Interacting matter

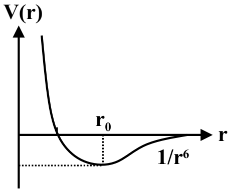
Classical real gas

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

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

For example, for nobel gases an excellent 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

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

Since the momentum variables appear only as quadratic in the kinetic energy terms they can be integrated and we get

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

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

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

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.

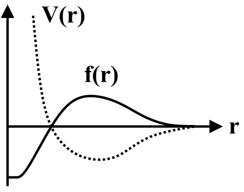
Ursell-Mayer graphs
Let's write

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

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 a small correction as compared with the term 1. 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

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

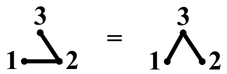
Graphs are build from the elements

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

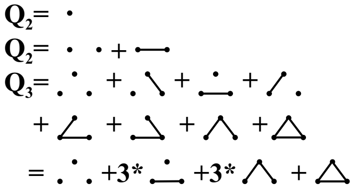
Permutations of particles do not change the values of the graphs, for example

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

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



Examle:



We classify the graphs:

- in *coupled graphs* or a *clusters* one can get from every black dot (•) to every black dot following a chain of lines ($\underline{\quad}$).
- in *uncoupled grpahs* there are parts that are not connected by a line ($\underline{\quad}$).

It is easy to see that an uncoupled graph can be factorized as the product of its coupled parts.
The sum of graphs of l coupled 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.
- $\displaystyle\sum_{\{\nu_l\}} = \sum_{\nu_1=0}^{\infty} \sum_{\nu_2=0}^{\infty} \sum_{\nu_3=0}^{\infty} \cdots$
- $\displaystyle\delta\left(N, \sum_l l\nu_l\right)$ restricts the number of the integration variables (black dots •) to N.
- $\displaystyle\frac{N!}{\prod_l (l!)^{\nu_l}}$ 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:

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

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

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

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.

$$\begin{aligned}
B_2(T) &= -b_2(T) = \frac{1}{2}\int d\boldsymbol{r}\left[1 - e^{-\beta v(r)}\right] \\
B_3(T) &= 4b_2^2 - 2b_3 \\
B_4(T) &= -20b_2^3 + 18b_2b_3 - 3b_4.
\end{aligned}$$

Second virial coefficient
We suppose 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

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

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 the particle j is in the range of the particle i (the particle N must also be in that range).
- 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

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

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

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

We can thus write

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

where

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

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.
- In spite of the possible incommutability of the operators $\hat{A}_\alpha$, $\hat{A}_\beta$ and $\hat{H}_0$ the results are exact in the classical mechanics. In quantum mechanics the incommutability 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

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

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 supposed 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

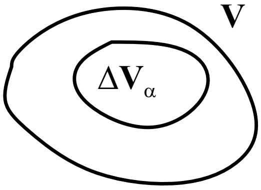
$$\begin{aligned}\int d\boldsymbol{r}\,\hat{\rho}(\boldsymbol{r}) &= \sum_{i=1}^N\int_V d\boldsymbol{r}\,\delta(\boldsymbol{r}-\hat{\boldsymbol{r}}_i)\\ &= \sum_{i=1}^N 1 = N,\end{aligned}$$

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

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

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 $\boldsymbol{r}'$.
- since 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
$$\lim_{|\boldsymbol{r}-\boldsymbol{r}'|\to\infty} g(\boldsymbol{r}-\boldsymbol{r}') = 1.$$

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

Compressibility
In the classical limit the density-density response function is
$$\begin{aligned} \chi(\boldsymbol{r},\boldsymbol{r}') &= \beta\left\langle\delta\hat\rho(\boldsymbol{r})\delta\hat\rho(\boldsymbol{r}')\right\rangle \\ &= \beta\left\langle(\hat\rho(\boldsymbol{r})-\rho)(\hat\rho(\boldsymbol{r}')-\rho)\right\rangle \\ &= \beta\left\langle\hat\rho(\boldsymbol{r})\hat\rho(\boldsymbol{r}')\right\rangle - \beta\rho^2 \\ &= \beta\left[\rho\delta(\boldsymbol{r}-\boldsymbol{r}') + \rho^2 g(\boldsymbol{r}-\boldsymbol{r}')\right] - \beta\rho^2 \end{aligned}$$
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
$$\begin{aligned} S(\boldsymbol{q}) &= \frac{1}{N}\left\langle\delta\hat\rho(\boldsymbol{q})\delta\hat\rho(-\boldsymbol{q})\right\rangle \\ &= 1+\rho\int d\boldsymbol{r}\, e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}[g(r)-1]. \end{aligned}$$
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
$$\delta\left\langle\hat\rho(\boldsymbol{r})\right\rangle = \int d\boldsymbol{r}'\,\chi(\boldsymbol{r}-\boldsymbol{r}')\delta a(\boldsymbol{r}').$$
Its Fourier transform is
$$\delta\rho(\boldsymbol{q}) = \chi(\boldsymbol{q})\delta a(\boldsymbol{q}).$$
We suppose that $\delta a(\boldsymbol{r}')$ is constant. Then we can interprete 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 get
$$\lim_{q\to 0}\chi(\boldsymbol{q}) = \rho^2\kappa_T$$
or
$$1+\rho\int d\boldsymbol{r}\,[g(\boldsymbol{r})-1] = \rho k_B T\kappa_T.$$

Fluctuation dissipation theorem
We suppose 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

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

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

- 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.

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

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

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

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

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

Approximating the pair correlation
To evaluate the state sum 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 supposes that

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

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

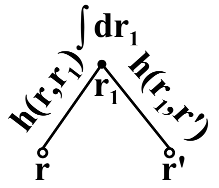
$$\begin{aligned} &G^{(3)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) = \\ &\qquad \frac{1}{\rho^3} G^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2) G^{(2)}(\boldsymbol{r}_2, \boldsymbol{r}_3) G^{(2)}(\boldsymbol{r}_3, \boldsymbol{r}_1). \end{aligned}$$

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

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

We define the graphical elements:

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

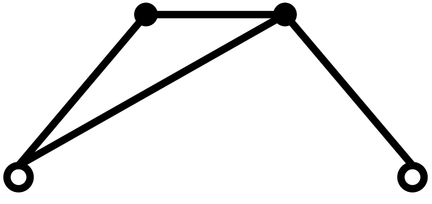


$$= \int d\boldsymbol{r}_1 \, h(\boldsymbol{r}, \boldsymbol{r}_1) h(\boldsymbol{r}', \boldsymbol{r}_1).$$

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.

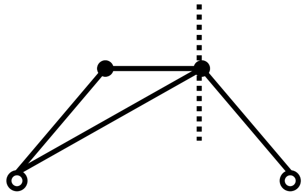


Thus this graph expansion of $B(r)$ depends on the pair correlation $g(r)$. Provided that we can sum the graph expansion, we can solve g iteratively:

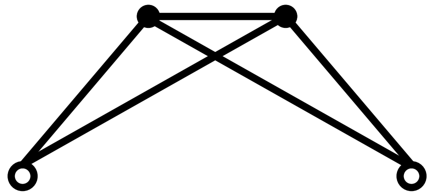
1. guess $g(r)$.
2. evaluate $B(r)$ using the graph expansion.
3. new $g(r)$ is now
$$g(r) = e^{-\beta v(r) + B(r)}.$$
4. if the new and old ones deviate from eachother remarkably we continue from 2.

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 uncoupled 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 suppose 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 suppose 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

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

We evaluate its expectation value in the state

$$\Psi=F\Phi.$$

One can easily see (integrating by parts) that

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

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

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

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

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

Thus the energy per particle is

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

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

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

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

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

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.*

Density fluctuations and correlation length

Let's consider the canonical partition sum

$$Z_N = e^{-\beta F_N} = \mathrm{Tr}_N e^{-\beta \hat{H}},$$

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

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

Here

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

where $\mathrm{Tr}_{\{N_\alpha\}}$ 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

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

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

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

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

$$f_1 = \frac{1}{\rho^2\kappa_T}\xrightarrow[\text{point}]{\text{critical}} 0.$$

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

$$f_2 = \frac{\xi^2}{\rho^2\kappa_T}\xrightarrow[\text{point}]{\text{critical}} 0.$$

That's why we can suppose 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.*

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

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

Now the state sum can be factorized:

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

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

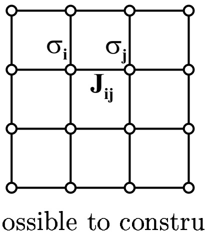
$$\begin{aligned} H_{\text{spin}} &= H(\boldsymbol{s}_1, \boldsymbol{s}_2, \ldots, \boldsymbol{s}_N) = H(\{\boldsymbol{s}_i\}) \\ &= -\frac{1}{\beta} \ln \operatorname{Tr}_{\{\boldsymbol{s}_i\}} e^{-\beta H}. \end{aligned}$$

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

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

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 suppose 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 cubical lattice $z = 6$ and in the two dimensional 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 break* has occured.
- is very degenerated. 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. Supposing 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 coupled to eigenstates of the operator

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

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-foldly degenerated. Hence at certain low 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.

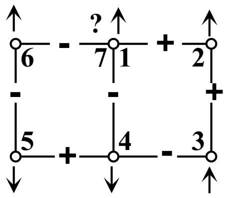
Spin glass
In the spin glass either the positions of atoms or their interactions (or both) vary randomly. For simplicity we assume that the spin glass Hamiltonian is of the form

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

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

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

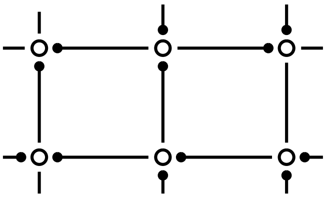
In the continuum limit we get the field theoretic model

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

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:

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

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

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