CHAPTER 10

APPROXIMATE METHODS

10.1 CLASSICAL CLUSTER EXPANSION

Many systems of physical interest can be treated classically. A large class of such systems is described by a classical Hamiltonian for N particles of the form

$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j} v_{ij} \tag{10.1}$$

where $\mathbf{p}_i$ is the momentum of the ith particle and $v_{ij} = v(|\mathbf{r}_i - \mathbf{r}_j|)$ is the potential energy of interaction between the ith and the jth particle. If the system occupies a volume V, the partition function is

$$Q_N(V, T) = \frac{1}{N!h^{3N}} \int d^{3N}p\, d^{3N}r \exp\left(-\beta \sum_i \frac{p_i^2}{2m} - \beta \sum_{i<j} v_{ij}\right) \tag{10.2}$$

where each coordinate $\mathbf{r}_i$ is integrated over the volume V. The integrations over momenta can be immediately effected, leading to

$$Q_N(V, T) = \frac{1}{\lambda^{3N} N!} \int d^{3N}r \exp\left(-\beta \sum_{i<j} v_{ij}\right) \tag{10.3}$$

where $\lambda = \sqrt{2\pi\hbar^2/mkT}$ is the thermal wavelength. The integral in (10.3) is called the *configuration integral*. For potentials v_{ij} of the usual type between molecules, a systematic method for the calculation of the configuration integral consists of expanding the integrand in powers of $\exp(-\beta v_{ij}) - 1$. This leads to the cluster expansion of Ursell and Mayer.* As we shall see, this expansion is of practical use if the system is a dilute gas.

*For original literature, see J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (Wiley, New York, 1940), Chapter 13.

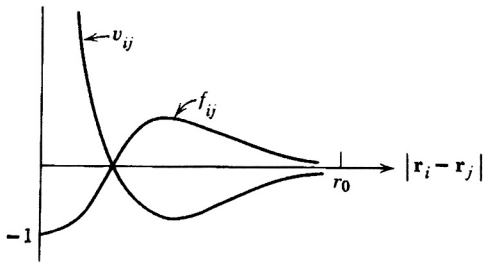


Fig. 10.1 Intermolecular potential v_{ij} and the function f_{ij}.

Let the configuration integral be denoted by $Z_N(V, T)$:

$$Z_N(V, T) \equiv \int d^3r_1 \cdots d^3r_N \exp\left(-\beta \sum_{i<j} v_{ij}\right) \tag{10.4}$$

in terms of which the partition function may be written as

$$Q_N(V, T) = \frac{1}{N!\lambda^{3N}} Z_N(V, T) \tag{10.5}$$

and the grand partition function as

$$\mathcal{Q}(z, V, T) = \sum_{N=0}^{\infty} \left(\frac{z}{\lambda^3}\right)^N \frac{Z_N(V, T)}{N!} \tag{10.6}$$

Let f_{ij} be defined by

$$e^{-\beta v_{ij}} \equiv 1 + f_{ij} \tag{10.7}$$

For the usual type of intermolecular potentials, v_{ij} and f_{ij} have the qualitative forms shown in Fig. 10.1. Thus f_{ij} is everywhere bounded and is negligibly small when $|\mathbf{r}_i - \mathbf{r}_j|$ is larger than the range of the intermolecular potential. In terms of f_{ij} the configuration integral may be represented by

$$Z_N(V, T) = \int d^3r_1 \cdots d^3r_N \prod_{i<j} (1 + f_{ij}) \tag{10.8}$$

in which the integrand is a product of $\frac{1}{2}N(N-1)$ terms, one for each distinct pair of particles. Expanding this product we obtain

$$Z_N(V, T) = \int d^3r_1 \cdots d^3r_N \left[1 + (f_{12} + f_{13} + \cdots) + (f_{12}f_{13} + f_{12}f_{14} + \cdots) + \cdots\right] \tag{10.9}$$

A convenient way to enumerate all the terms in the expansion (10.9) is to associate each term with a graph, defined as follows:

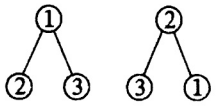
An N-particle graph is a collection of N distinct circles numbered $1, 2, \ldots, N$, *with any number of lines joining the same number of distinct pairs of circles. If the*

distinct pairs joined by lines are the pairs $\alpha, \beta, \ldots, \lambda$, *then the graph represents the term*

$$\int d^3r_1 \cdots d^3r_N f_\alpha f_\beta \cdots f_\gamma \tag{10.10}$$

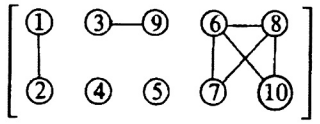
appearing in the expansion (10.9).

If the set of distinct pairs $\{\alpha, \beta, \ldots, \gamma\}$ is joined by lines in a given graph, replacing this set by a set $\{\alpha', \beta', \ldots, \gamma'\}$ that is not identical with $\{\alpha, \beta, \ldots, \gamma\}$ gives rise to a graph that is counted as distinct from the original one (although the integrals represented by the respective graphs have the same numerical value). For example, for $N = 3$, the following graphs are distinct:



but the following graphs are identical:

We may regard a graph as a picturesque way of writing the integral (10.10). For example, we may write, for $N = 10$,



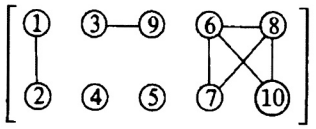
$$= \int d^3r_1 \cdots d^3r_{10} f_{12} f_{39} f_{67} f_{68} f_{8,10} f_{6,10} f_{78} \tag{10.11}$$

With such a convention, we can state that

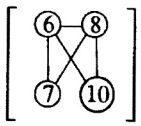
$$Z_N = (\text{sum of all distinct } N\text{-particle graphs}) \tag{10.12}$$

The proof is obvious.

Any graph can in general be decomposed into smaller units. For example, the graph (10.11) is a product of five factors, namely



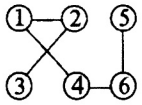
$$= [④] \cdot [⑤] \cdot [①—②] \cdot [③—⑨] \cdot$$



Each factor corresponds to a *connected graph*, in which every circle is attached to at least one line, and every circle is joined directly or indirectly to all other circles in the graph.

It would facilitate the analysis of Z_N if we first defined the basic units out of which an arbitrary graph can be composed. Accordingly we define an l-cluster to

be an l particle connected graph. For example, the following is a 6-cluster:



$$= \int d^3r_1 \cdots d^3r_6 \, f_{12} f_{23} f_{14} f_{46} f_{56} \tag{10.13}$$

We define a *cluster integral* $b_l(V, T)$ by

$$b_l(V, T) \equiv \frac{1}{l!\lambda^{3l-3}V} \text{ (sum of all possible } l\text{-clusters)} \tag{10.14}$$

The normalization factor is so chosen that

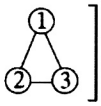
(a) $b_l(V, T)$ is dimensionless;

(b) $\tilde{b}_l(T) \equiv \lim_{V \to \infty} b_l(V, T)$ is a finite number.

The property (b) follows from the fact that f_{ij} has a finite range, so that in an l-cluster the only integration that gives rise to a factor V is the integration over the "center of gravity" of the l particles. Some of the cluster integrals are

$$b_1 = \frac{1}{V}[①] = \frac{1}{V}\int d^3r_1 = 1 \tag{10.15}$$

$$b_2 = \frac{1}{2!\lambda^3 V}[①—②] = \frac{1}{\lambda^3 2V}\int d^3r_1 \, d^3r_2 \, f_{12} = \frac{1}{2\lambda^3}\int d^3r_{12} \, f_{12} \tag{10.16}$$

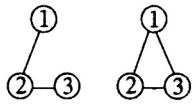
$$b_3 = \frac{1}{3!\lambda^6 V}\left[\right. \text{  } + \text{} + \text{  } + \text{  } \left.\right] \tag{10.17}$$

Any N-particle graph is a product of a number of clusters, of which m_l are l-clusters, with

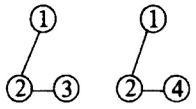
$$\sum_{l=1}^{N} l m_l = N \tag{10.18}$$

A given set of integers $\{m_l\}$ satisfying (10.18), however, does not uniquely specify a graph, because

(a) there are in general many ways to form an l-cluster, e.g.,



(b) there are in general many ways to assign which particle belongs to which cluster, e.g.,



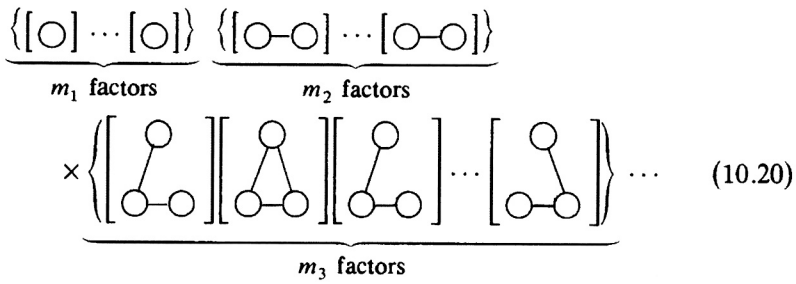
Thus a set of integers $\{m_l\}$ specifies a collection of graphs. Let the sum of all the

graphs corresponding to $\{m_l\}$ be denoted by $S\{m_l\}$. Then

$$Z_N = \sum_{\{m_l\}} S\{m_l\} \tag{10.19}$$

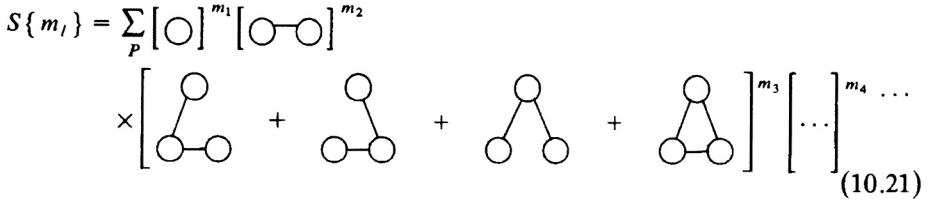
where the summation extends over all sets $\{m_l\}$ satisfying (10.18).

By definition, $S\{m_l\}$ can be obtained as follows. First write down an arbitrary N-particle graph that contains m_1 1-clusters, m_2 2-clusters, etc.; e.g.,



(10.20)

There are exactly N circles appearing in (10.20), and these N circles are to be filled in by the numbers $1, 2, \ldots, N$ in an arbitrary but definite order. We can write down many more examples like (10.20); e.g., we may change the choice of some of the 3-clusters (there being four distinct topological shapes for a 3-cluster). Again we may permute the numbering of all the N circles in (10.20), and that would lead to a distinct graph. If we add up all these possibilities, we obtain $S\{m_l\}$. Thus we may write



(10.21)

The meaning of this formula is as follows. Each bracket contains the sum over all l-clusters. If all the brackets $[\cdots]^{m_l}$ are expanded in multinomial expansions, the summand of $\sum_P$ will itself be a sum of a large number of terms in which every term contains exactly N circles. The sum $\sum_P$ extends over all distinct ways of numbering these circles from 1 to N.

Now each graph is an integral whose value is independent of the way its circles are numbered. Therefore $S\{m_l\}$ is equal to the number of terms in the sum $\sum_P$ times the value of any term in the sum. The number of terms in the sum $\sum_P$ can be found by observing that

(a) there are m_l l-clusters, and a permutation of these m_l things does not lead to a new graph;

(b) in the sum over all l-clusters, such as (10.17), a permutation of the l particles within it does not lead to a new graph. Hence the number of

terms in the sum $\sum_P$ is*

$$\frac{N!}{[(1!)^{m_1}(2!)^{m_2}\cdots][m_1!m_2!\cdots]} \tag{10.22}$$

and the value of any term is

$$(1!Vb_1)^{m_1}(2!\lambda^3 Vb_2)^{m_2}(3!\lambda^6 Vb_3)^{m_3}\cdots \tag{10.23}$$

Therefore

$$S\{m_l\} = N!\prod_{l=1}^{N}\frac{(V\lambda^{3l-3}b_l)^{m_l}}{m_l!} = N!\lambda^{3N}\prod_{l=1}^{N}\frac{1}{m_l!}\left(\frac{V}{\lambda^3}b_l\right)^{m_l} \tag{10.24}$$

From (10.5), (10.9), and (10.24) we obtain

Kanon. part. Suma

$$Q_N(V,T) = \sum_{\{m_l\}}\prod_{l=1}^{N}\frac{1}{m_l!}\left(\frac{V}{\lambda^3}b_l\right)^{m_l} \tag{10.25}$$

This formula is complicated by the restriction (10.18). The grand partition function is simpler in appearance:

GC part. Suma

$$\mathcal{Q}(z,V,T) = \sum_{m_1=0}^{\infty}\sum_{m_2=0}^{\infty}\cdots\left[\frac{1}{m_1!}\left(\frac{V}{\lambda^3}zb_1\right)^{m_1}\frac{1}{m_2!}\left(\frac{V}{\lambda^3}z^2b_2\right)^{m_2}\cdots\right]$$

or

$$\frac{1}{V}\log\mathcal{Q}(z,V,T) = \frac{1}{\lambda^3}\sum_{l=1}^{\infty}b_l z^l \tag{10.26}$$

from which we obtain the equation of state in parametric form:

$$\begin{cases}\dfrac{P}{kT} = \dfrac{1}{\lambda^3}\displaystyle\sum_{l=1}^{\infty}b_l z^l \\ \dfrac{1}{v} = \dfrac{1}{\lambda^3}\displaystyle\sum_{l=1}^{\infty}lb_l z^l\end{cases} \tag{10.27}$$

This is known as the cluster expansion for the equation of state.†

What we have described is historically the first graphical representation of a perturbation series. Graphs have become indispensable tools in the many-body problem and in quantum field theory, in which the analog of (10.26), known generally by the name of the *linked cluster theorem*, plays an important role. Generally it states that the sum of all graphs is the exponential of the sum of all connected graphs.

*To understand the method of counting the reader is advised to work out some simple examples.

†Compare this derivation with that outlined in Problem 7.6.

If the system under consideration is a dilute gas, we may expand the pressure in powers of $1/v$ and obtain the virial expansion. For this purpose we may take the equation of state to be

$$\begin{cases} \dfrac{P}{kT} = \dfrac{1}{\lambda^3} \displaystyle\sum_{l=1}^{\infty} \mathfrak{b}_l z^l \\ \dfrac{1}{v} = \dfrac{1}{\lambda^3} \displaystyle\sum_{l=1}^{\infty} l\mathfrak{b}_l z^l \end{cases} \tag{10.28}$$

where

$$\mathfrak{b}_l(T) \equiv \lim_{V \to \infty} b_l(V, T) \tag{10.29}$$

The virial expansion of the equation of state is defined to be

$$\frac{Pv}{kT} = \sum_{l=1}^{\infty} a_l(T) \left(\frac{\lambda^3}{v} \right)^{l-1} \tag{10.30}$$

where $a_l(T)$ is called the lth virial coefficient. We can find the relationship between the virial coefficients a_l and the cluster integrals $\mathfrak{b}_l$ by substituting (10.30) into (10.28) and requiring that the resulting equation be satisfied for every z:

$$\sum_{l=1}^{\infty} a_l \left(\sum_{n=1}^{\infty} n\mathfrak{b}_n z^n \right)^{l-1} = \frac{\displaystyle\sum_{l=1}^{\infty} \mathfrak{b}_l z^l}{\displaystyle\sum_{l=1}^{\infty} l\mathfrak{b}_l z^l} \tag{10.31}$$

This is equivalent to the condition

$$\begin{aligned} &(\mathfrak{b}_1 z + 2\mathfrak{b}_2 z^2 + 3\mathfrak{b}_3 z^3 + \cdots) \left[a_1 + a_2 \left(\sum_{n=1}^{\infty} n\mathfrak{b}_n z^n \right) + a_3 \left(\sum_{n=1}^{\infty} n\mathfrak{b}_n z^n \right)^2 + \cdots \right] \\ &\quad = \mathfrak{b}_1 z + \mathfrak{b}_2 z^2 + \mathfrak{b}_3 z^3 + \cdots \end{aligned} \tag{10.32}$$

By equating the coefficient of each power of z we obtain

$$\begin{aligned} a_1 &= \mathfrak{b}_1 = 1 \\ a_2 &= -\mathfrak{b}_2 \\ a_3 &= 4\mathfrak{b}_2^2 - 2\mathfrak{b}_3 \\ a_4 &= -20\mathfrak{b}_2^3 + 18\mathfrak{b}_2\mathfrak{b}_3 - 3\mathfrak{b}_4 \\ &\cdots \end{aligned} \tag{10.33}$$

Each virial coefficient therefore involves only a straightforward computation of a number of integrals.

Note that (10.28) differs from (10.27) in that the limit $V \to \infty$ is taken term by term in (10.28). In so doing we have lost all information about possible phase transitions, as we have remarked earlier in Section 9.3. The equation of state

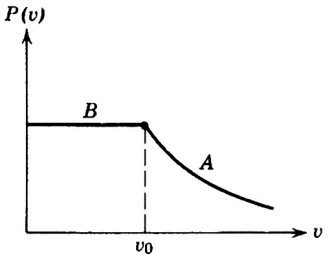


Fig. 10.2 Equation of state obtained by taking the virial expansion to be exact.

(10.30) of the gas phase cannot tell us if and when a phase transition will occur. Mayer* has demonstrated that the equation of state (10.30) has the general form shown in Fig. 10.2. The portion of the isotherm marked A is valid for $v > v_1$, but the value of v_1 is unrelated to v_0, and cannot be obtained from (10.30). The portion marked B is purely mathematical, and unrelated to how the isotherm actually behaves in that region.

10.2 QUANTUM CLUSTER EXPANSION

Kahn and Uhlenbeck† develop a cluster expansion in quantum statistical mechanics. The method they introduce applies equally well to classical statistical mechanics.

Consider N identical particles enclosed in a volume V. Let the Hamiltonian $\mathscr{H}$ of the system have the same form as (10.1) but be an operator instead of a number. In the coordinate representation, $\mathbf{p}_j = -i\hbar\nabla_j$, and v_{ij} is the same function of the number $|\mathbf{r}_i - \mathbf{r}_j|$ as that shown in Fig. 10.1. The partition function is

$$Q_N(V,T) = \operatorname{Tr} e^{-\beta H} = \int d^{3N}r \sum_\alpha \Psi_\alpha^*(1,\ldots,N)\, e^{-\beta\mathscr{H}} \Psi_\alpha(1,\ldots,N) \quad (10.34)$$

where $\{\Psi_\alpha\}$ is a complete set of orthonormal wave functions appropriate to the system considered, and the set of coordinates $\{\mathbf{r}_1,\ldots,\mathbf{r}_N\}$ is denoted in abbreviation by $\{1,\ldots,N\}$. It is important to use symmetric or antisymmetric wave functions, as required by the statistics of the particles (see Problem 10.4). Let us define

$$W_N(1,\ldots,N) \equiv N!\lambda^{3N} \sum_\alpha \Psi_\alpha^*(1,\ldots,N)\, e^{-\beta\mathscr{H}} \Psi_\alpha(1,\ldots,N) \quad (10.35)$$

The partition function can be written in the form

$$Q_N(V,T) = \frac{1}{N!\lambda^{3N}} \int d^{3N}r\, W_N(1,\ldots,N) \quad (10.36)$$

*See Mayer and Mayer, *loc. cit.*

†B. Kahn and G. E. Uhlenbeck, *Physica* **5**, 399 (1938).

1.3 viriálové koeficienty plynu tvrdých koulí

$$v(r) = \begin{cases} +\infty & r < R \\ 0 & r > R \end{cases}$$

NB: jsou to koule o poloměru $R/2$!

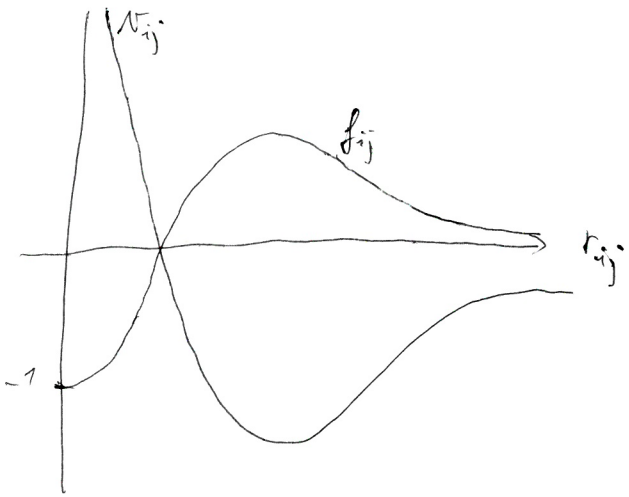
$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j} v_{ij}(r_{ij})$$

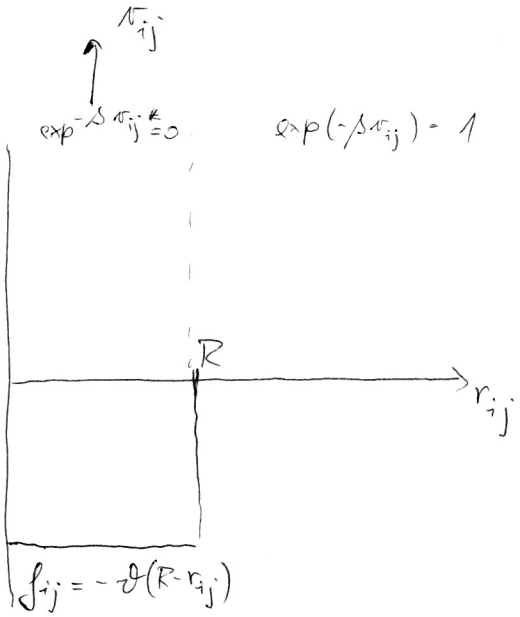
$$Z_C = \frac{1}{N!\,h^{3N}} \int d^{3N}q\, d^{3N}p\, e^{-\beta\mathcal{H}} = \frac{1}{\lambda^{3N} N!} \int d^{3N}r\, e^{-\beta \sum_{i<j} v(r_{ij})}$$

$$\Rightarrow \boxed{Z_C = \frac{Q_N}{\lambda^{3N} N!} \qquad \lambda = \left(\frac{h^2\beta}{2\pi m}\right) \qquad Q_N = \int d^{3N}r\, e^{-\beta \sum_{i<j} v(r_{ij})}}$$

$$Z_G = \sum_{N=0}^{\infty} \left(\frac{z}{\lambda^3}\right)^N \frac{Q_N}{N!} \qquad z = e^{\alpha} = e^{\beta\mu}$$

$$e^{-\beta v_{ij}} = 1 + f_{ij}(|r_i - r_j|)$$

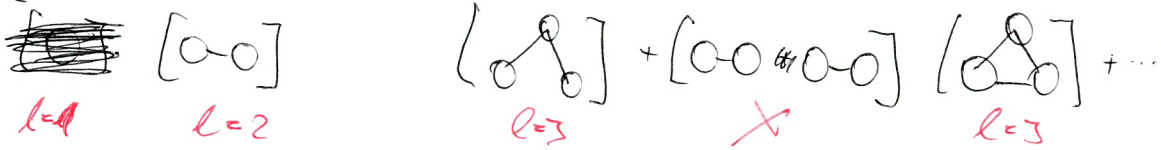




$$\Rightarrow Q_N = \int d^{3N}r \prod_{i<j} (1 + f_{ij})$$

zjevně $f_{ij} \ll 1$ neplatí! (jen pro vys. teplotu)

$$= \int d^{3N}r \left[1 + (f_{12} + f_{13} + \dots) + (f_{12}f_{13} + f_{12}f_{14} + \dots) + (f_{12}f_{23}f_{31} + \dots \right.$$



Kolik je takových příspěvků:

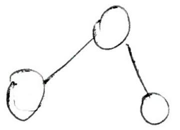
f^0 ~~[O]~~ ... 1 $\Big\}\ l=1$

$f^1 \Leftrightarrow [O-O]$: $\frac{1}{2}N(N-1) = \frac{N!}{2(N-2)!}$ $\Big\}\ l=2$

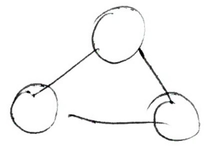
↑ nez. na pořadí O

f^2: $[O-O]^2$: ~~[přeškrtnuto]~~ ↑ nez. na pořadí párů ; $\frac{1}{2}\cdot\frac{1}{2^2}\frac{N!}{(N-4)!}$

↑ nez. na pořadí v párech ; ↑ nez. na pořadí párů

 : $\frac{1}{2}\frac{N!}{(N-3)!}$

↑ $f_{12}f_{23} = f_{23}f_{12}$, $f_{12}f_{23} \neq f_{12}f_{13}$ $\Big\}\ l=3$

f^3:  : $\frac{N!}{3!(N-3)!}$

↑ nezáleží na pořadí f-ek

Co dostanu: Clusterové integrály:

f^0: ~~$\int d^{3N}r = V^N = V^N b_1$~~

f^1: ~~$\int d^{3N}r\, f(|r_1-r_2|) = V^{N-1}\int d^3q\, f(|q|) = 2V^{N-1}\lambda^3 b_2$~~

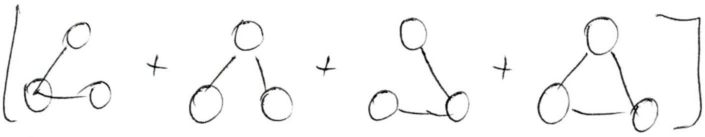
~~OTOČ~~

$b_l(V,T)$

$= \frac{1}{l!\,\lambda^{3l-3}V}\sum(\forall l\text{-clustery})$

clusterový integrál

$\bar{b}_l = \lim_{V\to\infty} b_l \in \mathbb{R}$!

f^2 & f^3: $b_3 = \frac{1}{3!\lambda^6 V}\Big[$  $\Big]$

$3\int d^9r\, f(r_{12})f(r_{23})$; $\int d^9r\, f(r_{12})f(r_{23})f(r_{13})$

↑ každá trojka bude to, proč výše u O-O-O je jen $\frac{1}{2}$ místo $\frac{1}{3!}$

⇒ linked cluster theorem

suma ∀ grafů = exp(~~spojité~~ souvislé grafy)

~~OTOČ~~

$$b_l = \frac{1}{l!\lambda^{3l-3}V} \int \Sigma(\text{l-clusters})\, d^{3l}r$$

$$b_1 = \frac{1}{V}\int d^3r = 1$$

$$b_2 = \frac{1}{2\lambda^3 V}\int d^3r_1 d^3r_2\, f(r_1 - r_2) = \frac{1}{2\lambda^3}\int d^3q\, f(q)$$

$$b_3 = \begin{cases} \text{a)} \quad \frac{3}{3!\lambda^6 V}\int d^3r_1 d^3r_2 d^3r_3\, f(r_1-r_2) f(r_1-r_3) & (I) \\ \quad = \frac{1}{2\lambda^6}\int d^3q_1 f(q_1)\int d^3q_2 f(q_2) = 2b_2^2 & \\ \frac{1}{6\lambda^6 V}\int d^3q_1 d^3q_2 d^3q_3\, f(|r_1-r_2|) f(|r_2-r_3|) f(|r_3-r_1|) & (II) \end{cases}$$

! každý integrál dá $1 \times V$ - jedna volná integrace

$\Rightarrow$ b_l jsou intenzivní

$$\Rightarrow Z_N = \sum_{\{m_l\}} \prod_{l=1}^{N} \frac{1}{m_l!}\left(\frac{V}{\lambda^3} b_l\right)^{m_l} \quad \& \quad \sum_{l=1}^{N} l m_l = N \quad \Rightarrow \sum_N Z_N z^N$$

$$\Rightarrow \log Z_G = \frac{V}{\lambda^3}\sum_{l=1}^{\infty} b_l z^l \qquad z = e^{\alpha} = e^{\beta\mu}$$

$$-pV = \Omega = -k_B T \log Z_G$$

$$\Rightarrow \frac{p}{kT} = \frac{1}{\lambda^3}\sum_{l=1}^{\infty} b_l z^l \qquad \frac{N}{V} = \frac{1}{v} = \frac{1}{\lambda^3}\sum_{l=1}^{\infty} l b_l z^l$$

clusterový rozvoj stavové rovnice

$$\frac{1}{v} = \frac{N}{V} = \frac{1}{V}\frac{\partial \log Z_G}{\partial \alpha} = \frac{1}{v}$$

Řídký plyn $\Rightarrow$ rozvoj p v $\frac{1}{v} \ll 1$ — potřebujeme to?

- provedeme $\lim_{V\to\infty}$ ve stav. rovnici člen po členu: $b_l \to \bar{b}_l$

(ztráta části info! – ~~člen po členu to se sleví.~~ – nejsou fáz. přechody)

$\Rightarrow$ Viriálový rozvoj

$$\frac{pv}{kT} = \sum_{l=1}^{\infty} a_l(T)\left(\frac{\lambda^3}{v}\right)^{l-1}$$

$$\Leftrightarrow \frac{\sum_{l=1}^{\infty} b_l z^l}{\sum_{l=1}^{\infty} l b_l z^l} = \sum_{l=1}^{\infty} a_l \left(\sum_{n=1}^{\infty} n b_n z^n\right)^{l-1}$$

a porovnáme mocniny z

$$\sum_{l=1}^{\infty} b_l z^l = \sum_{l=1}^{\infty} a_l \left(\sum_{n=1}^{\infty} n b_n z^n\right)^{l-1}\left(\sum_{m=1}^{\infty} m b_m z^m\right)$$

$z^1 \Rightarrow b_1 = a_1 b_1 \Rightarrow \boxed{a_1 = 1}$ NB: $b_1 = 1$

z^2: $b_2 = 2a_1 b_2 + a_2 b_1^2 \Rightarrow b_2 = 2b_2 + a_2 \Rightarrow \boxed{a_2 = -b_2}$

z^3:

$$b_3 = 3a_1 b_3 + a_2 (2b_2 b_1 + 2b_1 b_2) + a_3 b_1^3$$

$$= 3b_3 - 4b_2^2 + a_3$$

$$\Rightarrow \boxed{a_3 = 4b_2^2 - 2b_3}$$

KOULE

jsem v $\lim_{V\to\infty}$ => $\int$ přes celé koule, ostatní nevšímám ...)

=> počítáme $b_1 = 1$, b_2 a b_3

$$b_2 = \frac{1}{2}\frac{1}{\lambda^3}\int d^3q\, f(q) = -\frac{1}{2\lambda^3}\int_{K_0(R)} d^3q = -\frac{2}{3\lambda^3}\pi R^3$$

$$b_3(\text{⋔}) = 2b_2^2 = 2\frac{4}{9\lambda^6}\pi^2 R^6 = \frac{8\pi^2}{9\lambda^6}R^6$$

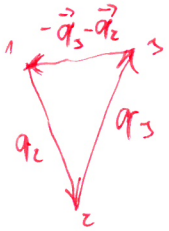
r_3

$q_2 = r_1 - r_2$ =>
$q_3 = r_2 - r_3$

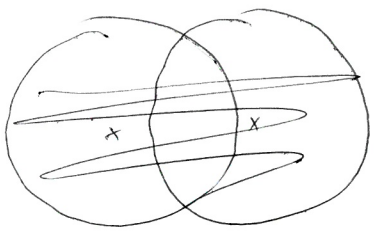
$$b_3(\text{||}) = \frac{1}{6\lambda^6 V}\int d^3r_1\, d^3q_2\, d^3q_3\, f(|\vec{q}_2|) f(|\vec{q}_3|) f(|\vec{q}_2+\vec{q}_3|)$$

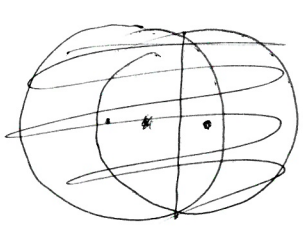
$$= -\frac{1}{6\lambda^6}\int d^3q_2 d^3q_3\, \vartheta(R-|q_2|)\vartheta(R-|q_3|)\vartheta(R-|\vec{q}_2+\vec{q}_3|)$$

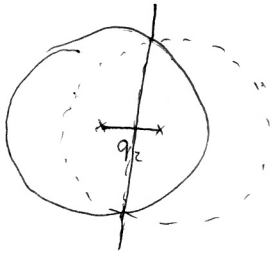
$K_R(0)$ $K_R(0)$ $K_R(\vec{q}_2)$

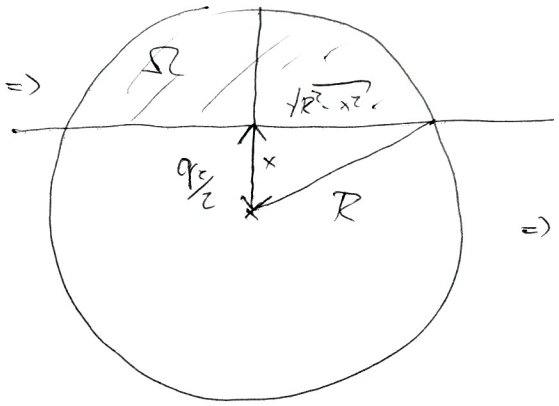


=> ~~přímek~~ pro fixní q_2 je $\int d^3q_3$ integrál přes průnik koulí okolo počátku a okolo bodu $\vec{q}_2$ $r \le R$









$\Rightarrow x \in \left(\frac{q_2}{2}, R\right)$

$$\Rightarrow \Omega = \int_{\frac{q_2}{2}}^{R} \pi\left(R^2 - x^2\right) dx$$

$$= \pi\left(R^2 x - \frac{1}{3}x^3\right)\Big|_{q_2/2}^{R} = \pi\left(\frac{2}{3}R^3 - R^2\frac{q_2}{2} + \frac{1}{24}q_2^3\right)$$

$$\Rightarrow b_3 = -\frac{1}{6\lambda^6}\int_{0}^{R} dq_2\, 2\Omega(q_2) = -\frac{8\pi}{6\lambda^6}\int_0^R dq_2\, q_2^2\,\Omega(q_2)$$

$$= -\frac{4\pi^2}{3\lambda^6}\left(R^3 q_2^3 - R^2\frac{q_2^4}{8} + \frac{1}{6\cdot 24}q_2^6\right)_0^R$$

$$= -\frac{4\pi^2}{3\lambda^6}R^6\left(\frac{2}{9} - \frac{1}{8} + \frac{1}{6\cdot 24}\right) = -\frac{4}{3}\frac{\pi^2}{\lambda^6}R^6\frac{5}{48} = -\frac{5\pi^2}{36\lambda^6}R^6$$

$$\Rightarrow \boxed{b_3 = \left(\frac{8}{9} - \frac{5}{36}\right)\frac{\pi^2}{\lambda^6}R^6 = \frac{3\pi^2}{4\lambda^6}R^6} \qquad \boxed{b_2 = -\frac{2\pi}{3\lambda^3}R^3 \qquad b_1 = 1}$$

$$\Rightarrow a_1 = 1$$

$$a_2 = -b_2 = \frac{2\pi}{3\lambda^3}R^3$$

$$a_3 = 4b_2^2 - 2b_3 = \frac{4\cdot 4\pi^2}{9\lambda^6}R^6 - \frac{6\pi^2}{4\lambda^6}R^6 = \frac{5\pi^2}{18\lambda^6}R^6$$

$$\Rightarrow \boxed{a_1 = 1 \qquad a_2 = \frac{2\pi}{3\lambda^3}R^3 \qquad a_3 = \frac{5\pi^2}{18\lambda^6}R^6 \qquad \lambda = \sqrt{\frac{2\pi u_1}{h^2/5}}}$$

$\Rightarrow$ skat. tvar

$$p v = kT\left(a_1 + a_2\frac{1}{v} + a_3\frac{1}{v^2}\right) = kT\left(1 + \frac{2}{3}\pi R^3\cdot\frac{1}{v} + \frac{5\pi^2}{18}R^6\frac{1}{v^2}\right)$$

---

vdW: $(v-b)\left(p+\frac{a}{v^2}\right) = kT$

$$\Rightarrow \frac{kT}{v} = \left(1-\frac{b}{v}\right)\left(p+\frac{a}{v^2}\right) \qquad \frac{1}{v} = \frac{N}{V} \ll 1$$

$$\Rightarrow \frac{1}{v}kT = p - p\frac{b}{v} + \frac{a}{v^2} - \frac{ba}{v^3}$$

$$\Rightarrow \frac{pv}{kT} = 1 + \frac{pv}{kT}\frac{b}{v} - \frac{a}{kTv} + \frac{ba}{kTv^2}$$

$$\Rightarrow \frac{pv}{kT} = 1 + A\frac{1}{v} + B\frac{1}{v^2}$$

$$\Rightarrow 1 + A\frac{1}{v} + B\frac{1}{v^2} = 1 + \left(1 + A\frac{1}{v} + B\frac{1}{v^2}\right)\frac{b}{v} - \frac{a}{kTv} + \frac{ba}{kTv^2}$$

$\left(\frac{1}{v}\right)^0$: $1 = 1$ ✓

$\frac{1}{v}$: $A = b - \frac{a}{kT}$

$\frac{1}{v^2}$: $B = Ab + \frac{ba}{kT} = b^2 - \frac{ab}{kT} + \frac{ab}{kT} = b^2$

Math:

$$\frac{p}{kT} = n + n^2\left(b - \frac{a}{kT}\right) + \sum_{k=2}^{\infty} b^k n^{k+1}$$

$$\Rightarrow \boxed{\frac{pv}{kT} = 1 + \left(b - \frac{a}{kT}\right)\frac{1}{v} + \frac{b^2}{v^2}}$$

$\Rightarrow b^2 \overset{?}{=} \frac{5\pi^2}{18}R^6 = \frac{10\pi^2}{36}R^6 \Rightarrow b = \frac{\sqrt{10}}{6}\pi R^3$

nebo: $\frac{a}{kT}$ zanedbám $\Rightarrow b = \frac{2}{3}\pi R^3$

NB: v odpovídá kouli o poloměru $\frac{R}{2}$; i pro střed druhé koule je nedostupný objem $\frac{4}{3}\pi R^3$, ale ten dělím mezi každou dvě koule