is again quite general: modes at non-zero real frequency invariably arise from the coupling of variables with opposite sign under time reversal via first-order differential equations in time. Obviously the first order equations (5.5) can be converted into a second-order differential equation of Newton's second law

$$\ddot{x} + \omega_0^2 x = 0 \tag{1}$$

This equation is invariant under time reversal and predicts modes with frequencies $\pm\omega_0$.

To introduce damping in an intuitive way, we place the particle of mass m into a viscous fluid. In constant motion, it experiences a friction force proportional to its velocity. This force can be written as

$$f_{vis} = -\alpha v \tag{2}$$

where α is the *friction constant*, and α^{-1} is the *mobility*. For a sphere of radius a moving in a fluid with *shear viscosity* η, α is given by Stoke's law

$$\alpha = 6\pi\eta a \tag{3}$$

In the presence of a viscous force and an external force f, Newton's equation for a one-dimensional harmonic oscillator becomes

$$\ddot{x} + \omega_0^2 x + \gamma \dot{x} = f/m \tag{4}$$

where $\gamma = \alpha/m$. The mode structure of the damped harmonic oscillator is determined by the equation

$$-\omega^2 + \omega_0^2 + i\gamma\omega = 0 \tag{5}$$

with solutions

$$\omega = \pm\left[\omega_0^2 - (\gamma^2/4)\right]^{1/2} - i\gamma/2 \equiv \pm\omega_1 - i\gamma/2 \tag{6}$$

If $\omega_0^2 > \gamma^2/4$, ω_1 is real, and solutions for x(t) will oscillate with frequency ω_1 and decay in time with time constant $\tau = 2/\gamma$. If $\omega_0^2 < \gamma^2/4$, is imaginary, and there will be no oscillatory component of x(t). In this case, the oscillator is said to be *overdamped* with inverse decay time

$$\tau_f^{-1} = \frac{1}{2}\gamma\left\{1 + (1 - 4\omega_0^2\gamma^{-2})^{1/2}\right\} \xrightarrow{\omega_0 \ll \gamma/2} \gamma$$

$$\tau_s^{-1} = \frac{1}{2}\gamma\left\{1 - (1 - 4\omega_0^2\gamma^{-2})^{1/2}\right\} \xrightarrow{\omega_0 \ll \gamma/2} \omega_0^2/\gamma = k/\alpha \qquad (1)$$

When $\omega_0^2 \ll (\gamma/2)^2$, the fast decay time τ_f is much shorter than the slow decay time τ_s. Thus for times long compared to τ_f, the first mode can be neglected. This corresponds to neglect the inertial term $m\ddot{x}$ in (64). We have then

$$\alpha\dot{x} = -kx + f \qquad (2)$$

This approximated equation of motion is often written as

$$\dot{x} = -\frac{k}{\alpha}x + \frac{1}{\alpha}f = -\Gamma\frac{dH_T}{dx} \qquad \Gamma \equiv \alpha^{-1}, \quad H_T = H - fx \qquad (3)$$

where H_T is the total Hamiltonian including $H_{ext} = -fx$. It is very useful for describing the dynamics of systems, such as polymers in solution, dominated by viscous effects.