10. Interacting matter

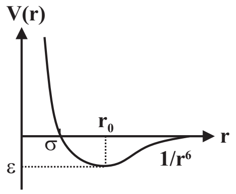
10.1. Classical real gas

We take into account the mutual interactions of atoms (molecules)
The Hamiltonian operator is

$$H^{(N)} = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} + \sum_{i<j} v(r_{ij}), \quad r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|.$$

For example, for noble gases a good approximation of the interaction potential is the *Lennard-Jones* 6–12 -potential

$$v(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right].$$



We evaluate the partition sums in the classical phase space. The canonical partition function is

$$\begin{aligned} Z_N(T,V) = Z(T,V,N) &= \mathrm{Tr}\,_N e^{-\beta H^{(N)}} \\ &\xrightarrow[\text{classical limit, Maxwell-Boltzmann}]{} \frac{1}{N!} \int d\Gamma\, e^{-\beta H}. \end{aligned}$$

Because the momentum variables appear only quadratically, they can be integrated and we obtain

$$\begin{aligned} Z_N &= \frac{1}{N!}\frac{1}{h^{3N}} \int \cdots \int d\boldsymbol{p}_1 \cdots d\boldsymbol{p}_N\, d\boldsymbol{r}_1 \cdots d\boldsymbol{r}_N \times \\ &\quad \exp\left[-\beta \sum_i \frac{p_i^2}{2m} + \sum_{i<j} v(r_{ij}) \right] \\ &= \frac{1}{N!}\frac{1}{\lambda_T^{3N}} Q_N(T,V), \end{aligned}$$

where

$$\lambda_T = \left(\frac{h^2}{2\pi m k_B T} \right)^{1/2}$$

is the thermal wave length and

$$Q_N(T,V) = \int d\boldsymbol{r}_1 \cdots d\boldsymbol{r}_N\, e^{-\beta \sum_{i<j} v(r_{ij})}.$$

The grand canonical partition function is

$$\begin{aligned} Z(T,V,\mu) &= \sum_N e^{\beta\mu N} Z_N(T,V) \\ &= \sum_N \frac{1}{N!} \left(\frac{z}{\lambda_T^3} \right)^N Q_N(T,V), \end{aligned}$$

when $z = e^{\beta\mu}$ is the fugacity.
We define an intensive function

$$\omega(z,T) = \frac{1}{V} \ln Z(T,V,\mu).$$

The grand potential is now

$$\Omega = -k_B T V \omega(z,T)$$

and

$$\begin{aligned} \frac{p}{k_B T} &= -\frac{\Omega}{V} = \omega(z,T) \\ \rho &= \frac{N}{V} = z \frac{\partial \omega(z,T)}{\partial z}. \end{aligned}$$

Eliminating z we can write the equation of state as

$$p = k_B T \varphi(\rho, T).$$

Expanding φ as the power series of ρ we end up with the virial expansion.

Ursell-Mayer graphs

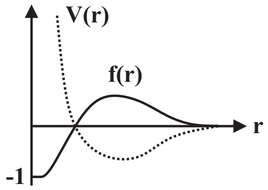
Let's write

$$\begin{aligned} Q_N &= \int d\boldsymbol{r}_1 \cdots \boldsymbol{r}_N \prod_{i<j} e^{-\beta v(r_{ij})} \\ &= \int d\boldsymbol{r}_1 \cdots \boldsymbol{r}_N \prod_{i<j} (1 + f_{ij}), \end{aligned}$$

where

$$f_{ij} = f(r_{ij}) = e^{-\beta v(r_{ij})} - 1$$

is *Mayer's function.*



The function f is bounded everywhere and it has the same range as the potential v. In general f is small (compared to 1), when r_{ij} is in the relevant range.
If $v(r) \equiv 0$, then $f \equiv 0$ and $Q_N = Q_N^0 = V^N$ i.e. we end up with the Maxwell-Boltzmann ideal gas. We write Q_N as the power series of Mayer functions f_{ij}:

$$\begin{aligned} Q_N &= \int d\boldsymbol{r}_1 \cdots \boldsymbol{r}_N \Bigg[1 + \sum_{(ij)} f_{ij} + \sum_{(ij)<(kl)} f_{ij} f_{kl} \\ &\quad \sum_{(ij)<(kl)<(mn)} f_{ij} f_{kl} f_{mn} + \cdots \Bigg]. \end{aligned}$$

Here

$$\begin{aligned} (ij) &\Leftrightarrow \text{pair } 1 \le i < j \le N, \frac{1}{2}N(N-1)\,\text{terms} \\ (ij) < (kl) &\Leftrightarrow (ij) \ne (kl) \text{ and only one} \\ &\quad\ \text{of terms } (ij)(kl), (kl)(ij) \text{ selected,} \\ &\quad\ \frac{1}{2}[\frac{1}{2}N(N-1)][\frac{1}{2}N(N-1) - 1]\,\text{terms} \\ &\vdots\ . \end{aligned}$$

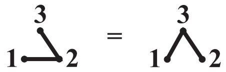
Graphs are build from the elements

$$\begin{aligned} \bullet^{i} &\Leftrightarrow \int d\boldsymbol{r}_i \\ {}_{i}\!\underline{\quad}\!{}_{j} &\Leftrightarrow f_{ij}. \end{aligned}$$

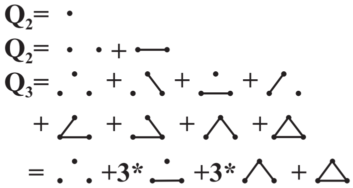
Permutations of particles do not change the values of the graphs, for example

$$\int\!\!\int\!\!\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3 f_{12} f_{23} = \int\!\!\int\!\!\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3 f_{13} f_{23},$$

as we can see by exchanging the integration variables $\boldsymbol{r}_2$ and $\boldsymbol{r}_3$.



Example:



We classify the graphs:

- in *connected (coupled) graphs* or a *clusters* one can get from every black dot (●) to every black dot following a chain of lines (▁).
- in *unconnected (uncoupled) graphs* there are parts that are not connected by a line (▁).

It is easy to see that an unconnected graph can be factorized as a product of its connected parts.
The sum of graphs of l connected points is called an l*-cluster*.
We define q_l so that it is the sum of all l-clusters, e.g.

$$\begin{aligned} q_1 &= \int d\boldsymbol{r}_{=}V \\ q_2 &= \int\!\!\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 f_{12} \\ q_3 &= \int\!\!\int\!\!\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3 (3 f_{12} f_{13} + f_{12} f_{23} f_{13}). \end{aligned}$$

One can show that

$$Q_N = \sum_{\{\nu_l\}} \delta\left(N, \sum_l l\nu_l\right) \frac{N!}{\prod_l (l!)^{\nu_l}} \prod_l \frac{q_l^{\nu_l}}{\nu_l!}.$$

Here

- ν_l tells the number of l-clusters.
- $\sum_{\{\nu_l\}} = \sum_{\nu_1=0}^{\infty} \sum_{\nu_2=0}^{\infty} \sum_{\nu_3=0}^{\infty} \cdots$
- $\delta\left(N, \sum_l l\nu_l\right)$ restricts the number of the integration variables (black dots ●) to N.
- $\frac{N!}{\prod_l (l!)^{\nu_l}}$ tells how many ways there are to pick the clusters from the set of N points.
- Everyone of the possible $\nu_l!$ permutations of the l-clusters gives an identical contribution and must be counted only once. That's why the divisor $\nu_l!$ in the factor $\frac{q_l^{\nu_l}}{\nu_l!}$.

Denote

$$\xi = \frac{z}{\lambda_T^3}.$$

The grand canonical partition function is now

$$\begin{aligned} Z(T,V,\mu) &= \sum_N \frac{1}{N!} \xi^N Q_N \\ &= \sum_{\{\nu_l\}} \prod_l \left[\frac{q_l^{\mu_l}}{\nu_l!(l!)^{\nu_l}}\right] \times \\ &\qquad \sum_N \frac{1}{N!} \xi^N N! \delta\left(N, \sum_l l\nu_l\right) \\ &= \sum_{\{\nu_l\}} \prod_l \left[\frac{q_l^{\nu_l}}{\nu_l!(l!)^{\nu_l}}\right] \xi^{\sum_l l\nu_l} \\ &= \sum_{\{\nu_l\}} \prod_l \frac{1}{\nu_l!} \left[\frac{q_l}{l!} \xi^l\right]^{\nu_l} \\ &= \prod_l \sum_{\nu_l=0}^{\infty} \frac{1}{\nu_l!} \left[\frac{q_l}{l!} \xi^l\right]^{\nu_l} = \prod_l e^{\frac{q_l}{l!} \xi^l}. \end{aligned}$$

We end up with the *cumulant expansion* of the grand canonical partition sum:

$$Z(T,V,\mu) = \sum_{N=0}^{\infty} \frac{1}{N!} \xi^N Q_N = \exp\left[\sum_{l=0}^{\infty} \frac{1}{l!} \xi^l q_l\right].$$

$\sum$ graphs = exp[$\sum$ connected graphs]

Virial expansion

In the cumulant expansion every q_l is proportional to the volume V. We define the *cluster integral* b_l depending only on temperature so that

$$\begin{aligned} b_l &= \frac{1}{l!} \frac{1}{V} q_l \\ &= \frac{1}{l!} \frac{1}{V} \int d\boldsymbol{r}_1 \cdots \int d\boldsymbol{r}_l \left[\prod_{i<j} (1 + f_{ij})\right]_{\text{connected graphs}}. \end{aligned}$$

Now

$$\omega(z,T) = \frac{1}{V} \ln Z(T,V,\mu) = \sum_{l=1}^{\infty} \xi^l b_l(T).$$

For the density we get

$$\rho = z \frac{\partial \omega}{\partial z} = \sum_{l=1}^{\infty} l \xi^l b_l(T).$$

We solve ξ as the power series of the density ρ, substitute it into the expression of ω and collect equal powers of ρ together and end up with the *virial expansion*

$$p = k_B T \omega(z,T) = k_B T [\rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots].$$

The virial coefficients $B_n(T)$ are now functions of the cluster integrals $\{b_l(T) | l \le n\}$, e.g.

$$\begin{aligned} B_2(T) &= -b_2(T) = \frac{1}{2} \int d\boldsymbol{r} \left[1 - e^{-\beta v(r)}\right] \\ B_3(T) &= 4b_2^2 - 2b_3 \\ B_4(T) &= -20 b_2^3 + 18 b_2 b_3 - 3 b_4. \end{aligned}$$

Second virial coefficient

We assume that

- the interaction has a *hard core*, i.e. the interaction is strongly repulsive when $r \lesssim \sigma$.
- on the average, the interaction is attractive when $r \gtrsim \sigma$, but the temperature is so high that $\beta v(r) \ll 1$ there.

Now

$$e^{-\beta v(r)} \approx \begin{cases} 0, & \text{when } r \lesssim \sigma \\ 1 - \beta v(r), & \text{when } r \gtrsim \sigma, \end{cases}$$

and

$$\begin{aligned} B_2 &= 2\pi \int_0^\infty dr\, r^2 \left[1 - e^{-\beta v(r)}\right] \\ &\approx 2\pi \int_0^\sigma dr\, r^2 + 2\pi \int_\sigma^\infty dr\, r^2 \beta v(r) \\ &= b - \frac{a}{T}. \end{aligned}$$

Here

$$\begin{aligned} b &= \frac{2\pi}{3} \sigma^3 \\ a &= -2\pi \int_\sigma^\infty dr\, r^2 v(r) > 0. \end{aligned}$$

With these approximations we end up with the van der Waals equation of state. For hard spheres the virial coefficients can be calculated exactly. Denoting

$$b_0 = \frac{2\pi}{3} \sigma^3$$

we get

n	B_n
2	b_0
3	$\frac{5}{8} b_0^2$
4	$0.287\, b_0^3$
5	$0.110\, b_0^4$
6	$0.039\, b_0^5$

Low density gas

We write

$$\begin{aligned} Q_N = & \int d\boldsymbol{r}_1 \cdots \int d\boldsymbol{r}_{N-1} e^{-\beta \sum_{i<j}^{N-1} v_{ij}} \times \\ & \int d\boldsymbol{r}_N e^{-\beta \sum_i^{N-1} v(r_{iN})}. \end{aligned}$$

With the help of Mayer's functions this is

$$\begin{aligned} \exp\left[-\beta \sum_i^{N-1} v_{iN}\right] &= \prod_i^{N-1} \left[1 + f_{iN}\right] \\ &= 1 + \sum_i^{N-1} f(r_{iN}) \\ &\quad + \sum_{i<j}^{N-1} f(r_{iN}) f(r_{jN}) + \cdots. \end{aligned}$$

Choose randomly two particles, i and j say. Now

- the function $f(r_{iN})$ deviates from zero only in the range of the interaction.
- the term $f(r_{iN}) f(r_{jN})$ can deviate from zero only if particles i and j are within the range of N.
- the probability that the particle j is in the range of the particle i is $\propto \frac{1}{V}$.
- if the particle j is in the range of the particle i, then the integral over the variable $\boldsymbol{r}_N$ is $\propto 1$, since the function f has a short range.

We see, that

$$\int d\boldsymbol{r}_N \sum_{i<j}^{N-1} f(r_{iN}) f(r_{jN}) \propto \sum_{i<j}^{N-1} \frac{1}{V} = \mathcal{O}\left(\frac{N^2}{V}\right).$$

In the low density limit we get

$$\begin{aligned} \int d\boldsymbol{r}_N e^{-\beta \sum_i^{N-1} v_{iN}} &= V + (N-1) \int d\boldsymbol{r}\, f(r) \\ &\quad + \mathcal{O}\left(\frac{N^2}{V}\right) \\ &\approx V + (N-1) \int d\boldsymbol{r}\, f(r). \end{aligned}$$

Iterating we have

$$\begin{aligned} Q_N &\approx \int d\boldsymbol{r}_1 \cdots \int d\boldsymbol{r}_{N-2} e^{-\beta \sum_{i<j}^{N-2} v_{ij}} \times \\ &\quad \left[V + (N-2) \int d\boldsymbol{r}\, f(r)\right] \times \\ &\quad \left[V + (N-1) \int d\boldsymbol{r}\, f(r)\right] \\ &\approx \cdots \approx V^N \prod_{n=0}^{N-1} \left[1 + \frac{n}{N} \rho \int d\boldsymbol{r}\, f(r)\right], \end{aligned}$$

where $\rho = N/V$. Now

$$\lim_{x \to 0} \left(1 + \frac{j}{N} x\right) \left(1 + \frac{N-j}{N} x\right) \approx \left(1 + \frac{x}{2}\right)^2$$

so

$$\lim_{x \to 0} \prod_{n=0}^{N-1} \left[1 + \frac{nx}{N}\right] \approx \left[1 + \frac{x}{2}\right]^N \approx e^{\frac{xN}{2}},$$

i.e. in the low density limit

$$Q_N \approx V^N e^{\frac{1}{2} N \rho \int d\boldsymbol{r}\, f(r)} = Q_N^{(0)} e^{\frac{1}{2} N \rho \int d\boldsymbol{r}\, f(r)}.$$

Here $Q_N^{(0)} = V^N$ is Q_N for the ideal gas. Since the canonical partition sum was

$$Z_N = \frac{1}{N! \lambda_T^{3N}} Q_N,$$

the energy can be written like

$$\begin{aligned} F(T, V, N) &= -k_B T \ln Z_N \\ &= F_0(T, V, N) - \frac{N^2 k_B T}{2V} \int d\boldsymbol{r}\, f(r), \end{aligned}$$

where $F_0(T,V,N)$ is the free energy of the ideal gas. The equation of state is now

$$\begin{aligned} p &= -\frac{\partial F}{\partial V} = -\frac{\partial F_0}{\partial V} - \frac{N^2 k_B T}{2V^2}\int d\boldsymbol{r}\, f(r) \\ &= \frac{N k_B T}{V}\left[1 - \frac{1}{2}\rho\int d\boldsymbol{r}\, f(r)\right]. \end{aligned}$$

Comparing with the virial expansion we see that the second virial coefficient is

$$B_2 = -\frac{1}{2}\int d\boldsymbol{r}\, f(r) = \frac{1}{2}\int d\boldsymbol{r}\left[1 - e^{-\beta v(r)}\right].$$

10.2. Correlation functions

Static linear response

Let $\hat{H}_0$ be the Hamiltonian of a system in the equilibrium and

$$\hat{\rho}_0 = \frac{1}{Z_0}\, e^{-\beta \hat{H}_0}$$

the corresponding density operator. We disturb the system with external time independent fields a_α, which couple to observables $\hat{A}_\alpha$ of the system:

$$\hat{H} = \hat{H}_0 - \sum_\alpha \hat{A}_\alpha a_\alpha.$$

The corresponding density operator is

$$\hat{\rho} = \frac{1}{Z}\, e^{-\beta \hat{H}},$$

where

$$Z = \mathrm{Tr}\, e^{-\beta \hat{H}} = \mathrm{Tr}\, e^{-\beta(\hat{H}_0 - \sum_\alpha \hat{A}_\alpha a_\alpha)}.$$

Now

$$\begin{aligned} \frac{\partial Z}{\partial a_\alpha} &= \beta \mathrm{Tr}\, \hat{A}_\alpha e^{-\beta(\hat{H}_0 - \sum_\alpha \hat{A}_\alpha a_\alpha)} \\ &= \beta Z \left\langle \hat{A}_\alpha \right\rangle \end{aligned}$$

and

$$\begin{aligned} \frac{\partial^2 Z}{\partial a_\alpha \partial a_\beta} &= \beta^2 \mathrm{Tr}\, \hat{A}_\alpha \hat{A}_\beta e^{-\beta(\hat{H}_0 - \sum_\alpha \hat{A}_\alpha a_\alpha)} \\ &= \beta^2 Z \left\langle \hat{A}_\alpha \hat{A}_\beta \right\rangle, \end{aligned}$$

when we assume that $\hat{H}_0$, $\hat{A}_\alpha$ and $\hat{A}_\beta$ commute. We define the *static linear response function* $\chi_{\alpha\beta}$ so that

$$\begin{aligned} \chi_{\alpha\beta} &= \frac{\partial \left\langle \hat{A}_\alpha \right\rangle}{\partial a_\beta} = \frac{1}{\beta}\frac{\partial}{\partial a_\beta}\frac{1}{Z}\frac{\partial Z}{\partial a_\alpha} \\ &= \frac{1}{\beta Z}\frac{\partial^2 Z}{\partial a_\alpha \partial a_\beta} - \frac{1}{\beta Z^2}\frac{\partial Z}{\partial a_\alpha}\frac{\partial Z}{\partial a_\beta} \\ &= \frac{1}{\beta}\frac{\partial^2}{\partial a_\alpha \partial a_\beta}\ln Z \\ &= \beta \left\langle \hat{A}_\alpha \hat{A}_\beta \right\rangle - \beta \left\langle \hat{A}_\alpha \right\rangle \left\langle \hat{A}_\beta \right\rangle. \end{aligned}$$

We can thus write

$$\delta \left\langle \hat{A}_\alpha \right\rangle = \sum_\beta \chi_{\alpha\beta}\delta a_\beta,$$

where

$$\begin{aligned} \chi_{\alpha\beta} &= \beta \left\langle \left(\hat{A}_\alpha - \left\langle \hat{A}_\alpha \right\rangle\right)\left(\hat{A}_\beta - \left\langle \hat{A}_\beta \right\rangle\right)\right\rangle \\ &= \beta \left\langle \delta\hat{A}_\alpha \delta\hat{A}_\beta \right\rangle. \end{aligned}$$

Notes:

- $\chi_{\alpha\beta}$ tells how much the expectation value of the observable $\hat{A}_\alpha$ changes when the observable $\hat{A}_\beta$ is influenced by one unit of disturbance.
- The response functions are related to the *correlations* of the fluctuations of observables. The correlation C_{AB} of the observables $\hat{A}$ and $\hat{B}$ is defined to be

  $$C_{AB} = \left\langle \delta\hat{A}\, \delta\hat{B} \right\rangle,$$

  where $\delta\hat{A} = \hat{A} - \left\langle \hat{A} \right\rangle$ is the fluctuating part of the observable $\hat{A}$.
- The *correlation functions* $\left\langle \delta\hat{A}_\alpha \delta\hat{A}_\beta \right\rangle$ can be calculated in the limit $\{a_\alpha = 0\}$. The responses $\chi_{\alpha\beta}$ are determined, in the limit of infinitesimal disturbances, by the undisturbed density matrix $\hat{\rho}_0$.
- The theory of linear responses can be generalized for dynamic disturbances.
- Despite of the possible incommutability of the operators $\hat{A}_\alpha$, $\hat{A}_\beta$ and $\hat{H}_0$ the results are exact in classical mechanics. In quantum mechanics the commutation relations must be taken into accout. One can show that the response function can be written as

  $$\chi_{\alpha\beta} = \left\langle \delta\tilde{A}_\beta^{(\hat{A}_\beta)} \delta\hat{A}_\alpha \right\rangle,$$

  where the operator $\tilde{A}^{(\hat{B})}$ is

  $$\tilde{A}^{(\hat{B})} = \hat{A} + \frac{1}{2!}\left[\hat{A}, \hat{B}\right] + \frac{1}{3!}\left[\left[\hat{A}, \hat{B}\right], \hat{B}\right] + \cdots.$$

Particle density

Let $\hat{\boldsymbol{r}}_1, \hat{\boldsymbol{r}}_2, \ldots, \hat{\boldsymbol{r}}_N$ be position operators, i.e.

$$\hat{\boldsymbol{r}}_i \psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) = \boldsymbol{r}_i \psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N).$$

The *number density operator* is

$$\hat{\rho}(\boldsymbol{r}) = \sum_i \delta(\boldsymbol{r} - \hat{\boldsymbol{r}}_i).$$

For example, in the pure state $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$ we get

$$\begin{aligned} \langle \hat{\rho}(\boldsymbol{r}) \rangle &= \sum_i \int d\boldsymbol{r}_1 \cdots \int d\boldsymbol{r}_{i-1} \int d\boldsymbol{r}_{i+1} \cdots \int d\boldsymbol{r}_N \\ &\qquad |\psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_{i-1}, \boldsymbol{r}, \boldsymbol{r}_{i+1}, \ldots, \boldsymbol{r}_N)|^2. \end{aligned}$$

When the particles are identical bosons or fermions $|\psi|^2$ is symmetric under permutations $\boldsymbol{r}_i \leftrightarrow \boldsymbol{r}_j$, so

$$\langle\hat\rho(\boldsymbol{r})\rangle = N\int d\boldsymbol{r}_2\cdots\int d\boldsymbol{r}_N|\psi(\boldsymbol{r},\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)|^2.$$

We assumed that the system is closed into the volume V and ψ normalized. Then

$$\begin{aligned}\int_V\langle\hat\rho(\boldsymbol{r})\rangle\, d\boldsymbol{r} &= N\int d\boldsymbol{r}_1\cdots\int d\boldsymbol{r}_N|\psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N)|^2\\ &= N.\end{aligned}$$

In general, we have

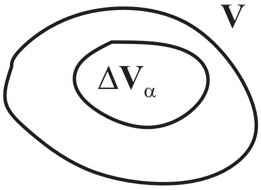
$$\begin{aligned}\left\langle\int d\boldsymbol{r}\,\hat\rho(\boldsymbol{r})\right\rangle &= \sum_{i=1}^N\left\langle\int_V d\boldsymbol{r}\,\delta(\boldsymbol{r}-\hat{\boldsymbol{r}}_i)\right\rangle\\ &= \sum_{i=1}^N 1 = N,\end{aligned}$$

so we can write

$$\hat N = \int d\boldsymbol{r}\,\hat\rho(\boldsymbol{r}).$$

Density-density response function

We divide the volume V into elements ΔV_α.



Let

$$\hat N_\alpha = \int_{\Delta V_\alpha} d\boldsymbol{r}\,\hat\rho(\boldsymbol{r}) = N_\alpha$$

be the number of particles in the element ΔV_α. Let a_α be a field coupling to $\hat N_\alpha$. The Hamiltonian of the system is

$$\begin{aligned}\hat H &= \hat H_0 - \sum_\alpha \hat N_\alpha a_\alpha\\ &= \hat H_0 - \sum_\alpha\int_{\Delta V_\alpha} d\boldsymbol{r}\,\hat\rho(\boldsymbol{r})a_\alpha.\end{aligned}$$

In the continuum limit we get

$$\begin{aligned}\hat H &= \hat H_0 - \int_V d\boldsymbol{r}\,\hat\rho(\boldsymbol{r})a(\boldsymbol{r})\\ &= \hat H_0 - \sum_i\int d\boldsymbol{r}\,\delta(\boldsymbol{r}-\hat{\boldsymbol{r}}_i)a(\boldsymbol{r})\\ &= \hat H_0 - \sum_i a(\hat{\boldsymbol{r}}_i).\end{aligned}$$

Thus the field $-a(\boldsymbol{r})$ is a *1-particle potential.*
The state sum Z can be thought to be a function of variables $\{a_\alpha\}$ or a functional of the function $a(\boldsymbol{r})$:

$$Z = Z(\{a_\alpha\})\underset{\text{continuum}}{\longrightarrow} Z[a(\boldsymbol{r})].$$

Now

$$\left\langle\hat N_\alpha\right\rangle = \frac{1}{\beta}\frac{\partial\ln Z}{\partial a_\alpha}$$

and in the continuum limit

$$\rho(\boldsymbol{r}) = \langle\hat\rho(\boldsymbol{r})\rangle = \frac{1}{\beta}\frac{\delta\ln Z}{\delta a(\boldsymbol{r})}.$$

We define the *density-density response function* χ so that

$$\chi_{\alpha\beta} = \frac{\partial\left\langle\hat N_\alpha\right\rangle}{\partial a_\beta}\approx\beta\left\langle\delta\hat N_\alpha\delta\hat N_\beta\right\rangle$$

and in the continuum limit

$$\begin{aligned}\chi(\boldsymbol{r},\boldsymbol{r}') &= \frac{\delta\langle\hat\rho(\boldsymbol{r})\rangle}{\delta a(\boldsymbol{r}')}\\ &\approx \beta\langle\delta\hat\rho(\boldsymbol{r})\delta\hat\rho(\boldsymbol{r}')\rangle.\end{aligned}$$

Here

$$\delta\hat\rho(\boldsymbol{r}) = \hat\rho(\boldsymbol{r}) - \langle\hat\rho(\boldsymbol{r})\rangle = \hat\rho(\boldsymbol{r}) - \rho(\boldsymbol{r})$$

is the fluctuation of the density.
The approximativity of the last formulas is due to the non commutativity the Hamiltonian with the operators $\delta\hat\rho(\boldsymbol{r})$ and $\delta\hat\rho(\boldsymbol{r}')$.

Pair correlation function

We restrict to homogeneous matter. Then

$$\langle\hat\rho(\boldsymbol{r})\rangle = \rho(\boldsymbol{r}) = \rho.$$

Let us consider the function

$$\begin{aligned}\langle\hat\rho(\boldsymbol{r})\hat\rho(\boldsymbol{r}')\rangle &= \sum_i\langle\delta(\boldsymbol{r}-\hat{\boldsymbol{r}}_i)\delta(\boldsymbol{r}'-\hat{\boldsymbol{r}}_i)\rangle\\ &\quad+\sum_{i\neq j}\langle\delta(\boldsymbol{r}-\hat{\boldsymbol{r}}_i)\delta(\boldsymbol{r}'-\hat{\boldsymbol{r}}_j)\rangle\\ &= \delta(\boldsymbol{r}-\boldsymbol{r}')\langle\hat\rho(\boldsymbol{r})\rangle\\ &\quad+\sum_{i\neq j}\langle\delta(\boldsymbol{r}-\hat{\boldsymbol{r}}_i)\delta(\boldsymbol{r}'-\hat{\boldsymbol{r}}_j)\rangle.\end{aligned}$$

We define the *pair correlation function* $g(\boldsymbol{r}-\boldsymbol{r}')$ so that

$$\boxed{\langle\hat\rho(\boldsymbol{r})\hat\rho(\boldsymbol{r}')\rangle = \rho\delta(\boldsymbol{r}-\boldsymbol{r}') + \rho^2 g(\boldsymbol{r}-\boldsymbol{r}')}$$

or

$$\rho^2 g(\boldsymbol{r}-\boldsymbol{r}') = \sum_{i\neq j}\langle\delta(\boldsymbol{r}-\hat{\boldsymbol{r}}_i)\delta(\boldsymbol{r}'-\hat{\boldsymbol{r}}_j)\rangle.$$

It can be shown that in a homogenous pure state $\psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N)$ of N particles one has

$$\begin{aligned}g(\boldsymbol{r}-\boldsymbol{r}') &= \frac{N(N-1)}{\rho^2}\times\\ &\quad\int d\boldsymbol{r}_3\cdots\int d\boldsymbol{r}_N|\psi(\boldsymbol{r},\boldsymbol{r}',\boldsymbol{r}_3,\ldots,\boldsymbol{r}_N)|^2.\end{aligned}$$

We see that

- $g(\boldsymbol{r}-\boldsymbol{r}')$ is proportional to the probability for finding two different particles at the points $\boldsymbol{r}$ and $\boldsymbol{r}'$.

- Because simultaneous events far away from each other cannot be correlated we have
$$\lim_{|\boldsymbol{r}-\boldsymbol{r}'|\to\infty}\left\langle \hat{A}(\boldsymbol{r})\hat{B}(\boldsymbol{r}')\right\rangle \longrightarrow \left\langle \hat{A}(\boldsymbol{r})\right\rangle \left\langle \hat{B}(\boldsymbol{r}')\right\rangle$$
so that
$$\lim_{|\boldsymbol{r}-\boldsymbol{r}'|\to\infty} g(\boldsymbol{r}-\boldsymbol{r}') = 1.$$
Note that for completely uncorrelated particles we have
$$g(\boldsymbol{r}-\boldsymbol{r}') = 1, \quad \text{or} \quad \langle \hat{\rho}(\boldsymbol{r})\hat{\rho}(\boldsymbol{r}')\rangle = \rho\delta(\boldsymbol{r}-\boldsymbol{r}') + \rho^2$$

The function
$$G^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \rho^2 g(\boldsymbol{r}_1 - \boldsymbol{r}_2)$$
is called the *pair distribution function.* Distribution functions of higher rank are defined analogously. In particular, for a pure state the distribution function of rank (degree) n is
$$\begin{aligned} &G^{(n)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \dots \boldsymbol{r}_n) = \\ &\quad N(N-1)(N-2)\cdots(N-n+1)\times \\ &\quad \int d\boldsymbol{r}_{n+1}\cdots\int d\boldsymbol{r}_N |\psi(\boldsymbol{r}_1,\dots,\boldsymbol{r}_n,\boldsymbol{r}_{n+1},\dots,\boldsymbol{r}_N)|^2. \end{aligned}$$
The pair correlation function (like the higher rank functions) can be generalized for nonhomogenous systems, for example, in a pure state we have
$$\begin{aligned} &\rho(\boldsymbol{r})\rho(\boldsymbol{r}')g(\boldsymbol{r},\boldsymbol{r}') = \\ &\quad N(N-1)\int d\boldsymbol{r}_3\cdots\int d\boldsymbol{r}_N|\psi(\boldsymbol{r},\boldsymbol{r}',\boldsymbol{r}_3,\dots,\boldsymbol{r}_N)|^2. \end{aligned}$$

Compressibility

In the classical limit the density-density response function is
$$\begin{aligned} \chi(\boldsymbol{r},\boldsymbol{r}') &= \beta\langle\delta\hat{\rho}(\boldsymbol{r})\delta\hat{\rho}(\boldsymbol{r}')\rangle \\ &= \beta\langle(\hat{\rho}(\boldsymbol{r})-\rho)(\hat{\rho}(\boldsymbol{r}')-\rho)\rangle \\ &= \beta\langle\hat{\rho}(\boldsymbol{r})\hat{\rho}(\boldsymbol{r}')\rangle - \beta\rho^2 \\ &= \beta\left[\rho\delta(\boldsymbol{r}-\boldsymbol{r}') + \rho^2 g(\boldsymbol{r}-\boldsymbol{r}')\right] - \beta\rho^2 \end{aligned}$$
or
$$\chi(\boldsymbol{r}-\boldsymbol{r}') = \beta\rho\delta(\boldsymbol{r}-\boldsymbol{r}') + \beta\rho^2[g(\boldsymbol{r}-\boldsymbol{r}')-1].$$
Its Fourier transform
$$\chi(\boldsymbol{q}) = \int d\boldsymbol{r}\, e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}\chi(\boldsymbol{r})$$
is
$$\chi(q) = \beta\rho + \beta\rho^2\int d\boldsymbol{r}\, e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}[g(r)-1].$$
The *structure function* $S(\boldsymbol{q})$ is defined so that
$$\begin{aligned} S(\boldsymbol{q}) &= \frac{1}{N}\langle\delta\hat{\rho}(\boldsymbol{q})\delta\hat{\rho}(-\boldsymbol{q})\rangle \\ &= 1 + \rho\int d\boldsymbol{r}\, e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}[g(r)-1]. \end{aligned}$$

Now
$$\begin{aligned} \delta\hat{\rho}(\boldsymbol{q})^\dagger &= \left[\int d\boldsymbol{r}\, e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}\delta\hat{\rho}(\boldsymbol{r})\right]^\dagger \\ &= \int d\boldsymbol{r}\, e^{i\boldsymbol{q}\cdot\boldsymbol{r}}\delta\hat{\rho}(\boldsymbol{r}) = \delta\hat{\rho}(-\boldsymbol{q}), \end{aligned}$$
so $S(\boldsymbol{q})$ is a real and non negative function of the variable q.

According to the definition of the response we have
$$\delta\langle\hat{\rho}(\boldsymbol{r})\rangle = \int d\boldsymbol{r}'\,\chi(\boldsymbol{r}-\boldsymbol{r}')\delta a(\boldsymbol{r}').$$
Its Fourier transform is
$$\delta\rho(\boldsymbol{q}) = \chi(\boldsymbol{q})\delta a(\boldsymbol{q}).$$
We assume that $\delta a(\boldsymbol{r}')$ is constant. Then we can interpret that
$$\delta a(\boldsymbol{r}') = \delta\mu$$
is a change in the chemical potential, so
$$\delta\rho(\boldsymbol{r}) = \frac{\delta N}{V} = \delta\mu\int d\boldsymbol{r}'\,\chi(\boldsymbol{r}-\boldsymbol{r}') = \delta\mu\lim_{q\to 0}\chi(\boldsymbol{q}).$$
We see that
$$\lim_{q\to 0}\chi(\boldsymbol{q}) = \frac{1}{V}\left(\frac{\partial N}{\partial\mu}\right)_{T,V}.$$
It follows from Maxwell's relations that
$$\left(\frac{\partial N}{\partial\mu}\right)_{T,V} = \frac{1}{V}N^2\kappa_T,$$
where κ_T is the compressibility
$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N}.$$
Thus we obtain
$$\lim_{q\to 0}\chi(\boldsymbol{q}) = \rho^2\kappa_T$$
or
$$1 + \rho\int d\boldsymbol{r}\,[g(\boldsymbol{r})-1] = \rho k_B T\kappa_T.$$

Fluctuation dissipation theorem

We assume that fields $a_\alpha(t)$ are time dependent. Then also the Hamiltonian
$$\hat{H}(t) = \hat{H}_0 - \sum_\alpha \hat{A}_\alpha a_\alpha(t)$$
depends on time.

Let
$$\hat{A}(t) = e^{\frac{i}{\hbar}\hat{H}_0 t}\hat{A}e^{-\frac{i}{\hbar}\hat{H}_0 t}$$
be the Heisenberg picture of the operator $\hat{A}$. We use the notation
$$\langle\cdots\rangle^0 = \mathrm{Tr}\,\hat{\rho}_0\cdots$$
for expectation values in undisturbed states.

It can be shown that in the linear limit one gets

$$\begin{aligned}\delta A_\alpha(t) &\equiv \mathrm{Tr}\,\delta\hat{\rho}(t)\hat{A}_\alpha \\ &= \sum_\beta \int_{-\infty}^{\infty} dt'\,\chi_{\alpha\beta}(t-t')a_\beta(t'),\end{aligned}$$

where

$$\chi_{\alpha\beta}(t-t') = \frac{i}{\hbar}\,\theta(t-t')\left\langle\left[\hat{A}_\alpha(t),\hat{A}_\beta(t')\right]\right\rangle^0 .$$

Because

$$\left[\delta\hat{A},\delta\hat{B}\right] = \left[\hat{A}-\left\langle\hat{A}\right\rangle,\hat{B}-\left\langle\hat{B}\right\rangle\right] = \left[\hat{A},\hat{B}\right],$$

we can in fact write

$$\chi_{\alpha\beta}(t-t') = \frac{i}{\hbar}\,\theta(t-t')\left\langle\left[\delta\hat{A}_\alpha(t),\delta\hat{A}_\beta(t')\right]\right\rangle^0 ,$$

i.e. the response function depends only on the fluctuating parts of the operator.
The Fourier transform with respect to time is defined as

$$\chi_{\alpha\beta}(\omega) = \int_{-\infty}^{\infty} dt\,e^{i\omega t}\chi_{\alpha\beta}(t).$$

The inverse transform is then

$$\chi_{\alpha\beta}(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\,e^{-i\omega t}\chi_{\alpha\beta}(\omega).$$

We rewrite the response function as

$$\chi_{\alpha\beta}(t-t') = 2i\theta(t-t')\chi''_{\alpha\beta}(t-t'),$$

where

$$\chi''_{\alpha\beta}(t-t') = \frac{1}{2\hbar}\left\langle\left[\hat{A}_\alpha(t),\hat{A}_\beta(t')\right]\right\rangle^0 .$$

It can be shown that $\chi_{\alpha\beta}(\omega)$ is analytic in the half plane $\mathrm{Im}\omega \geq 0$ and that

$$\chi_{\alpha\beta}(\omega) = \frac{1}{\pi}\int_{-\infty}^{\infty} d\omega'\,\frac{\chi''_{\alpha\beta}(\omega')}{\omega'-\omega-i0},$$

where $i0$ stands for an infinitesimal imaginary number.
The static response or *susceptivity* is

$$\chi_{\alpha\beta} = \chi_{\alpha\beta}(\omega=0) = \frac{1}{\pi}\int_{-\infty}^{\infty} d\omega\,\frac{\chi''_{\alpha\beta}(\omega)}{\omega}.$$

This is the microscopic form of thermodynamic response functions.
The time dependent correlation function $C_{\alpha\beta}(t-t')$ is defined as

$$C_{\alpha\beta}(t-t') = \left\langle\delta\hat{A}_\alpha(t)\delta\hat{A}_\beta(t')\right\rangle^0 .$$

So we can write the response function like

$$\chi_{\alpha\beta}(t-t') = \frac{i}{\hbar}\,\theta(t-t')\left[C_{\alpha\beta}(t-t') - C_{\beta\alpha}(t'-t)\right].$$

One can show that in the frequency space one has

$$\boxed{C_{\alpha\beta}(\omega) = \frac{2\hbar}{1-e^{-\beta\hbar\omega}}\,\chi''_{\alpha\beta}(\omega).}$$

This relation is called the *fluctuation dissipation theorem*, because

- the left side, $C_{\alpha\beta}(\omega)$, describes spontaneous fluctuations of the system.
- it can be shown that an external field oscillating with the frequency ω loses energy with the power $\omega\chi''_{\alpha\beta}(\omega)$, i.e. the right side is associated with dissipations.

skip until 10.4

Pair correlation function and equation of state

We consider homogenous matter. According to the definition of the pair correlation,

$$\rho^2 g(\boldsymbol{r}-\boldsymbol{r}') = \sum_{i\neq j}\left\langle\delta(\boldsymbol{r}-\hat{\boldsymbol{r}}_j)\delta(\boldsymbol{r}'-\hat{\boldsymbol{r}}_j)\right\rangle,$$

we have in a classical system

$$\begin{aligned}\rho^2 g(\boldsymbol{r}-\boldsymbol{r}') &= \frac{1}{Z_N}\sum_{i\neq j}\int d\Gamma\,\delta(\boldsymbol{r}-\boldsymbol{r}_i)\delta(\boldsymbol{r}'-\boldsymbol{r}_j)e^{-\beta H} \\ &= \frac{1}{Q_N}\sum_{i\neq j}\int d\boldsymbol{r}_1\cdots\int d\boldsymbol{r}_{i-1}\,\times \\ &\quad \int d\boldsymbol{r}_{i+1}\cdots\int d\boldsymbol{r}_{j-1}\,\times \\ &\quad \int d\boldsymbol{r}_{j+1}\cdots\int d\boldsymbol{r}_N e^{-\beta\sum_{k<l}v_{kl}} \\ &= \frac{N(N-1)}{Q_N}\int d\boldsymbol{r}_3\cdots d\boldsymbol{r}_N e^{-\beta\sum_{i<j}v_{ij}}.\end{aligned}$$

The pressure is

$$p = -\frac{\partial E}{\partial V}$$

where

$$E = \langle H\rangle$$

is the expectation value of the energy. We think that the system is bounded by an L-sided cube. then

$$p = -\frac{\partial E}{\partial V} = -\frac{1}{3L^2}\frac{\partial E}{\partial L}$$

and we can write

$$\begin{aligned}3pV &= -L\frac{\partial E}{\partial L} = -L\lim_{\epsilon\to 0}\frac{E_{L(1+\epsilon)}-E_L}{\epsilon L} \\ &= -\frac{1}{\epsilon}\left\langle H_{L(1+\epsilon)}-H_L\right\rangle,\end{aligned}$$

where $H_{\lambda L}$ stands for the Hamiltonian in a λL-sided cube and $E_{\lambda L}$ for the corresponding expectation value.
When we restrict to linear terms in ϵ we obviously have

$$E_{L(1+\epsilon)} = E_L + \left\langle H_{L(1+\epsilon)}-H_L\right\rangle_{H_L} + \mathcal{O}(\epsilon^2).$$

Here $\langle\cdots\rangle_{H_L}$ means that the expectation value is evaluated in a L-sided cube with the weight $e^{-\beta H_L}$. The Hamiltonian $H_{L(1+\epsilon)}$ deviates from H_L only in that the coordinates x_i, y_i and z_i can have values between $[0, L(1+\epsilon)]$, while in H_L they are restricted to $[0, L]$. We rewrite the Hamiltonian $H_{L(1+\epsilon)}$ with the help of the scaled variables

$$\boldsymbol{r}'_i = \frac{1}{1+\epsilon}\boldsymbol{r}_i$$

like

$$\begin{aligned}H_{L(1+\epsilon)} &= \sum_i \frac{\boldsymbol{p}'^2_i}{2m(1+\epsilon)^2} + \sum_{i<j} v((1+\epsilon)r'_{ij}) \\ &\approx \sum_i \frac{\boldsymbol{p}'^2_i}{2m} + \sum_{i<j} v(r'_{ij}) \\ &\quad +\epsilon\left[-2\sum_i \frac{\boldsymbol{p}'^2_i}{2m} + \sum_{i<j} r'_{ij}v'(r'_{ij})\right]\end{aligned}$$

. Here we have used the relation

$$\boldsymbol{p}' = -i\hbar\nabla_{\boldsymbol{r}'} = (1+\epsilon)\boldsymbol{p}.$$

Since the new, primed, coordinates span the same range as the originals we can replace the new ones with the originals. Now

$$\left\langle H_{L(1+\epsilon)} - H_L\right\rangle_{H_L} = \epsilon\left[-2\langle T\rangle + \left\langle \sum_{i<j} r_{ij}v'(r_{ij})\right\rangle\right],$$

where $\langle T\rangle$ is the expectation value of the energy. For the equation of state we get

$$3pV = 2\langle T\rangle - \left\langle \sum_{i<j} r_{ij}v'(r_{ij})\right\rangle.$$

Now the kinetic energy is same as for the ideal gas, i.e.

$$\langle T\rangle = \frac{3}{2}Nk_BT.$$

The latter term is evaluated like:

$$\begin{aligned}\left\langle \sum_{i<j} r_{ij}v'(r_{ij})\right\rangle &= \frac{N(N-1)}{2}\langle r_{12}v'(r_{12})\rangle \\ &= \frac{N(N-1)}{2Q_N}\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 r_{12}v'(r_{12}) \times \\ &\quad \int d\boldsymbol{r}_3\cdots d\boldsymbol{r}_N e^{-\beta\sum_{i<j}v(r_{ij})} \\ &= \frac{V}{2}\rho^2\int d\boldsymbol{r}_{12} r_{12}v'(r_{12})g(r_{12}).\end{aligned}$$

Thus the equation of state is

$$pV = Nk_BT - \frac{2\pi V}{3}\rho^2\int dr\, r^3v'(r)g(r).$$

The internal energy of the system

$$E = -\frac{\partial \ln Z_N}{\partial\beta} = \frac{3}{2}Nk_BT - \frac{1}{Q_N}\frac{\partial Q_N}{\partial\beta}$$

can also be expressed with the help of the pair correlation. Now

$$\begin{aligned}\frac{1}{Q_N}\frac{\partial Q_N}{\partial\beta} &= -\frac{1}{Q_N}\sum_{k<l}\int d\boldsymbol{r}_1\cdots d\boldsymbol{r}_N v(r_{kl}) \times \\ &\quad e^{-\beta\sum_{i<j}v(r_{ij})} \\ &= -\frac{1}{2}\frac{N(N-1)}{Q_N}\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 v(r_{12}) \times \\ &\quad \int d\boldsymbol{r}_3\cdots d\boldsymbol{r}_N e^{-\beta\sum_{i<j}v(r_{ij})} \\ &= -\frac{1}{2}\rho^2\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 v(r_{12})g(r_{12}),\end{aligned}$$

or the internal energy is

$$E = \frac{3}{2}Nk_BT + 2\pi V\rho^2\int dr\, r^2v(r)g(r).$$

We see that the thermodynamic properties of the system are determined by the pair correlation.

Approximating the pair correlation

To evaluate the partition function Z_N we have to perform $3N$-fold integration. Correspondingly, for the pair correlation, or for the pair distribution

$$\begin{aligned}G^{(2)}(r_{12}) &= \rho^2 g(r_{12}) \\ &= \frac{N(N-1)}{Q_N}\int d\boldsymbol{r}_3\cdots d\boldsymbol{r}_N e^{-\beta\sum_{i<j}v(r_{ij})},\end{aligned}$$

we need $3N-6$ integrations. In macroscopic systems N is of order 10^{23}, so the evaluation of both of them is equally tough. Like for the partition sum one can develop approximative methods for the pair correlation. We rewrite $G^{(2)}$ like

$$\begin{aligned}G^{(2)}(\boldsymbol{r}_1,\boldsymbol{r}_2) &= \frac{N(N-1)}{Q_N}\int d\boldsymbol{r}_3\cdots d\boldsymbol{r}_N \times \\ &\quad e^{-\beta\sum_{i\neq 1}v(r_{1i})}e^{-\beta\sum_{1<i<j}v(r_{ij})}.\end{aligned}$$

Its gradient with respect to $\boldsymbol{r}_1$ is

$$\begin{aligned}\nabla_1 G^{(2)}(\boldsymbol{r}_1,\boldsymbol{r}_2) &= -\frac{\beta N(N-1)}{Q_N}\int d\boldsymbol{r}_3\cdots d\boldsymbol{r}_N \times \\ &\quad \left[\nabla_1 v(r_{12}) + \sum_{i>2}\nabla_1 v(r_{1i})\right] \times \\ &\quad e^{-\beta\sum_{i<j}v(r_{ij})}.\end{aligned}$$

We employ the three body distribution

$$\begin{aligned}G^{(3)}(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3) &= \frac{N(N-1)(N-2)}{Q_N} \times \\ &\quad \int d\boldsymbol{r}_4\cdots d\boldsymbol{r}_N e^{-\beta\sum_{i<j}v(r_{ij})}.\end{aligned}$$

Now we can write

$$\begin{aligned}&\nabla_1 G^{(2)}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \\ &\quad -\beta\nabla_1 v(r_{12})G^{(2)}(\boldsymbol{r}_1,\boldsymbol{r}_2) \\ &\quad -\beta\int d\boldsymbol{r}_3\nabla_1 v(r_{13})G^{(3)}(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3).\end{aligned}$$

This equation is know as the Born-Green equation. *Repeating the procedure described above one can derive a relation which expresses $\nabla_1 G^{(3)}(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3)$ as a functional of the four body distribution $G^{(4)}$. Continuing further we would get a recursive chain of relations binding together the n- ja $n+1$-body distributions. To exploit the hierarchy of the relations we have to cut the chain somewhere. In the* Kirkwood approximation *one assumes that*

$$G^{(3)}(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3) \longrightarrow G^{(2)}(\boldsymbol{r}_1,\boldsymbol{r}_2)\rho,$$

when $\mathbf{r}_3$ *moves far from the points* $\mathbf{r}_1$ *ja* $\mathbf{r}_2$*. Since* $G^{(3)}$ *is symmetric with respect its arguments one can write*

$$G^{(3)}(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3) = \frac{1}{\rho^3}G^{(2)}(\boldsymbol{r}_1,\boldsymbol{r}_2)G^{(2)}(\boldsymbol{r}_2,\boldsymbol{r}_3)G^{(2)}(\boldsymbol{r}_3,\boldsymbol{r}_1).$$

This is know as the Kirkwood approximation *or as the* superposition approximation *One can also derive diagram expansions for the pair correlation. Since* $g(\boldsymbol{r})$ *is a non negative function it can be written as*

$$g(r) = e^{-\beta v(r)+B(r)}.$$

We define the graphical elements:

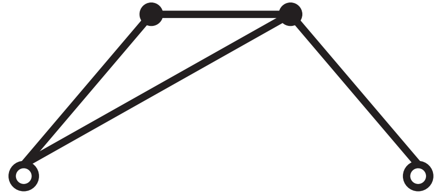
$$\circ^{\boldsymbol{r}} \quad \Leftrightarrow \quad \textit{free variable } \boldsymbol{r}$$
$$\bullet^{\boldsymbol{r}} \quad \Leftrightarrow \quad \int d\boldsymbol{r}$$
$$\boldsymbol{r}\underline{\quad}\boldsymbol{r}' \quad \Leftrightarrow \quad h(\boldsymbol{r},\boldsymbol{r}') = g(\boldsymbol{r}-\boldsymbol{r}')-1.$$

$$= \int d\boldsymbol{r}_1\, h(\boldsymbol{r},\boldsymbol{r}_1)h(\boldsymbol{r}',\boldsymbol{r}_1).$$

In the relevant graphs

- *there are two white points* $\circ^{\boldsymbol{r}}$ *and* $\circ^{\boldsymbol{r}'}$ *together with one or more black points,* $\bullet^{\boldsymbol{r}_i}$.
- *there is no direct link* ($\underline{\quad}$) *from one white point to the other white point.*
- *there is a path from every point to every other point, i.e. they are connected.*

One can show that $B(r)$ *is the sum of all these graphs.*

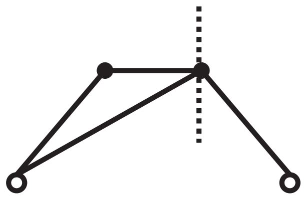


Thus this graph expansion of $B(r)$ *depends on the pair correlation* $g(r)$*. Provided that we can sum the graph expansion, we can solve* g *iteratively:*

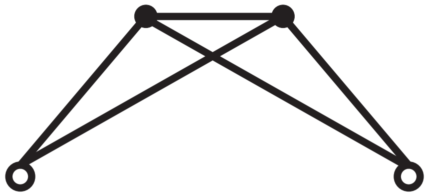
1. *guess* $g(r)$.
2. *evaluate* $B(r)$ *using the graph expansion.*
3. *new* $g(r)$ *is now*
$$g(r) = e^{-\beta v(r)+B(r)}.$$
4. *if the new and old ones deviate from eachother remarkably we continue from 2.*

We divide the graphs in the expansion of $B(r)$ *into two classes:*

- nodal graphs *are such diagrams that can be splitted into two or more unconnected parts by cutting them at some black point.*



- bridge *or* elementary diagrams *cannot be separated in parts by cutting them at any black point.*



We rewrite the pair correlation as

$$g(r) = e^{-\beta v(r)+N(r)+E(r)},$$

where $N(r)$ *is the sum of the nodal diagrams* $E(r)$ *the sum of the elementary diagrams. The* HNC *(*HyperNetted Chain*) approximation assumes that* $E(r)$ *is insignificant, i.e.*

$$g(r) \approx e^{-\beta v(r)+N(r)}.$$

It can be shown that the nodal diagrams can be summed. They satisfy the Ornstein-Zernike relation

$$N(r) = \rho\int d\boldsymbol{r}'[g(|\boldsymbol{r}-\boldsymbol{r}'|)-1-N(|\boldsymbol{r}-\boldsymbol{r}'|)][g(\boldsymbol{r}')-1].$$

Via Fourier transformation we end up with the algebraic relation

$$\tilde{N}(k) = \frac{(S(k)-1)^2}{S(k)},$$

where $S(k)$ *is the structure function and*

$$\tilde{N}(k) = \rho\int d\boldsymbol{r}\, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}N(r).$$

Jastrow's theory

Although the previous cumulant expansion and approximative methods for the pair correlation are valid only for a classical system it turns out that these methods are useful also in quantum mechanical systems.
We consider the ground state *of* N *identical particles (the temperature is* $T=0$*), so the system is in a pure quantum state* Ψ.
We assume that, due to the interactions, the particles are strongly correlated, i.e. the independent particle model is

not applicable. A good guess for the ground state wave function is then the function, known as the Jastrow trial,

$$\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N) = \Phi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N) \prod_{1\le i<j\le N} f(|\boldsymbol{r}_i-\boldsymbol{r}_j|).$$

Here the pair correlation

$$f_{ij} = f(|\boldsymbol{r}_i-\boldsymbol{r}_j|)$$

describes the mutual correlation between the particles. Since the factor

$$F = \prod_{1\le i<j\le N} f_{ij}$$

is symmetric with respect to the exchange of particles the possible Fermionic character is embedded into the function Φ*:*

- *for bosons*
$$\Phi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N) \equiv 1.$$
- *for fermions* Φ *is, for example, the Slater determinant of* N *non interacting particles and thus antisymmetric with respect to the exchange of particles.*

When Φ *takes care of the statistics we can assume that in the ground state* F *is real (in fact we could assume that* F *is positive since the ground state wave function has no zeros).*
The Hamiltonian operator of the system is

$$H = -\sum_{i=1}^{N} \frac{\hbar^2}{2m}\nabla_i^2 + \frac{1}{2}\sum_{i\ne j} v(|\boldsymbol{r}_i-\boldsymbol{r}_j|).$$

We evaluate its expectation value in the state

$$\Psi = F\Phi.$$

One can easily see (integrating by parts) that

$$\begin{aligned}\int d\boldsymbol{r}_1\cdots d\boldsymbol{r}_N\,\Psi^*\nabla_i^2\Psi = \\ \frac{1}{4}\int d\boldsymbol{r}_1\cdots d\boldsymbol{r}_N|\Phi|^2\nabla_i^2\ln F^2 \\ -\frac{1}{4}\int d\boldsymbol{r}_1\cdots d\boldsymbol{r}_N F^2\nabla_i^2|\Phi|^2 \\ +\int d\boldsymbol{r}_1\cdots d\boldsymbol{r}_N F^2\Phi^*\nabla_i^2\Phi.\end{aligned}$$

This relation is know as the Jackson-Feenberg energy form. *Employing the pair distribution*

$$g(|\boldsymbol{r}_1-\boldsymbol{r}_2|) = \frac{N(N-1)}{\rho^2\,\langle\Psi|\,\Psi\rangle}\int d\boldsymbol{r}_3\cdots d\boldsymbol{r}_N|\Psi|^2$$

and writing

$$f_{ij}^2 = e^{u_{ij}}$$

we get for the expectation of the kinetic energy

$$\begin{aligned}\langle T\rangle &= \left\langle -\sum_{i=1}^{N}\frac{\hbar^2}{2m}\nabla_i^2\right\rangle \\ &= -\frac{1}{\langle\Psi|\,\Psi\rangle}\frac{\hbar^2}{2m}\sum_{i=1}^{N}\int d\boldsymbol{r}_1\cdots d\boldsymbol{r}_N\,\Psi^*\nabla_i^2\Psi \\ &= -N\rho\frac{\hbar^2}{8m}\int d\boldsymbol{r} g(r)\nabla^2 u(r) + T_\Phi,\end{aligned}$$

where T_Φ *is composed of the Fermionic terms* $\int d\boldsymbol{r}_1\cdots d\boldsymbol{r}_N F^2\nabla_i^2|\Phi|^2$ *and* $\int d\boldsymbol{r}_1\cdots d\boldsymbol{r}_N F^2\Phi^*\nabla_i^2\Phi$*. The expectation value of the potential energy will be correspondingly*

$$\begin{aligned}\langle v\rangle &= \left\langle \frac{1}{2}\sum_{i\ne j} v_{ij}\right\rangle \\ &= \frac{1}{\langle\Psi|\,\Psi\rangle}\frac{1}{2}\sum_{i\ne j}\int d\boldsymbol{r}_1\cdots d\boldsymbol{r}_N|\Psi|^2 v_{ij} \\ &= N\rho\frac{1}{2}\int d\boldsymbol{r}\,g(r)v(r).\end{aligned}$$

Thus the energy per particle is

$$\epsilon = -\frac{\hbar^2}{8m}\rho\int d\boldsymbol{r}\,g(r)\nabla^2 u(r) + \frac{1}{2}\rho\int d\boldsymbol{r}\,g(r)v(r) + \frac{1}{N}T_\Phi.$$

Assuming that the particles are bosons the pair distribution can be written as

$$\rho^2 g(r_{12}) = \frac{N(N-1)}{\langle\Psi|\,\Psi\rangle}\int d\boldsymbol{r}_3\cdots d\boldsymbol{r}_N e^{\sum_{i<j}u_{ij}}.$$

This is exactly the same as in the classical system. Now, however, the potential term $-\beta v_{ij}$ *is replaced with the correlation factor* $u_{ij} = \ln f_{ij}^2$*. So, we can apply diagram expansions of classical systems. In particular we can write*

$$g(r) = e^{u(r)+N(r)+E(r)},$$

where $N(r)$ *is the sum of the nodal diagrams and* $E(r)$ *stands for the contribution of the elementary diagrams. In HNC-approximation we write*

$$g(r) \approx e^{u(r)+N(r)}.$$

*A corresponding approximation can be derived also for Fermionic systems but then the nodal and bridge diagrams are not composed only of black and white points and connecting links. That approximation is called the FHNC (*Fermi HyperNetted Chain*) approximation. In the following we consider only bosonic systems.*
Unlike in the classical systems the function $u(r)$ *is now unknown. We use the HNC equation to eliminate* u *from the energy expression. For one particle energy we get*

$$\begin{aligned}\epsilon \approx &-\frac{\hbar^2}{8m}\rho\int d\boldsymbol{r}\,g(r)\nabla^2\ln g(r) \\ &+\frac{\hbar^2}{8m}\rho\int d\boldsymbol{r}\,g(r)\nabla^2 N(r) \\ &+\frac{1}{2}\rho\int d\boldsymbol{r}\,g(r)v(r).\end{aligned}$$

Since the functions $N(r)$ and $g(r)$ are related by the Ornstein-Zernike relation

$$N(r) = \rho \int d\boldsymbol{r}' \, [g(r') - 1 - N(r')][g(|\boldsymbol{r} - \boldsymbol{r}'|) - 1],$$

one can take the energy ϵ as a functional of the pair distribution $g(r)$ only. It turns out that in fact a more convenient variable is $\sqrt{g(r)}$, so

$$\epsilon = \epsilon[\sqrt{g}].$$

As well known, the ground state wave function is that Ψ, whose expectation value

$$\langle H \rangle = \frac{1}{\langle \Psi | \, \Psi \rangle} \int d\boldsymbol{r}_1 \cdots d\boldsymbol{r}_N \Psi^* H \Psi$$

is minimized. We now seek the minimum of the expectation of the Hamiltonian among all the functions of Jastrow form. Equivalently, find out such a $\sqrt{g}$, that the energy $\epsilon[\sqrt{g}]$ attains its minimum. A condition for the existence of the extremum is that the variation

$$\delta\epsilon = \epsilon[\sqrt{g} + \delta\sqrt{g}] - \epsilon[\sqrt{g}]$$

vanishes up to linear order in $\delta\sqrt{g}$. A straightforward calculation shows that

$$\delta\epsilon = \int d\boldsymbol{r} \, L[\sqrt{g(r)}] \, \delta\sqrt{g(r)},$$

where

$$L[\sqrt{g(r)}] = -\frac{\hbar^2}{2m} \nabla^2 \sqrt{g(r)} + v(r)\sqrt{g(r)} + W(r)\sqrt{g(r)}.$$

In order $\delta\epsilon$ to vanish independent on the variation $\delta\sqrt{g}$, the coefficient L must vanish, i.e.

$$-\frac{\hbar^2}{2m} \nabla^2 \sqrt{g(r)} + v(r)\sqrt{g(r)} + W(r)\sqrt{g(r)} = 0.$$

The function $W(r)$ is the so called induced potential. Its Fourier transform is

$$\begin{aligned} W(k) &= \rho \int d\boldsymbol{r} \, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} W(r) \\ &= -\frac{\hbar^2 k^2}{2m} \, \frac{(S-1)^2(2S+1)}{S^2}. \end{aligned}$$

Although the above Euler-Lagrange equation *for $\sqrt{g}$ looks like a Schrödinger equation at 0 energy it is*

- *strongly nonlinear since the induced potential W depends (nonlinearly) on the structure factor S, which in turn depends via the (linear) Fourier transform on $(\sqrt{g})^2$.*
- *solvable only numerically. There are several solution methods but they all are iterative.*
- *an equation for the ground state only. Even if there are more solutions the solutions associated with other energies have no physical meaning.*

In the Jastrow theory the excited states are constructed explicitely. For example

- *let* every *particle in the system have the momentum $\hbar k$, i.e.*
- *excite the particle i with the operator $e^{i\boldsymbol{k}\cdot\hat{\boldsymbol{r}}_i}$.*
- *every particle is excited with the* same *phase, i.e.*
- *if the ground state is Ψ_0 the excited state is*

$$\begin{aligned} \Psi_k &= \left[\sum_{i=1}^{N} e^{i\boldsymbol{k}\cdot\hat{\boldsymbol{r}}_i} \right] \Psi_0 \\ &= \hat{\rho}(\boldsymbol{k})\Psi_0, \end{aligned}$$

where $\hat{\rho}(\boldsymbol{k})$ is the Fourier transform of the density operator

$$\hat{\rho}(\boldsymbol{r}) = \sum_{i=1}^{N} \delta(\hat{\boldsymbol{r}}_i - \boldsymbol{r}).$$

One can show that for bosons this kind of collective excitation *Ψ_k in the long wave length (small wave vector k) limit is energetically most favorable.*
The excitation energy can be obtained evaluating the expectation

$$E_k = \langle H \rangle_{\Psi_k} = \frac{\langle \Psi_k | \, H \, | \Psi_k \rangle}{\langle \Psi_k | \, \Psi_k \rangle}.$$

A straightforward calculation shows that

$$E_k = E_0 + \frac{\hbar^2 k^2}{2mS(k)},$$

when E_0 is the energy of the ground state Ψ_0. The excitation energy is thus

$$\epsilon_k = E_k - E_0 = \frac{\hbar^2 k^2}{2mS(k)}.$$

These kind of excitations and corresponding excitation energies are called Bijl-Feynman ecitations.

10.3. Density fluctuations and correlation length

Let's consider the canonical partition sum

$$Z_N = e^{-\beta F_N} = Tr_N e^{-\beta\hat{H}},$$

where F_N is the free energy. We divide the volume into elements V_α, whose particle numbers are

$$N_\alpha = 0, 1, 2, \ldots.$$

Let $\delta(\hat{N}_\alpha, N_\alpha)$ be an operator satisfying

$$\delta(\hat{N}_\alpha, N_\alpha) \, |N\rangle = \begin{cases} |N\rangle, & \text{if } \hat{N}_\alpha \, |N\rangle = N_\alpha \, |N\rangle \\ 0, & \text{if } \hat{N}_\alpha \, |N\rangle \neq N_\alpha \, |N\rangle, \end{cases}$$

i.e. $\delta(\hat{N}_\alpha, N_\alpha)$ is the Kronecker delta function. The identity operator operating in the volume element α can be written as

$$\hat{I}_\alpha = \sum_{N_\alpha=0}^{\infty} \delta(\hat{N}_\alpha, N_\alpha).$$

The identity operator of the whole system can be written, for example, as

$$\begin{aligned}\hat{I} &= \prod_\alpha \hat{I}_\alpha = \prod_\alpha \left[\sum_{N_\alpha=0}^{\infty} \delta(\hat{N}_\alpha, N_\alpha) \right] \\ &= \sum_{\{N_\alpha\}} \prod_\alpha \delta(\hat{N}_\alpha, N_\alpha).\end{aligned}$$

Here $\sum_{\{N_\alpha\}}$ stands for the summation over all possible configurations, i.e.

$$\sum_{\{N_\alpha\}} [\cdots] = \sum_{N_1=0}^{\infty} \sum_{N_2=0}^{\infty} \cdots [\cdots].$$

The partition sum is now

$$\begin{aligned}Z_N &= Tr_N e^{-\beta \hat{H}} \\ &= Tr_N \sum_{\{N_\alpha\}} \prod_\alpha \delta(\hat{N}_\alpha, N_\alpha) e^{-\beta \hat{H}} \\ &= \sum_{\{N_\alpha\}} Tr \prod_\alpha \delta(\hat{N}_\alpha, N_\alpha) e^{-\beta \hat{H}} \\ &= \sum_{\{N_\alpha\}} e^{-\beta \tilde{F}_N}.\end{aligned}$$

Here

$$\begin{aligned}e^{-\beta \tilde{F}_N} &= Tr \prod_\alpha \delta(\hat{N}_\alpha, N_\alpha) e^{-\beta \hat{H}} \\ &= Tr_{\{N_\alpha\}} e^{-\beta \hat{H}},\end{aligned}$$

where $Tr_{\{N_\alpha\}}$ means that in the evaluation of the trace the summation is over all microscopical degrees of freedom keeping, however, the particle numbers N_α constant and fixing for the total number

$$N = \sum_\alpha N_\alpha.$$

The function

$$\tilde{F}_N = \tilde{F}_N(T, V, \{N_\alpha\})$$

is the free energy or the reduced free energy of the configuration $\{N_\alpha\}$.
The quantity $e^{-\beta \tilde{F}_N}$ is proportional to the probability for the configuration $\{N_\alpha\}$. Thus the most probable configuration is such where the reduced free free energy $\tilde{F}_N(T, V, \{N_\alpha\})$ attains its minimum.

Density functional theory

In the continuum limit the configuration $\{N_\alpha\}$ is described by the density $\rho(\boldsymbol{r})$ and the reduced free energy will become a functional of the density:

$$\tilde{F}_N = \tilde{F}_N[\rho].$$

Now all the microscopical degrees of the freedom are reduced to the single density distribution. This kind of model is call the density functional theory. Normally the reduced free energy cannot be calculated exactly. A phenomenological method is the Local Density Approximation, LDA):

- the reduced free energy is the volume integral of the free energy density f_N.
- the free energy density at every spatial point depends only on the local particle density and its low order derivatives at that particular point.

Thus the energy functional of the system is

$$\tilde{F}_N[\rho] = \int d\boldsymbol{r}\, f_N[\rho(\boldsymbol{r}), \nabla\rho(\boldsymbol{r}), \nabla\nabla\rho(\boldsymbol{r}), \ldots].$$

If there is an external potential $u(\boldsymbol{r})$, there is the additional term $\int d\boldsymbol{r}\, u(\boldsymbol{r})\rho(\boldsymbol{r})$ in the functional. As we noted above the most probable configuration corresponds to the minimum of the reduced free energy. We restrict to homogenous systems so that the constant density ρ_0 minimizes the functional $\tilde{F}_N[\rho]$. Let

$$\delta\rho(\boldsymbol{r}) = \rho(\boldsymbol{r}) - \rho_0$$

be a small deviation from the constant density. The simplest model for the variation of the energy functional is

$$\begin{aligned}&\tilde{F}_N[\delta\rho] = \\ &\quad \int d\boldsymbol{r} \left[f_0 + \frac{1}{2} f_1 \left(\delta\rho(\boldsymbol{r})\right)^2 + \frac{1}{2} f_2 \left(\nabla\delta\rho(\boldsymbol{r})\right)^2 \right],\end{aligned}$$

where f_0, f_1 and f_2 are constants independent on the position $\boldsymbol{r}$ (but can depend on the temperature and the constant density ρ_0). In the expansion

- there is no linear term in the variation $\delta\rho$, since according to the hypothesis ρ_0 minimizes the energy.
- due to the minimum condition the coefficients f_1 and f_2 must be positive.
- the gradient term $(\nabla\rho)^2$ favors slowly varying densities, so the wave lengthts of the density fluctuations cannot be arbitrary short. At points $\boldsymbol{r}$ and $\boldsymbol{r}'$ close to each other the deviations $\delta\rho(\boldsymbol{r})$ ja $\delta\rho(\boldsymbol{r}')$ are roughly the same.
- physically the gradient term can be motivated by the tendency of the stochastic thermal motion to smooth down the density differences in close by volume elements. Thus the factor f_2 depends on the correlations of the particles in volumes close to each other.

Since the particle number is constant we have

$$\delta N = \int d\boldsymbol{r}\, \delta\rho(\boldsymbol{r}) = \delta\rho(\boldsymbol{q} = 0) = 0,$$

and, with the help of the Fourier transform, the free energy can be written as

$$\tilde{F}_N = \tilde{F}_N^0 + \frac{1}{2V} \sum_{\boldsymbol{q}}{}' (f_1 + f_2 q^2) \delta\rho(\boldsymbol{q}) \delta\rho(-\boldsymbol{q}),$$

where $\sum_{\boldsymbol{q}}'$ means that the term $\boldsymbol{q} = 0$ is not to be summed. Since the variation $\delta\rho(\boldsymbol{r})$ is real its Fourier transform satisfies

$$\delta\rho(-\boldsymbol{q}) = \delta\rho(\boldsymbol{q})^*,$$

so

$$\delta\rho(\boldsymbol{q})\delta\rho(-\boldsymbol{q}) = |\delta\rho(\boldsymbol{q})|^2.$$

The physical meaning of this term is that $\langle\delta\rho(\boldsymbol{q})\delta\rho(-\boldsymbol{q})\rangle$, *as we recall, describes density correlations.*
the probability for the fluctuation $\delta\rho$ *is now*

$$\begin{aligned} P[\delta\rho] &\propto e^{-\beta\tilde{F}_N} \\ &\propto \exp\left[-\frac{1}{2k_BTV}\sum_{\boldsymbol{q}}{}'\left(f_1+f_2q^2\right)|\delta\rho(\boldsymbol{q})|^2\right]. \end{aligned}$$

Correlation length

Since the distribution $P[\delta\rho]$ *derived above is of Gaussian shape one can directly read from it the correlation function*

$$\begin{aligned} \langle\delta\rho(\boldsymbol{q})\delta\rho(-\boldsymbol{q})\rangle &= \frac{k_BTV}{f_1+f_2q^2} \\ &= \frac{k_BTV}{f_2}\,\frac{1}{q^2+q_c^2}, \end{aligned}$$

where

$$q_c^2 = \frac{f_1}{f_2}.$$

The density-density response $\chi(\boldsymbol{q})$ *was defined so that*

$$\chi(\boldsymbol{q}) = \beta\rho S(\boldsymbol{q}) = \frac{\beta}{V}\,\langle\delta\rho(\boldsymbol{q})\delta\rho(-\boldsymbol{q})\rangle\,,$$

when $S(\boldsymbol{q})$ *is the structure factor. So we get*

$$\chi(\boldsymbol{q}) = \frac{1}{f_2}\,\frac{1}{q^2+q_c^2}.$$

Its inverse Fourier transform is

$$\chi(r) = \frac{1}{f_2}\,\frac{1}{4\pi r}e^{-r/\xi}.$$

The parameter

$$\xi = \frac{1}{q_c} = \sqrt{\frac{f_2}{f_1}}$$

is the correlation length.
Since we had $\lim_{\boldsymbol{q}\to 0}\chi(\boldsymbol{q}) = \rho^2\kappa_T$ *we must have*

$$f_1 = \frac{1}{\rho^2\kappa_T},$$

so

$$f_2 = \frac{\xi^2}{\rho^2\kappa_T}.$$

The pair correlation $h(r) = g(r)-1$ *can be written with the help of the density-density response (excluding the autocorrelation proportional to* δ*-function) as*

$$h(r) = \frac{1}{\beta\rho^2}\chi(r).$$

We see that

$$h(r) = \frac{k_BT\kappa_T}{\xi^2}\,\frac{1}{4\pi r}\,e^{-r/\xi}.$$

Note: *The results are characteristically qualitative because they are derived using a nonmicroscopic model.*

Scattering in medium

We consider the scattering of photons or massive particles in a medium. One can show that the intensity of the elastic scattering is proportional to the structure factor, i.e.

$$I(\boldsymbol{k},\boldsymbol{q}) \propto S(\boldsymbol{q}) = \frac{1}{N}\,\langle\delta\hat{\rho}(\boldsymbol{q})\,\delta\hat{\rho}(-\boldsymbol{q})\rangle\,.$$

Here $\boldsymbol{k}$ *is the wave vector of the incoming particle and* $\boldsymbol{q}$ *its change due to the scattering, i.e. the wave vector of the scattered particle is*

$$\boldsymbol{k}' = \boldsymbol{k}-\boldsymbol{q}.$$

Since the scattering is elastic we have

$$|\boldsymbol{k}'| = |\boldsymbol{k}|.$$

The intensity of the inelastic scattering in turn is proportional to the dynamic structure factor:

$$I(\boldsymbol{k};\boldsymbol{q},\omega) \propto S(\boldsymbol{q},\omega),$$

where $\boldsymbol{q}$ *the change in wave vector and* $\hbar\omega$ *in the energy. When the temperature approaches the critical point from above the isothermal compressibility* κ_T *diverges, i.e. an infinitesimal change in the pressure causes an finite change in the volume. Then*

$$f_1 = \frac{1}{\rho^2\kappa_T} \underset{\substack{critical\\point}}{\longrightarrow} 0.$$

On the other hand, there is no reason to assume that, for example, the correlations would become independent on the wave vector at the critical point, as would happen if

$$f_2 = \frac{\xi^2}{\rho^2\kappa_T} \underset{\substack{critical\\point}}{\longrightarrow} 0.$$

That's why we can assume the correlation length ξ *diverges at the critical point.*
Consider elastic scattering of light. When the scattering angle is θ *the change in the wave vector is*

$$q = 2k\sin\frac{\theta}{2},$$

the wave length being

$$\lambda = \frac{2\pi}{k}.$$

We see that the intensity is

$$I(\theta) \propto \frac{1}{f_1+f_2q^2} \propto \frac{1}{\sin^2\frac{\theta}{2}+\left(\frac{\lambda}{4\pi\xi}\right)^2}.$$

Then at the critical point

$$I(\theta) \propto \frac{1}{\sin^2\frac{\theta}{2}},$$

i.e. the scattering intensity is strongly peaked at forward directions and the total cross section ($\propto \int d\Omega I(\theta)$) diverges. Thus the radiation cannot pass through the medium: in the vicinity of the critical point tranparent matter becomes opaque. The phenomenon is called the critical opalescence.

10.4. Discrete interaction models

We first consider interaction between atomic spins in a solid. Assuming that the atoms are bound to their lattice sites the spin degrees of freedom are independent on other degrees of freedom, that is

$$H \approx H_{spin} + H_{other}.$$

Now the partition function can be factorized:

$$Z = Tr e^{-\beta H} \approx Z_{spin} Z_{other}.$$

In the case where the factorization is not complete one can define the spin Hamiltonian

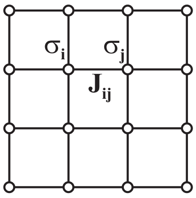
$$\begin{aligned} H_{spin} &= H(\boldsymbol{s}_1, \boldsymbol{s}_2, \ldots, \boldsymbol{s}_N) = H(\{\boldsymbol{s}_i\}) \\ &= -\frac{1}{\beta} \ln Tr_{\{\boldsymbol{s}_i\}} e^{-\beta H}. \end{aligned}$$

Here $Tr_{\{\boldsymbol{s}_i\}}$ means that the trace is evaluated keeping the spin configuration fixed. The total partition function is

$$Z = Tr^{spin} e^{-\beta H(\{\boldsymbol{s}_i\})},$$

where now the trace is over spins. In the spin model

- the most important interactions are between nearest neighbours.
- the interactions are associated with the links connecting the lattice points.
- the spins associated with the lattice points are the dynamical variables.



In some cases it is possible to construct spin models also for continuum systems by discretizing the field variables. We denote the lattice points by $i, j, \ldots$. If the spin quantum number of the particles in the model is s, the state sum is

$$\begin{aligned} Z &= \sum_{\{\sigma_i\}} e^{-\beta H(\{\boldsymbol{s}_i\})} \\ &= \sum_{\sigma_1=-s}^{s} \cdots \sum_{\sigma_N=-s}^{s} e^{-\beta H(\{\boldsymbol{s}_i\})}. \end{aligned}$$

Heisenberg's model

In the external field $\boldsymbol{B}_0$ the Hamiltonian according to the Heisenberg model is

$$H = -\frac{1}{2} \sum_{ij} J_{ij} \boldsymbol{s}_i \cdot \boldsymbol{s}_j - \gamma \boldsymbol{B}_0 \cdot \sum_i \boldsymbol{s}_i$$

when the magnetic moment of the particles is

$$\boldsymbol{\mu}_i = \gamma \boldsymbol{s}_i.$$

We use notation $< ij >$ for such spins i j, which are closest neighbours of each other and count this kind of pair only once. We assume further that the interactions do not depend on the lattice sites, i.e. $J_{ij} = J$. Then

$$H = -J \sum_{<ij>} \boldsymbol{s}_i \cdot \boldsymbol{s}_j,$$

when the external field is $\boldsymbol{B}_0 = 0$. Ferromagnetic coupling $J > 0$

The interaction favors parallel spins. One can easily see that the state

$$\bigotimes_i |\sigma_i = s\rangle = |s, s, \ldots, s\rangle\,,$$

where the spins at all lattice points are parallel is the ground state.

Let z be the coordination number of the lattice (the number of nearest neighbours at each lattice point). For example, in the 3-dim. cubic lattice $z = 6$ and in 2-dim. square lattice $z = 4$. It is easy to see that the ground state energy is

$$E_0 = -N \frac{z}{2} J s^2.$$

Since the scalar product $\boldsymbol{s}_i \cdot \boldsymbol{s}_j$ is invariant under rotations the Hamiltonian of the system is also rotationally invariant. The ground state

- does not obey the symmetry of the Hamiltonian. It is said that a spontaneous symmetry breaking has occured.
- is degenerate: rotating all spins equally we end up with a state with the same energy.

Antiferromagnetic coupling $J < 0$

The interaction favors neighbours with opposite spins. Assuming that opposite configurations were possible for all nearest neighbours the classical ground state energy were

$$E_0 = N \frac{z}{2} J s^2.$$

This kind state of alternating spins,

$$\bigotimes_i |\sigma_i = \pm s\rangle = |s, -s, s, \ldots\rangle\,,$$

is, however, not a quantum mechanical eigenstate of the operator

$$\begin{aligned} H &= -J \sum_{<ij>} \boldsymbol{s}_i \cdot \boldsymbol{s}_j \\ &= -\frac{J}{2} \sum_{<ij>} \left[(\boldsymbol{s}_i + \boldsymbol{s}_j)^2 - \boldsymbol{s}_i^2 - \boldsymbol{s}_j^2\right] \end{aligned}$$

since the spin pairs are not connected to eigenstates of the operator

$$\boldsymbol{s}_{ij}^2 = (\boldsymbol{s}_i + \boldsymbol{s}_j)^2.$$

The correct eigenstate can be solved only in the one dimensional system (so called Bethe's Ansatz *method).*

Ising's model

We simplify the Heisenberg model by restricting the spin quantum number to the case $s_i = \frac{1}{2}$ *and taking into account only the* z *components. Then*

$$H = -J \sum_{<ij>} \sigma_i \sigma_j - h \sum_i \sigma_i,$$

where $\sigma_i = \pm 1$ *and* h *is proportional to the external magnetic field.*
The Ising model can be solved (i.e. the partition function evaluated) exactly for one and two dimensional systems.
Analogical to Ising's model are for example

- binary mixture *composed of two species of atoms, A ja B, where each lattice point is occupied by either A or B type atom.*
- *lattice gas, where at each lattice point there either is an atom or is nothing.*

Potts' model

We let the spin take q *different values,*

$$\sigma_i = 1, 2, \ldots, q,$$

but only the neighbouring spins in the same spin state are allowed to interact, i.e.

$$H = -J \sum_{<ij>} \delta(\sigma_i, \sigma_j).$$

We see that this Potts model *reduces to Ising's model when* $q = 2$.
When the coupling is ferromagnetic ($J > 0$) *the ground state is such that every spin is in the same state. The ground state is thus* q*-fold degenerate. Hence at a certain temperature the system transforms to a phase where one of the values of the variable is dominant. The number of these ordered phases is* q.

Spin glass

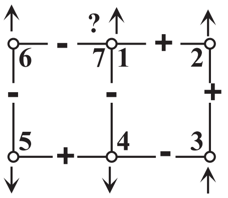
In the spin glass either the positions of atoms or their interactions (or both) vary randomly. For simplicity we assume that the spin glass Hamiltonian is of the form

$$H = -\sum_{<ij>} J_{ij} \sigma_i \sigma_j,$$

where the couplings J_{ij} *are random quantities.*
The simpliest choice is

$$J_{ij} = \pm J$$

the sign being stochastic. This is known as Ising's spin glass. *In a system of this type there are* frustrations *i.e. going around a closed path along links setting the spins so that the energy of each link is minimized the last spin direction will differ from the one we started with. That's why all interactions cannot be minimized simultaneously and the ground state cannot be determined.*



XY model

We confine the spins in the Heisenberg model to a two dimensional plane, i.e.

$$\boldsymbol{s}_i = s_{ix}\boldsymbol{i} + s_{iy}\boldsymbol{j}.$$

When the spins are treated classically the XY model *Hamiltonian can be written as*

$$H = -J \sum_{<ij>} \cos\theta_{ij},$$

where $\theta_{ij} = \theta_i - \theta_j$ *is the angle between neighbour spins. If the coupling is ferromagnetic,* $J > 0$, *all spins are parallel in the ground state. The we can assume that at low temperatures the angles* θ_i *vary slowly as a function of the position. Thus one can write*

$$\theta(\boldsymbol{r}_i + a\boldsymbol{i}) - \theta(\boldsymbol{r}_i) \approx a\,\frac{\partial\theta(x,y)}{\partial x}$$

and

$$\cos\theta_{ij} \approx 1 - \frac{1}{2}\theta_{ij}^2 \approx 1 - \frac{1}{2}a^2\left(\frac{\partial\theta}{\partial x}\right)^2.$$

In the continuum limit we get the field theoretic model

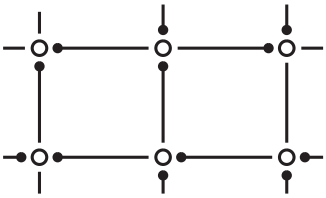
$$H \approx E_0 + \frac{1}{2}K \int\!\!\int dx\,dy\,|\nabla\theta|^2.$$

Vertex models

In the vertex models the dynamical variables are associated with the links and the interactions to the lattice points common to the links. As an example we consider models for crystalline phases of water (H_2O) *(*ice models*):*

- *in the ice the oxygen atoms correspond to the lattice points.*
- *the links binding oxygen atom pairs are* hydrogen bonds.
- *the hydrogen bond is unsymmetric: the hydrogen ion is always closer to one of the atoms.*
- *the state of the hydrogen bond can be described by the two valued spin variable* $\sigma_{ij} = \pm 1$.
- *the hydrogen ions must satisfy so called* ice conditions*: each oxygen atom must have exactly two hydrogen as neighbours. The water molecules of the ice are thus binded together by weak hydrogen bonds.*

We approximate the ice structure with two dimensional square lattice. There are 6 possible link configuration for each lattice point. We have a so called 6 vertex model.



Let θ_i *be the ice condition for the lattice point* i*:*

$$\theta_i = \begin{cases} 1, \textit{condition satisfied} \\ 0, \textit{condition not satisfied.} \end{cases}$$

A suitable Hamiltonian for the system is such that the energy of the forbidden configurations is infinite, e.g.

$$H = \lim_{U\to\infty} \sum_i U(1-\theta_i).$$

Now the energy of an allowed configuration is zero. One can also associate different energy ϵ_k *with each vertex type* k*. The the total energy of the lattice, in an allowed configuration, is*

$$E = \sum_{k=1}^{6} N_k \epsilon_k.$$

Here N_k *is the total number of the* k *type verteces. One can easily see that the state sum is*

$$Z = \sum_{\{\sigma_{ij}\}} e^{-\beta \sum_{k=1}^{6} N_k\epsilon_k} \prod_i \theta_i.$$

11. Phase transitions

11.1. Lee-Yang theory

A phase transition happens at an exactly determined temperature which depends on the density, pressure and other intensive properties of the system. Since the state variables behave differently on each side of the transition point the partition sum must be non analytic at the transition point. The energy spectrum $\{E_n\}$ *of finite number particles in a finite volume is discrete so the partition function*

$$Z_N = \sum_n e^{-\beta E_n}$$

is a positive and, on the positive real axis $\beta > 0$ *and in the neighbourhood of it, an analytic function of its argument* β*. In this kind of a system there can be no sharp phase transition point. Phase transition can thus occur only in the* thernodynamic limit *where*

$$V \to \infty \textit{ and } N \to \infty \textit{ but } \frac{N}{V} \to \rho = \textit{constant.}$$

The model by Lee and Yang explains how the analytic partition function develops toward non-analytic form when we approach the thermodynamic limit. We consider a system of hard spheres confined in the volume V*. Let* V_0 *be the volume of one sphere. Then*

$$N_m \approx \frac{V}{V_0}$$

is the maximum number of spheres. The partition function

$$Z_G(T,V,\mu) = \sum_{N=0}^{N_m} z^N Z(T,V,N)$$

is a polynomial of degree N_m *of the fugacity*

$$z = e^{\beta\mu}.$$

We use the shorthand notation

$$Z(z) = Z_G(T,V,\mu).$$

Let $\xi_1, \xi_2, \ldots, \xi_{N_m}$ *be the zeros of the polynomial* $Z(z)$*. Since* $Z(0) = 1$*, we have, according to the fundamental theorem of algebra,*

$$Z(z) = \prod_{n=1}^{N_m} \left(1 - \frac{z}{\xi_n}\right).$$

Because $Z(z)$ *is real when* z *is real the zeros must occur as conjugate pairs, i.e. for every root* ξ_n *there must be the root* ξ_n^**.*
When we approach the thermodynamic limit the number of zeros of the partition function $Z(z)$ *tends to infinity. One can assume that the real axis remains clean of the zeros excluding, maybe, some separate points. In the vicinity of those points the density of zeros is very high and the function* $Z(z)$ *non-analytic.*

Let's assume that the zeroes of the partition function $Z(z)$ close to the real axis condense on the curve C. The function $Z(z)$ is analytic on both sides of the curve but its analytic properties are different on different sides. When the zeros lying on the curve C condense to continuum we can write

$$\begin{aligned}\ln Z(z) &= \sum_n \ln\left(1-\frac{z}{\xi_n}\right)\\ &\to \int_C d\xi\, w(\xi)\ln\left(1-\frac{z}{\xi}\right).\end{aligned}$$

Here

$$dn = d\xi\, w(\xi)$$

is the number of zeroes on the arc $d\xi$ of the curve. The density $w(\xi)$ is $\propto N_m \propto V$ and so an extensive quantity. From this expression for the partition function one can clearly see that $Z(z)$ is not analytic if z happens to lie on the curve formed by the zeroes. As an example we consider the partition function which in the vicinity of z_0 behaves like

$$Z(z) \approx e^{\Phi(z)}\cosh\left[\frac{\pi}{b}(z-z_0)\right],$$

where $\Phi(z)$ is analytic. The zeroes of the partition function are then at the points

$$\xi_n = z_0 + ib\left(n+\frac{1}{2}\right),\ n = 0,\pm1,\pm2,\ldots.$$

Since

$$\ln Z(z) = \Phi(z) + \ln\cosh\left[\frac{\pi}{b}(z-z_0)\right]$$

is extensive the argument $\pi/b(z-z_0)$ must be extensive. The only possibility is that $1/b \propto V$. We denote

$$b = \frac{v_0}{V},$$

so in the thermodynamic limit

$$V\to\infty \text{ or } b\to 0 \text{ but } v_0 = constant$$

we get

$$\begin{aligned}\frac{1}{V}\ln Z &= \frac{1}{V}\Phi(z) + \frac{1}{V}\ln\cosh\left[\frac{\pi V}{v_0}(z-z_0)\right]\\ &\to \begin{cases}\frac{1}{V}\Phi(z) + \frac{1}{V}\ln\frac{1}{2} + \frac{\pi}{v_0}(z_0-z), & z<z_0\\ \frac{1}{V}\Phi(z) + \frac{1}{V}\ln\frac{1}{2} + \frac{\pi}{v_0}(z-z_0), & z>z_0.\end{cases}\end{aligned}$$

Because in the grand canonical ensemble we have

$$\begin{aligned}pV &= k_BT\ln Z\\ N &= z\frac{\partial\ln Z}{\partial z},\end{aligned}$$

we see that now

$$\begin{aligned}pV &= k_BT\Phi(z) + \frac{\pi}{v_0}k_BTV|z-z_0|\underset{z\to z_0}{\to} k_BT\Phi(z_0)\\ N &= z\frac{\partial\Phi(z)}{\partial z} + \pi\frac{V}{v_0}z\,sgn(z-z_0).\end{aligned}$$

We are thus dealing with a typical first order phase transition where the density jump is

$$\Delta\rho = \frac{2\pi z_0}{v_0}.$$

11.2. Ising model

Practically the only exactly solvable models are the one and two dimensional models by Ising.
We consider one dimensional chain of spins

$$\begin{matrix}\uparrow\uparrow\downarrow\uparrow & & \downarrow\\ 1234 & \cdots & N,\end{matrix}$$

where we apply periodic boundary conditions, i.e. we set

$$\sigma_{N+1} = \sigma_1.$$

The Hamiltonian operator of the system is then

$$\begin{aligned}H &= -J\sum_{i=1}^{N}\sigma_i\sigma_{i+1} - h\sum_{i=1}^{N}\sigma_i\\ &= -J\sum_{i=1}^{N-1}\sigma_i\sigma_{i+1} - J\sigma_N\sigma_1 - h\sum_{i=1}^{N}\sigma_i,\end{aligned}$$

where each spin variable can attain the values

$$\sigma_i = \pm1.$$

The partition function is

$$\begin{aligned}Z &= \sum_{\sigma_1}\sum_{\sigma_2}\cdots\sum_{\sigma_N} e^{\beta J\sum_{i=1}^{N}\sigma_i\sigma_{i+1} + \beta h\sum_{i=1}^{N}\sigma_i}\\ &= \sum_{\sigma_1}\sum_{\sigma_2}\cdots\sum_{\sigma_N}\prod_{i=1}^{N} e^{\beta J\sigma_i\sigma_{i+1} + \frac{1}{2}\beta h(\sigma_i+\sigma_{i+1})}.\end{aligned}$$

We define the 2×2 transition matrix T so that

$$T_{\sigma\sigma'} = e^{\beta J\sigma\sigma' + \frac{1}{2}\beta h(\sigma+\sigma')},$$

where $\sigma,\sigma' = \pm1$. The partition function can now be written as

$$\begin{aligned}Z &= \sum_{\sigma_1}\sum_{\sigma_2}\cdots\sum_{\sigma_N} T_{\sigma_1\sigma_2}T_{\sigma_2\sigma_3}\cdots T_{\sigma_N\sigma_1}\\ &= \sum_{\sigma_1}\left(T^N\right)_{\sigma_1\sigma_1} = TrT^N.\end{aligned}$$

Looking at the matrix

$$T = \begin{pmatrix} e^{\beta J+\beta h} & e^{-\beta J}\\ e^{-\beta J} & e^{\beta J-\beta h}\end{pmatrix}$$

we see that the transition matrix is symmetric. Thus its eigenvalues

$$\lambda^{\pm} = e^{\beta J}\left[\cosh(\beta J) \pm \sqrt{\sinh^2(\beta h) + e^{-4\beta J}}\right],$$

are real. Let S be a orthoganal matrix diagonalizing T (composed of the eigenvectors of T), i.e.

$$T = S^{-1}\begin{pmatrix}\lambda^+ & 0\\ 0 & \lambda^-\end{pmatrix} S.$$

Now

$$T^N = S^{-1}\begin{pmatrix}\left(\lambda^+\right)^N & 0\\ 0 & \left(\lambda^-\right)^N\end{pmatrix} S$$

and, due to the cyclic property of the trace,

$$\begin{aligned} Z &= Tr T^N = Tr S S^{-1}\begin{pmatrix}\left(\lambda^+\right)^N & 0\\ 0 & \left(\lambda^-\right)^N\end{pmatrix}\\ &= \left(\lambda^+\right)^N + \left(\lambda^-\right)^N.\end{aligned}$$

The logarithm of the partition function is

$$\begin{aligned} \ln Z &= \ln\left[\left(\lambda^+\right)^N + \left(\lambda^-\right)^N\right]\\ &= N\ln\lambda^+ + \ln\left[1 + \left(\frac{\lambda^-}{\lambda^+}\right)^N\right].\end{aligned}$$

Since in the thermodynamic limit, $N \to \infty$,

$$\left(\frac{\lambda^-}{\lambda^+}\right)^N \to 0,$$

holds we get

$$\lim_{N\to\infty}\ln Z \to N\left[\ln\lambda^+ + \frac{1}{N}\left(\frac{\lambda^-}{\lambda^+}\right)^N\right] \underset{N\to\infty}{\to} N\ln\lambda^+.$$

Just like in the free spin system the free energy is interpreted as the magnetic Gibbs function. Its value per spin is

$$\begin{aligned} \frac{G}{N} &= -\frac{k_BT}{N}\ln Z\\ &= -J\\ &\quad -k_BT\ln\left[\cosh(\beta h) + \sqrt{\sinh^2(\beta h) + e^{-4\beta J}}\right].\end{aligned}$$

The equilibrium values of other thermodynamic variables can be calculated from the Gibbs function. In particular, the average of the spin variable is

$$\begin{aligned} \sigma &\equiv \langle\sigma_i\rangle = \frac{1}{N\beta}\frac{\partial\ln Z}{\partial h} = -\frac{\partial G/N}{\partial h}\\ &= \frac{\sinh(\beta h)}{\sqrt{\sinh^2(\beta h) + e^{-4\beta J}}}.\end{aligned}$$

The expectation value σ is an order parameter *of the system: $\sigma = 0$ corresponds to completely stochastically oriented spins whereas $|\sigma| = 1$ corresponds to the case where all spins are ordered themselves parallely. The order parameter σ is analogous to the magnetization M of the free spin system when h corresponds to the magnetic field H. The susceptivity is analogically*

$$\chi = \frac{\partial M}{\partial H} \Leftrightarrow \frac{\partial\sigma}{\partial h}.$$

In the weak field limit $h \to 0$ we get then

$$\chi = \left.\frac{\partial\sigma}{\partial h}\right|_{h=0} = \frac{1}{k_BT}\,e^{\frac{2J}{k_BT}}.$$

When the coupling is ferromagnetic ($J > 0$) the system magnetizes strongly at low temperatures. When the external field is removed the system returns to the disordered state $\sigma = 0$: there is no spontaneous symmetry break.
If the coupling is antiferromagnetic ($J < 0$) the polarization is damped exponentially.
The one dimensional Ising chain is thus a paramagnetic system without any phase transitions. However, since it does not obey Curie's law it is not a Curie paramagnet.
Two dimensional Ising model *can be solved exactly generalizing the transition matrix method (Onsager, 1944). It turns out that in this case there is a phase transition at the temperature*

$$T_c = \frac{2J}{\ln(1+\sqrt{2})} \approx 2.269\,J.$$

The specific heat diverges logarithmically at the critical point $T = T_c$ and the phase transition is continuous.

Monte Carlo methods

Because, in general, interacting systems can not be solved analytically numerical methods are of great value. An important class of numerical methods, Monte Carlo methods, *handles interacting systems using stochastic simulations. Suitable simulations for continuum systems, like ^{3}He- ^{4}He-liquids and electron gas, are mostly based on* Green's function Monte Carlo. *In discretized systems one can often apply* Metropolis' Monte Carlo method*:*

- *Let the possible configurations of the system be*

  $$j \in J = \{1, 2, \ldots, K\}$$

  and $E(j)$ the corresponding energies.
- *Form a chain $j_1, j_2, \ldots, j_n$ of configurations.*
- *Choose the next configuration, $(n+1)$'th, in the chain drawing randomly from the set J of the possible configurations. The drawed configuration, j', will be*
  - *accepted if $\Delta E = E(j') - E(j_n) < 0$.*
  - *accepted with the probability $\propto e^{-\beta\,\Delta E}$ if $\Delta E > 0$.*
- *When the length N of the chain $\{j_n\}$ increases ($N \to \infty$) the probability for each configuration j approaches*

  $$P(j) \propto e^{-\beta E(j)}.$$
- *The chain is thus a canonical ensemble which can be used to evaluate expectation values.*

Note: *The method assumes that the energy eigenstates of the system are known. So it can be applied for handling of e.g. Ising models and all classical systems.*
If the energy states are unknown the quantization must be included in the simulation.

12. Critical phenomena

In a second order phase transition the system normally goes from a higher temperature phase to a lower temperature phase with less symmetry. We say that a symmetry is broken spontaneously. For example, ferromagnetic material will get polarized below a certain critical temperature. The spin rotation symmetry is broken. The amount of the symmetry break is described by an order parameter, which is usually assigned to the expectation value of some observable of the system. In the ferromagnetic system a suitable order parameter is the magnetization $\boldsymbol{m}$. In the symmetric phase $\boldsymbol{m} = 0$ and in the ordered, i.e. symmetry breaking phase $\boldsymbol{m} \neq 0$.
Let the order parameter be m and h the external field coupling to the corresponding observable. We consider the system close to the critical point $T = T_c$. When we denote

$$\tau = T - T_c,$$

the critical point is at origin of the (τ, h)-plane.
Since the critical point is a singular point of thermodynamic potentials we divide them into regular and singular parts. For example, we write

$$\begin{aligned} F(T,m) &= F_0(T,m) + F_s(T,m) \\ G(T,h) &= G_0(T,h) + G_s(T,h) = F - hm, \end{aligned}$$

where the functions F_0 and G_0 are regular at the vicinity of the point $(\tau = 0, h = 0)$ whereas the functions F_s and G_s are singular there. Their differentials are

$$\begin{aligned} dF(T,m) &= -S\,dT + h\,dm \\ dG(T,h) &= -S\,dT - m\,dh. \end{aligned}$$

12.1. Critical exponents

Close to the critical point the singular parts are (with great accuracy) proprtional to some powers of the thermodynamical quantities τ and h. The critical exponents or the critical indeces are defined as follows:

- α, α' determine the singular part of the specific heat so that

$$\begin{aligned} C_h &= -T\left(\frac{\partial^2 G}{\partial T^2}\right)_h \\ &= \begin{cases} K\,\tau^{-\alpha}, & \text{when } T > T_c \\ K'\,(-\tau)^{-\alpha'}, & \text{when } T < T_c. \end{cases} \end{aligned}$$

  In practice we have $\alpha' = \alpha$.

- β tells how the order parameter behaves:

$$m(T) = \begin{cases} 0, & \text{when } T > T_c \\ K\,(-\tau)^{\beta}, & \text{when } T < T_c. \end{cases}$$

- γ, γ' are related with the susceptivity:

$$\begin{aligned} \chi &= \left(\frac{\partial m}{\partial h}\right)_T = -\left(\frac{\partial^2 G}{\partial h^2}\right)_T \\ &= \begin{cases} K\,\tau^{-\gamma}, & \text{when } T > T_c \\ K'\,(-\tau)^{-\gamma'}, & \text{when } T < T_c. \end{cases} \end{aligned}$$

  Within the experimental accuracy $\gamma' = \gamma$.

- δ tells how the order parameter depends on the external field h at the critical temperature $T = T_c$:

$$m(T_c, h) = K\,h^{1/\delta}.$$

- ν determines the dependence of the correlation length on the temperature,

$$\xi = K\,|\tau|^{-\nu}.$$

  The index ν is not actually a thermodynamic quantity since it is related with the microscopical parameter ξ.

12.2. Scaling theory

A scalable equation is such that it remains invariant under the scale transformations if the units of measurements are selected by scaling them properly. As an example we consider Navier-Stokes' equation of flow:

$$\frac{\partial \boldsymbol{v}}{\partial t} + (\boldsymbol{v}\cdot\nabla)\boldsymbol{v} = \boldsymbol{f} - \frac{1}{m\rho}\nabla p + \nu\nabla^2\boldsymbol{v},$$

where $\boldsymbol{v}$ is the velocity, ρ the density, p the pressure and $\boldsymbol{f}$ the force. The coefficient

$$\nu = \frac{\eta}{m\rho}$$

is the kinematic viscosity and η the viscosity. Let T, L, V and M be the dimensional units of the time, length, velocity and mass. With the help of the corresponding measures t', $\boldsymbol{r}'$, $\boldsymbol{v}'$ and m' (for example the mass is $m = m'M$) the Navier-Stokes equation takes the form

$$\frac{\partial \boldsymbol{v}'}{\partial t'} + (\boldsymbol{v}'\cdot\nabla')\boldsymbol{v}' = \boldsymbol{f}' - \frac{1}{m'\rho'}\nabla' p' + \frac{1}{R}\nabla'^2\boldsymbol{v}'.$$

The parameter R is the dimensionless Reynolds number

$$R = \frac{L^2}{T\nu} = \frac{VL}{\nu} = \frac{m\rho VL}{\eta},$$

which characterizes the flow: if $R \lesssim 10\ldots100$, the flow is usually laminar and if $R \gtrsim 10\ldots100$, it's turbulent.
Looking at the Navier-Stokes equation written using the measurement numbers we see that the behaviour of the system is dictated by the Reynolds number. If one can go from a system S to a system S_1 by scaling the measuring units so that the Reynolds number remains fixed, the equation describing the system as well as its solution remain also invariant. We say that the systems S ja S_1 are similar.
As a concrete example we consider two systems which are composed of same material, i.e.

$$\rho = \rho_1 \text{ ja } \nu = \nu_1.$$

We scale the linear measure by the factor s i.e.

$$L_1 = sL.$$

If we want the systems to be similar the Reynolds number must stay invarinat. For example

$$R = \frac{L^2}{T\nu} = \frac{L_1^2}{T_1\nu_1} = \frac{s^2L^2}{s_T T\nu},$$

so the scaling factor of the time s_T *must be*

$$s_T = s^2.$$

Let A *and* A_1 *be some dimensional units of measure corresponding to similar systems* S *and* S_1*. It turns out that all scaling laws are of the form*

$$A_1 = s^{-d_a}A,$$

where is d_a *is a rational number.*

Scaling hypothesis

In dense matter (liquid, solid, ...)

- *the microscopical length scale is determined by the distance between atoms or molecules.*
- *when macroscopic properties are considered the microscopic structure is invisible.*
- *the only macroscopically essential parameter related to microscopical properties is the correlation length* ξ*, because in the vicinity of the critical point it grows macroscopically large.*

We can thus assume that when we approach the critical point the classical similarity will hold:

- *Consider two systems of same material with correlation lengths* ξ *and* ξ_1*.*
- *The correlation length tells the scale of the fluctuations, i.e. the scale of structure of the matter (provided that we cannot observe the atomic structure).*
- *When the systems are observed using such magnifications that* ξ *and* ξ_1 *seem to be of equal length (and possibly adjusting sampling frequencies) no differences between the systems can be found.*

Since the correlation length at the critical point is infinite all sizes of fluctuations related to the order parameter are present. Except the atomic scale, there is no natural measure of length in the system. Thus the system looks similar no matter what scale is used, the system is self similar*. The self similarity assumption is formulated mathematically as the* scaling hypothesis*:*

- *The singular parts of all thermodynamic potentials scale as exponential functions of the correlation length* ξ *only.*
- *The quantity* A *behaves in the vicinity of the critical point like*

  $$A \propto \xi^{-d_A},$$

  where d_A *is the* scaling dimension *of* A*.*

The scaling dimension of the correlation length is then obviously $d_\xi = -1$*. Further, we see that the scaling dimension of the quatity* $A^xB^y\cdots$ *is*

$$d_{(A^xB^y\cdots)} = xd_A + yd_B + \cdots.$$

Because the critical index ν *was defined so that*

$$\xi \propto |\tau|^{-\nu},$$

the scaling dimension of the temperature is

$$d_\tau = \nu^{-1}.$$

The scaling dimensions of the most important quantities are

- Correlation length ξ: *We saw above that*

  $$d_\xi = -1.$$

- Temperature τ: *We had*

  $$d_\tau = \frac{1}{\nu}.$$

- Length ℓ: *Since the correlation length determines the length scale of the system* ℓ *scales like* ξ *i.e.*

  $$d_\ell = -1.$$

- Wave vector q: *The wave vector is inversely proportional to the length so*

  $$d_q = 1.$$

- Order parameter m: *The index* β *was defined so that* $m \propto (-\tau)^\beta$*, so*

  $$d_m = \beta d_\tau = \frac{\beta}{\nu}.$$

- Free energy G: *Scale transformation do not affect the free energy of the system, so*

  $$d_G = 0.$$

- Free energy per volume element g: *Since* $g = G/V$*, we have*

  $$d_g = d_G - d_V = -dd_\ell = d,$$

  when d *is the spatial dimension.*

- Specific heat c: *Since the specific heat (density) is*

  $$c \approx -T_c\frac{\partial^2 g}{\partial\tau^2},$$

  the scaling dimension d_c *satisfies the condition*

  $$d_c = d_g - 2d_\tau = d - \frac{2}{\nu}.$$

  Thus we have for the specific heat

  $$c \propto \xi^{(2/\nu)-d} \propto |\tau|^{d\nu-2}$$

and, according to the definition of the critical index α*,*

$$c \propto |\tau|^{-\alpha}.$$

Hence the critical indeces are related via the scaling law

$$\alpha = 2 - \nu d.$$

- Field h: *In an equilibrium the order parameter* m *is*

  $$m = -\frac{\partial g}{\partial h},$$

  so

  $$d_m = d - d_h.$$

  For the field h *we thus have*

  $$d_h = d - d_m = d - \frac{\beta}{\nu}.$$

The suceptivity obeys according to the definition of the index γ *the relation*

$$\chi = \frac{\partial m}{\partial h} \propto |\tau|^{-\gamma},$$

so

$$d_m - d_h = -\gamma d_\tau.$$

Comparing the dimension obtained from this for d_h *with our earlier result we end up with the scaling law*

$$\gamma = \nu d - 2\beta.$$

Further, the index δ *was defined so that at the critical temperature*

$$m \propto h^{1/\delta}.$$

Then we have

$$d_m = \frac{d_h}{\delta},$$

from which, using our earlier result, we get the scaling law

$$\delta = \frac{\nu d}{\beta} - 1.$$

The hard to measure index ν*, which is related to the microscopical correlation length, can be eliminated from the three scaling laws derived above. We are left with scaling laws relating thermodynamic indeces:*

$$\begin{aligned} \alpha + 2\beta + \gamma &= 2 \\ \beta(\delta - 1) &= \gamma. \end{aligned}$$

Note: *Although the scaling laws derived above are based on phenomenological arguments they are valid within experimental accuracy.*

Widom scaling

We consider the Gibbs function per primitive cell (or particle)

$$g(\tau, h) = g_0(\tau, h) + g_s(\tau, h),$$

where we have again separated the regular and singular parts from eachother at the singular point $(\tau = 0, h = 0)$*. Its differential is*

$$dg = -s\, d\tau - m\, dh,$$

when $s = S/N$ *is the entropy per primitive cell (or particle). Since the order parameter* m *is zero at temperatures above the critical point the critical exponents related to it must come from the singular function* g_s*.*
The functio f *is a* generalized homogenous function *if it satisfies the condition*

$$f(\lambda^{\alpha_1} x_1, \lambda^{\alpha_2} x_2, \ldots) = \lambda f(x_1, x_2, \ldots).$$

According to Widom's hypothesis *the function* g_s *behaves in the vicinity of the critical point like a generalized homogenous function, i.e. it* scales *like*

$$g_s(\lambda^p \tau, \lambda^q h) = \lambda g_s(\tau, h),$$

when $\lambda > 0$ *and* p *and* q *are system independent exponents.*
Because the scaling equation holds for all positive values of λ *it holds when* $\lambda = h^{-1/q}$*, in which case* $\lambda^q h = 1$*. Thus we can write the scaling hypothesis as*

$$\begin{aligned} g_s(\tau, h) &= h^{1/q} g_s\left(\frac{\tau}{h^{p/q}}, 1\right) \\ &= h^{1/q} \phi\left(\frac{\tau}{h^{p/q}}\right). \end{aligned}$$

Here we have defined

$$\phi(x) = g_s(x, 1).$$

The critical indeces can be obtained as follows

- β*. Take the derivative of the scaling equation*

  $$g_s(\lambda^p \tau, \lambda^q h) = \lambda g_s(\tau, h),$$

  with respect to the field h *and recall that the order parameter is*

  $$m(\tau, h) = -\frac{\partial g_s(\tau, h)}{\partial h},$$

  so we have the scaling condition

  $$\lambda^q m(\lambda^p \tau, \lambda^q h) = \lambda m(\tau, h). \qquad (*)$$

  Since the order parameter is supposed to be $m \neq 0$*, we have* $\tau < 0$*. Then we can choose* λ *so that* $\lambda^p \tau = -1$*. Setting* $h = 0$ *we get*

  $$m(\tau, 0) = (-\tau)^{(1-q)/p} m(-1, 0).$$

  According to the definition we have

  $$m(\tau, 0) \propto (-\tau)^\beta,$$

  so

  $$\beta = \frac{1-q}{p}.$$

- δ. We set in the equation $(*)$ $\tau = 0$ and $\lambda^q = 1/h$, so
$$m(0,h) = h^{1/q-1} m(0,1).$$
According to the definition $m(0,h) \propto h^{1/\delta}$, so
$$\delta = \frac{q}{1-q}.$$

- γ, γ'. According to the definition the susceptivity is
$$\chi(\tau,h) = \frac{\partial m(\tau,h)}{\partial h},$$
which close to the critical point behaves like
$$\chi \propto \begin{cases} \tau^{-\gamma}, & \text{when } \tau > 0 \\ (-\tau)^{-\gamma'}, & \text{when } \tau < 0. \end{cases}$$
Differentiating $(*)$ with respect to the field h we get
$$\lambda^{2q} \chi(\lambda^p \tau, \lambda^q h) = \lambda \chi(\tau, h).$$
Setting $h = 0$ and $\lambda^p \tau = \pm 1$ we have
$$\chi(\tau, 0) = |\tau|^{-(2q-1)/p} \chi(\pm 1, 0).$$
From this we can read for γ and γ'
$$\gamma = \gamma' = \frac{2q-1}{p}.$$

- α, α'. The specific heat is
$$c_h \propto \frac{\partial^2 g}{\partial \tau^2}.$$
Differentiating the scaling equation
$$g_s(\lambda^p \tau, \lambda^q h) = \lambda g_s(\tau, h)$$
twice with respect to τ we get
$$\lambda^{2p} c_h(\lambda^p \tau, \lambda^q h) = \lambda c_h(\tau, h).$$
We set $h = 0$ and $\lambda^p \tau = \pm 1$ and compare the result with the definitions of α and α':
$$c_h \propto \begin{cases} \tau^{-\alpha}, & \text{kun } \tau > 0 \\ (-\tau)^{-\alpha'}, & \text{kun } \tau < 0. \end{cases}$$
We see that
$$\alpha = \alpha' = 2 - \frac{1}{p}.$$

It is easy to verify that the Widom scaling hypothesis leads to the scaling laws
$$\begin{aligned} \alpha + 2\beta + \gamma &= 2 \\ \beta(\delta - 1) &= \gamma. \end{aligned}$$

Kadanoff scaling theory

Unlike the Widom scaling hypothesis the method developed by Kadanoff (1966) is based on the microscopic properties of matter.
Outlines of Kadanoffs method:

- Combine the original microscopical state variables blockwise to block variables.
- Determine the efective interactions between the blocks. This coarsing of the system is called the block transform.
- The block transforms form a semigroup, so called renormalization group. One can perform transforms sequentially.
- Because in a system at the critical point there is no natural length scale the transformed systems look copies of eachother. Thus the critical point corresponds to a fixed point of the transformations.

We apply the method to the d-dimensional Ising spin system.

Block transform

We denote by $i, j, \ldots$ the origininal lattice points and the blocks obtained by combining them by indeces $I, J, \ldots$. The block spin σ'_I of the block I is defined so that
$$\sigma'_I = \sum_{i \in I} \sigma_i.$$

If we end up with the blocks I by scaling the length measure by the factor L, each block has L^d spins. Because in the Ising model each spin can get the values $\sigma_i = \pm 1$ the block spin can get the values
$$\sigma'_I = -L^d, -L^d + 2, \ldots, L^d$$
i.e. alltogether $L^d + 1$ different values.
Let H be the original Hamiltonian. We denote
$$\mathcal{H}[\sigma_i] = \beta H = -K \sum_{\langle ij \rangle} \sigma_i \sigma_j - h \sum_i \sigma_i.$$

The state sum is
$$Z = e^{-\mathcal{G}} = Tr\, e^{-\mathcal{H}[\sigma_i]} = \sum_{\{\sigma_i\}} e^{-\mathcal{H}[\sigma_i]},$$
where $\mathcal{G} = \beta G$, G is the Gibbs function. We divide the trace summation into two parts
$$\begin{aligned} Z &= \sum_{\{\sigma_i\}} e^{-\mathcal{H}[\sigma_i]} \\ &= \sum_{\{\sigma'_I\}} \sum_{\{\sigma_i\}} e^{-\mathcal{H}[\sigma_i]} \prod_I \delta\left(\sigma'_I, \sum_{i \in I} \sigma_i\right) \\ &= \sum_{\{\sigma'_I\}} e^{-\mathcal{H}[\sigma'_I]}. \end{aligned}$$

Here we have defined
$$\begin{aligned} e^{-\mathcal{H}[\sigma'_I]} &= Tr_{\{\sigma'_I\}} e^{-\mathcal{H}[\sigma_i]} \\ &= \sum_{\{\sigma_i\}} e^{-\mathcal{H}[\sigma_i]} \prod_I \delta\left(\sigma'_I, \sum_{i \in I} \sigma_i\right). \end{aligned}$$

As can be seen from the definition

$$\mathcal{H}[\sigma'_I] = \ln Tr_{\{\sigma'_I\}} e^{-\mathcal{H}[\sigma_i]}$$

the Hamilton block function $\mathcal{H}[\sigma'_I]$ is actually the reduced free energy. Thus it can be written as

$$\mathcal{H}[\sigma'_I] = \overline{\mathcal{H}[\sigma_i]}\Big|_{\{\sigma'_I\}} - TS|_{\{\sigma'_I\}},$$

where $\overline{\mathcal{H}[\sigma_i]}\Big|_{\{\sigma'_I\}}$ is the expectation value of the energy (the internal energy) evaluated in the block configuration $\{\sigma'_I\}$. Hence the Hamiltonian block function contains the internal entropy related to the internal variables of the blocks.

Close to the critical point, due to the scale invariance, we assume the reduced free energy to take approximately the same form as the original Hamiltonian. To achieve this we scale the range of the block spins so that

$$\sigma'_I = z\sigma_I,$$

where $\sigma_I = \pm 1$. Because the maximum of the block spin is L^d we must have $z \leq L^d$.

Critical exponents

According to Kadanoff effectively the most important values of the block variable are $\pm z$. We denote

$$\mathcal{H}_L[\sigma_I] = \mathcal{H}[z\sigma_I].$$

We let the new Hamiltonian $\mathcal{H}_L$ to be of the same form as the original $\mathcal{H}$:

$$\mathcal{H}_L[\sigma_I] = -K_L \sum_{\langle IJ\rangle} \sigma_I\sigma_J - h_L \sum_I \sigma_I.$$

The parameters K_L and h_L depend now on the scale L. Let the values of the parameters at the critical point to be

$$\begin{aligned} K &= K_c \\ h &= h_c = 0. \end{aligned}$$

Since at the critical point nothing changes while scaling we must also have

$$\begin{aligned} K_L &= K_c \\ h_L &= h_c = 0. \end{aligned}$$

We consider the neighbourhood of the critical point. We suppose that $h \neq 0$, so also the corresponding scaled field satisfies $h_L \neq 0$. We write the original coupling constant as

$$K = K_c + \Delta K$$

and the corresponding scaled coupling constant as

$$K_L = K_c + \Delta K_L.$$

We now vary the scale factor L by a (small) amount δL. The relative variation of the scale is then $\delta L/L$. we can assume (as a good approximation) that the relative variations of the scaled parameters are proportional to the relative variation of the scale, i.e.

$$\begin{aligned} \frac{\delta\Delta K_L}{\Delta K_L} &= x\,\frac{\delta L}{L} \\ \frac{\delta h_L}{h_L} &= y\,\frac{\delta L}{L}, \end{aligned}$$

where x and y are constants.

When the change in the ratio is infinitesimal we get the differential equations

$$\begin{aligned} x &= \frac{\partial \ln \Delta K_L}{\partial \ln L} \\ y &= \frac{\partial \ln h_L}{\partial \ln L}, \end{aligned}$$

which after integration give

$$\begin{aligned} K_L &= K_c + L^x(K - K_c) \\ h_L &= L^y h. \end{aligned}$$

To obtain the same energy from the original and scaled Hamiltonians the coupling to the external field must satisfy the condition

$$h \sum_{i\in I} \sigma_i = h\sigma'_I = hz\sigma_I = h_L\sigma_I,$$

so the field scales like $h_L = zh$. We see that

$$z = L^y \text{ and } y \leq d.$$

The same reasoning allows us to assume that the relative deviation of the temperature from the critical point,

$$\tau = \frac{T - T_c}{T_c},$$

behaves like the relative deviation of the coupling constant K from the critical value, i.e.

$$\tau_L = L^x\tau.$$

Thus the Gibbs function per spin unit scales like

$$g(\tau_L, h_L) = g(L^x\tau, L^y h) = L^d g(\tau, h),$$

where the factor L^d is due to the fact that the new block contains L^d old spins. Writing

$$\begin{aligned} x &= pd \\ y &= qd \end{aligned}$$

we end up with the Widom scaling.

Renormalization group

Let us suppose that the Hamiltonian $\mathcal{H}$ depends on the parameters

$$\mu = (\mu_1, \mu_2, \ldots),$$

For example $\mu = (K, h)$, as above. Block transforms are now mappings in the parameter space

$$\mu \longrightarrow \mu_L.$$

Let $\boldsymbol{R}_L$ *be the operator corresponding to the block transform, i.e.*

$$\mu \longrightarrow \mu_L = \boldsymbol{R}_L \mu.$$

Since the block transform is a change in the scale we must have

$$\boldsymbol{R}_L \boldsymbol{R}_{L'} = \boldsymbol{R}_{LL'}.$$

Furthermore, it does not matter in which order the scale transforms are performed:

$$\boldsymbol{R}_L \boldsymbol{R}_{L'} = \boldsymbol{R}_{L'} \boldsymbol{R}_L.$$

In the block transform we loose information, for example the detailed knowledge of the values of the original spin variables. Thus it is impossible to return to the original system by scaling: the operation $\boldsymbol{R}_{L'}$ *has no inverse transformation among the operations* $\{\boldsymbol{R}_L\}$*. We see that the operations*

$$\mathcal{R} = \{\boldsymbol{R}_L\}$$

form a commutative semigroup *which is called the* renormalization group.
A point μ^* *which satisfies the condition*

$$\mu^* = \boldsymbol{R}\mu^* \quad \forall \boldsymbol{R} \in \mathcal{R},$$

is called a fixed point. *A system corresponding to the parameter values* μ^* *is at the critical point since any transformation of that systems results an exactly identical system. The set of those points that after sequential block transforms lead to the fixed point* μ^* *is called the* critical surface. *If the system is on the critical surface, but not at the critical point, it is at a critical point of the phase transition. However, one can still observe it using the scale where microscopical details are visible.*