Virial Expansion – A Brief Introduction

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Abstract

The existence of interactions among the particles of a system is a common situation in statistical physics, for instance in real gases or weak liquid solutions. On the one hand, these interactions limit the range of applicability of the ideal equation of state. On the other hand, they give rise to a whole new class of exciting phenomena, such as thermodynamic instability and metastability, phase transition, phase separation, and self-assembled micro-structuring. The virial expansion is the simplest and most general theory addressing these effects, and constitutes the foundation for more advanced and specific models, such as Ornstein-Zernike Integral Schemes, Path Integral Statistical Physics, and Phase Field Theories. In these notes, we introduce the virial expansion using elementary mathematical methods. The reader needs to be only familiar with the contents of first- and second-year university courses. A basic understanding of classical mechanics and thermodynamics is recommended, including the equation of state of the ideal gas.

In the first section, we briefly review the equation of state of the ideal gas. We discuss the problems encountered when trying to extend that result to systems of interacting particles, and elucidate the general strategy of the virial expansion. Then, we introduce the second virial coefficient and derive the corresponding second-order virial equation of state in two different ways, using the virial theorem and the cluster expansion. Finally, we present an example based on the square well potential, and connect the virial expansion to the familiar van der Waals equation of state for real gases, and thus connect microscopic interaction parameters to macroscopic equation of state, one of the key points in condensed matter.

Starting point: equation of state

Matter can be found in different thermodynamic phases. For instance, H_2O in a closed box is a liquid under normal conditions, but can be converted into a vapor or a solid upon a change of temperature. For pure substances, a complete description (of all phases) is possible through a thermodynamic potential as a function of its natural variables:

Energy	$E(S, V, N)$
...	...
Free energy	$F(T, V, N)$
Free enthalpy	$G(T, P, N)$

Most frequently and conveniently, experiments use the variable set T, V, P, V. There is an equation connecting these variables , the so-called **equation of state** (EOS):

$$P = P(V, T, N) \; . \tag{1}$$

Since the pressure is an intensive quantity (i.e. independent of the system size), it is possible to express it as a function of purely intensive quantities. The equation (1) is restated introducing the **density** $\rho := N/V$, becoming:

$$P = P(T, \rho) \; . \tag{2}$$

Ideal gas

The EOS of the ideal gas reads simply:

$$P = \frac{NkT}{V} = \rho kT \; , \tag{3}$$

the pressure is linear both in the temperature and in the density. Note that $P = P(T, \rho)$ is entirely invertible in both variables; at every (P, T), a single phase with density $\rho = P/kT$ is predicted.

This EOS can be verified experimentally measuring (T,V,P,N) for real gases at high T and low P. Moreover, it can be derived theoretically under the assumptions that *molecules in the gas are point-like and do not interact with each other.*

Real systems

If the simplifying assumptions of the ideal gas are given up, i.e. if interactions between the particles and a finite particle volume of these is allowed for, this many-particle system is much more difficult to solve.

Many different techniques have been developed to cope with this problem. The standard way proceeds in two steps. First of all, one has to find a *reference state* which is not very different from the real system, and whose Hamiltonian is known. For instance, an ideal, zero-temperature crystal is a reference state for a real crystal; the hard-sphere system is a reference state for real colloidal dispersions. Then, one may use a type of perturbation theory around this state in the thermodynamic variables (T,P,ρ) to get a better approximation. Of course, this approach is doomed to fail if the interactions are too strong and the density too high. The virial expansion is such a perturbation theory. It is used when the interactions are dominated by two-body interactions, whereas many-body ones are rare. The virial expansion is thus suited for modeling not only real gases. Also, liquid mixtures where one component is much less abundant and bigger than the other (solution, or suspension) can be simplified to a picture of big colloidal particles (solute) in a homogeneous background (solvent). The latter argument is a common paradigm in colloid theory and allows a connection of colloid theory and thermodynamics of real gases and simple liquids.

The virial equation of state

Let us study the thermodynamics of a real gas at low density and high temperature. The theory for dilute solutions is analogous. In this gas, it is rare for two particles to come close to one another; for *three or more* particles it is even less frequent.

We assume that the total potential energy can be written as a sum of two-particle interactions:

$$\mathcal{V}(q) = \frac{1}{2} \sum_{k=1}^{N} \sum_{j=1, j \neq k}^{N} V_2(q_k, q_j) \, , \tag{4}$$

where the pair potential V_2 is equal for all pairs. In this simplified form, $\mathcal{V}(q)$ becomes much more tractable than in the general, multi-particle interaction case. In fact, we only need a theoretical model for the potential between *two* molecules, instead of $3N$ ones.

Now, we start the second step of the strategy, i.e. perturbation theory. In the usual *virial expansion*, one expands in powers of the density, keeping the temperature dependence of the coefficients. One seeks a so-called **virial equation of state**:

$$P(T, \rho) = kT \cdot \left[\rho + \sum_{i=2}^{\mathrm{MAX}} B_i(T) \rho^i \right] \quad , \tag{5}$$

where $B_i(T)$ are the expansion coefficients and MAX is the maximum order of the expansion. The first correction to the ideal gas EOS is given by the **second virial coefficient** B_2, and is written:

$$P(T, \rho) = kT \cdot \left[\rho + B_2 \, \rho^2 \right] = kT \cdot \rho \left[1 + B_2 \rho \right]$$

Therefore, for a real gas, B_2 is the main physical quantity that distinguishes it from the ideal gas, and that estimates the overall interactions among the particles. We derive the virial EOS below, but for the impatient reader we already state the main result:

$$B_2 = -2\pi \int_0^\infty \left(e^{-\frac{V_2(R)}{kT}} - 1 \right) R^2 \, \mathrm{d}R \, . \tag{6}$$

Two paths are common to get the virial EOS from the potential (4), the derivation based on the virial theorem and the cluster expansion. In these notes, the former will be less formal but easier to follow.

Derivation based on the virial theorem

This derivation is mathematically easier and physically more instructive, but not quite direct. As a first step, it is necessary to translate the existence of $\mathcal{V}(q)$ into a general correction for the EOS. Then, this correction has to be recast in terms of a power expansion of the density.

The definition from classical mechanics of the **virial** G reads:

$$G = \sum_{i=1}^{N} q_i \cdot p_i$$

Even at thermodynamic equilibrium, G will change all the time because of fluctuations. However, the mean of its time derivative is zero; using the ergodic hypothesis, one can write:

$$\begin{aligned} \left\langle \frac{\mathrm{d}G}{\mathrm{d}t} \right\rangle &= \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau \frac{\mathrm{d}G}{\mathrm{d}t} \, \mathrm{d}t \\ &= \lim_{\tau \to \infty} \frac{1}{\tau} \left(G(\tau) - G(0) \right) \\ &= 0 \, . \end{aligned} \tag{7}$$

The last equality follows because G is a limited function (both volume and energy of the system are finite).

From the definition of the virial, and using Hamilton's equation of motion, one obtain:

$$\begin{aligned} \frac{\mathrm{d}G}{\mathrm{d}t} &= \frac{\mathrm{d}}{\mathrm{d}t} \left[\sum_{i=1}^{N} q_i \cdot p_i \right] \\ &= 2 \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=1}^{N} q_i \cdot f_i(q) \\ &= 2\mathcal{K}(p) + \sum_{i=1}^{N} q_i \cdot f_i(q) \, . \end{aligned} \tag{8}$$

Here $\mathcal{K}(p)$ is the kinetic energy as a function of momenta, and $f_i(q)$ is the total force acting on the i-th particle:

$$f_i(q) := -\partial_{q_i}\mathcal{V}(q) + f_{\text{ext}}(q_i) \, ,$$

which is the sum of internal and external forces (the last ones coming from the walls confining the gas). $\partial_x := \partial/\partial x$ is the partial derivative.

The external force term in (8) is proportional to the pressure, because f_{ext} is different from zero only on the container walls:

$$\begin{aligned} \left\langle \sum_{i=1}^{N} q_i \cdot f_{\text{ext}}(q_i) \right\rangle &= N \cdot \langle q_1 \cdot f_{\text{ext}}(q_1) \rangle \\ &= 3N \langle q_1^x \cdot f_{\text{ext}}(q_1^x) \rangle \\ &= 3PV \, , \end{aligned} \tag{9}$$

where the last equality follows from the usual molecular theory of gases.

The mean kinetic energy is proportional to the temperature (equipartition theorem):

$$2 \langle \mathcal{K} \rangle = 3NkT \, , \tag{10}$$

From (7), the average of (8) using (9) and (10) has to vanish, ensuring the conservation of the mean virial. We recast this conservation as a function of the pressure, obtaining the following result:

$$P(T,\rho) = \rho kT - \left[\frac{1}{3V} \left\langle \sum_{i=1}^{N} q_i \cdot \partial_{q_i}\mathcal{V}(q) \right\rangle \right] \tag{11}$$

Compared to the ideal gas, we have an additional factor, the so-called virial correction, which is due to the interactions:

$$\mathcal{X} = - \left[\frac{1}{3V} \left\langle \sum_{i=1}^{N} q_i \cdot \partial_{q_i}\mathcal{V}(q) \right\rangle \right]$$

Now we will express the last equality in a more convenient form, using the hypothesis of pairwise interactions. The partial derivative of V becomes:

$$\begin{aligned} \partial_{q_i}\mathcal{V}(q) &= \frac{1}{2} \left[\sum_{j=1, j\neq i}^{N} \partial_{q_i} V_2(q_i, q_j) + \sum_{k=1, k\neq i}^{N} \partial_{q_i} V_2(q_k, q_i) \right] \\ &= \sum_{j=1, j\neq i}^{N} \partial_{q_i} V_2(q_i, q_j) \, , \end{aligned}$$

In the second line we used the identity of particles, i.e. $V_2(q_i, q_j) = V_2(q_j, q_i)$. We get:

$$\begin{aligned} \mathcal{X} &= \frac{1}{3V} \left\langle \sum_{i,j\neq i} q_i \cdot \partial_{q_i} V_2(q_i, q_j) \right\rangle \\ &= \frac{1}{6V} \left\langle \sum_{i,j\neq i} r_{ij} \partial_{r_{ij}} V_2(r_{ij}) \right\rangle \ , \end{aligned}$$

where $r_{ij} := q_i - q_j$ is the position difference, and the translational symmetry of the potential, i.e. $V_2(q_i, q_j) = V_2(r_{ij})$, has been used.

Pair correlation function

At this point, in terms of notation it is more convenient to trade in the double sum for a distribution function:

$$g(r) := \frac{1}{\rho^2} \sum_{i,j\neq i} \delta(r - r_{ij}) \ ,$$

This quantity is, strictly speaking, a function of all particle positions at a given time, i.e. a dynamic variable. In practice, $\rho^2\, g(r)$ is a map of the molecule separations, the probability distribution of finding, among all molecules, two of them separated by a vector r. Its mean value $\langle \rho^2\, g(r) \rangle$ is the equilibrium probability distribution that two particles are separated by a vector r, and is called **pair correlation function**.

Therefore, it is clear that g and V_2 are closely related. The mean inter-particle separation takes exactly the value that minimizes the free energy(enthalpy); in turn, the total interaction energy V_2 depends on the relative positions of particles. Obviously, the pair correlation function also depends on the temperature and the density, i.e. $g = g(r, T, \rho)$.

In terms of pair correlations, the virial correction can be rewritten as follows:

$$\mathcal{X} = \frac{\rho^2}{6V} \int_V \int_V g(r) \cdot r \cdot \partial_r V_2(r) \, \mathrm{d}q \mathrm{d}q' \ , \tag{12}$$

in which $r := q - q'$.

Radial distribution function

Now, if the potential is also radially symmetric, one can simplify this expression further. We have to assume that g is also radially symmetric; this is explained in the following. First we introduce the inter-particle distance $R := |r|$. Now, given a particle at a certain point in space, $\rho^2\, g(R)$ is the probability distribution to find another particle at a distance R. Clearly, if both the Hamiltonian and the entropy are radially symmetric, the condition of minimizing the free energy (enthalpy) implies the same symmetry for $g(r)$. Then, g only depends on the distance between two particles, and is called **radial distribution function**.

Inserting $\mathcal{X}$ from (12) into the EOS (11), we find the **virial EOS**:

$$P(T,\rho) = \rho kT - \frac{2\pi\rho^2}{3} \int_0^\infty g(R)\, R^3\, V_2'(R)\, \mathrm{d}R\,, \tag{13}$$

where we used the identity $r \cdot \partial_r f(r) = R\, f'(R)$, valid for every radially symmetric function f.

Sign of the virial correction

From the minus sign in the virial EOS (13), one could think that the virial correction is always negative. This is not true, as we will see in the following.

The sign of the whole correction $\mathcal{X}$ depends on that of the integrand function $g\, R^3\, V_2'$. g is always positive because it is proportional to a probability distribution via a positive factor ρ^2; R^3 is also positive, since the integration is performed from zero upwards. So, the key factor here is V_2', the derivative of the pairwise potential.

If the potential between two particles increases with the distance, as for gravity or Coulomb attraction, the virial correction will be negative. In contrast, if the potential decreases with distance, as for Coulomb repulsion, the virial correction will be positive.

It is also possible that V_2 is not a monotonic function, because a certain distance between particles is energetically favored. In fact, this is the usual case, i.e. attractive and repulsive contributions to V_2. For instance, atoms in a crystal possess harmonic potentials centered at certain lattice spacings, and colloidal particles in an electrolyte solution can have a non-trivial potential. In both cases, it is clear that interactions play an important role for the EOS, but the sign of the virial correction is not obvious at first glance.

Second-order expansion of the virial EOS

Now we are able to perform perturbation theory on the virial EOS. In practice, the virial correction is the product of two quantities, i.e. V_2' and g. If the potential is known, the whole power expansion is encoded in the radial distribution function.

As a first approximation, it is natural to assume that g is Boltzmann-distributed according to the potential V_2:

$$g(R) \approx \exp\left[-\frac{V_2(R)}{kT}\right]\,. \tag{14}$$

With such a choice, the virial EOS can be integrated by parts and, for sufficiently regular potentials, we get the second-order expansion:

$$P(T,\rho) = \rho kT - 2\pi kT\,\rho^2 \int_0^\infty \left(e^{-\frac{V_2(R)}{kT}} - 1\right) R^2\,\mathrm{d}R\,. \tag{15}$$

Because of the approximation (14), all coefficients above the second one have been neglected. The reader can (indeed, should) verify that the second-order coefficient is consistent with B_2 as in (6). Furthermore, as for the full virial correction, attractive (repulsive) potentials will give rise to negative (positive) B_2. Conversely, the sign of B_2 is an indicator of the "degree of attractiveness and repulsiveness" of inter-particle interactions.

Higher-order expansion

In principle, refining the approximation for g up to the n-th order, the final virial EOS will be of $(n+2)$-th order. However, this refinement is very difficult to perform in practice.

One could even get the impression that we only shifted the expansion problem from $P(T,\rho)$ over to $g(r,T,\rho)$. As a matter of fact, our whole derivation enabled us to calculate a single virial coefficient, namely B_2. However, from the second-order EOS it is possible to calculate $g(r,T,\rho)$ approximately, up to first order in the density. Recursively, this delivers the third-order virial coefficient B_3, an so on. So, from the single parameter B_2, it is possible to compute approximately the full correction due to interactions. This procedure is called **Kirkwood superposition approximation**.

Cluster expansion

The second path for including the interactions into the EOS, in a power expansion of the density, is the cluster expansion. This approach is much more direct than the mechanical derivation and, in a sense, more powerful. The drawback lies in its mathematical abstraction and computational complexity.

The starting point is the following: apart from exotic examples, all thermodynamic potentials are equivalent for describing a system, as long as they are expressed as functions of their natural variables. A good choice is the free energy, because it depends on both V and N, so it is easily expressed as a function of the density. In the canonical formalism, the pressure is derived from the partition function Z as follows:

$$P(T,V,N) = -\partial_V F(T,V,N) = kT\cdot\partial_V \log Z(T,V,N)\,. \tag{16}$$

The expansion of P is then translated into an expansion of Z. If the Hamiltonian is in a form that allows a decoupling of the momenta p_i from the positions q_i, we can define a reduced partition function:

$$Z_Q(T,V,N) := \left(\frac{2\pi mkT}{h^2}\right)^{-3N/2} \cdot Z(T,V,N)\,,$$

which is an integral over the Gibbs distribution of the potential $\mathcal{V}$ alone, i.e.:

$$Z_Q(T,V,N) = \frac{1}{N!}\int_{V^N} \exp\left[-\frac{\mathcal{V}(q)}{kT}\right]\,\mathrm{d}q\,.$$

We want to expand Z_Q around the limit of vanishing density, so that small correction to the ideal gas are taken into account. In the ideal gas, particles never meet in the sense of interactions. In a weakly interacting gas, pairs of particles will interact rarely, and three-particle clusters will form even less commonly. But the probability of meeting is clearly linked to the density. So, we develop an expansion around the number of molecules meeting in a cluster and hope, in the end, to recover a density expansion. The general theory, which includes non-pairwise forces, is called **Ursell expansion**; however, for the sake of brevity, we will only study the pairwise approximated theory due to Mayer, called the **Mayer expansion**.

Mayer f-function

We have already met the basic ingredient in equation (15). In order to derive that expression, we have integrated (13) by parts , using the following choice of functions:

$$\begin{array}{ccc}
V_2'(R)\,e^{-\frac{V_2(R)}{kT}} & \xrightarrow{\int \mathrm{d}R} & -kT\left(e^{-\frac{V_2(R)}{kT}}-1\right) \\
R^3 & \xrightarrow{\partial/\partial R} & 3\,R^2
\end{array}$$

In the integrated part, the "minus one" part looks superfluous; its derivative is zero. However, its presence is essential for the elimination of the boundary integral at $R \to \infty$. Without the "minus one", the exponential function would stay finite and the integral would diverge! So, the function:

$$f(R) := e^{-\frac{V_2(R)}{kT}} - 1$$

seems to be a key piece in our previous derivation; it is called **Mayer f-function**. In ideal systems, where there are no interactions, the Mayer f-function vanishes everywhere. The stronger the interactions V_2, the larger the absolute value of f. In this sense, the Mayer f-function looks like a promising candidate as smallness parameter for a perturbation approach starting from the ideal gas. This is indeed the essence of the cluster expansion, as we will see in the following. For now, note that, in general, the Mayer f-function is zero at large distances, and takes finite values only in the interaction region, where the pairwise potential is different from zero.

Mayer expansion

Now look at the reduced partition function Z_Q. In the approximation of pairwise interactions, we assume that V_2 only depends on the position difference $r_{ij} = q_i - q_j$, symmetrically under exchange of the two particles. Z_Q becomes:

$$\begin{aligned} Z_Q(T, V, N) &= \frac{1}{N!} \int_{V^N} \exp\left[-\frac{\sum_{j>k} V_2(r_{kj})}{kT} \right] \, \mathrm{d}q \\ &= \frac{1}{N!} \int_{V^N} \prod_{j>k} \exp\left[-\frac{V_2(R_{kj})}{kT} \right] \, \mathrm{d}q \\ &= \frac{1}{N!} \int_{V^N} \prod_{j>k} \{1 + f(r_{kj})\} \, \mathrm{d}q \, . \end{aligned} \tag{17}$$

In the last expression we used the Mayer f-function.

Since the Mayer f-function is zero at large r_{kj}, the effective integration volume in the space of configurations is much smaller than V^N. In other words, in most of V^N we are integrating the identity function. This remark shows the way how to expand Z_Q. As a zero-order approximation, we assume that the integrand is indeed the identity. Secondly, we calculate the correction for one pair of interacting particles. Then, we take into account two pairs, three pairs, one 3-body cluster, one 3-body and one pair, etc., up to large clusters.

Mathematically, this is expressed in the following series expansion:

$$\prod_{j>k} \{1 + f(r_{kj})\} = 1 + \sum_{j>k} f_{kj} + \sum_{j>k,\ m>l,\ l \geq k,\ (kj) \neq (lm)} f_{kj} f_{lm} + \ldots \tag{18}$$

which is called the **Mayer expansion**.

Cluster diagrams and combinatorics

Equation (18) get notationally complex as the order of the expansion increases, for the indices are not free to run from 1 to N, but are constrained in order to avoid double-counting.

Moreover, (18) groups together terms quite different from one another. For instance, consider the following terms:

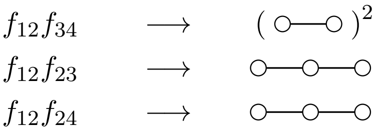
$$f_{12} f_{23} \qquad \text{and} \qquad f_{12} f_{34}$$

In the first one, particle 2 builds an interaction bridge between 1 and 3, forming a 3-body cluster, 1-2-3. In the last one, two spatially separated pairs are formed, i.e. 1-2 and 3-4. Both terms are written in the form $f_{kj} f_{lm}$, so that they appear in the same group in (18).

Another obvious drawback of the expansion as written in (18) is that we do not recognize identical clusters formed by different particles. For instance, it is clear that the terms $f_{12}f_{23}$ and $f_{12}f_{24}$ contribute with the same amount to the reduced partition function, but equation (18) does not show it at all.

To get over these three issues, a graphical approach has been taken. This is analogous to the Feynman diagrams in Quantum Field Theory, but in the real rather than in the reciprocal space. Following the convention of e.g. Croxton, we denote every particle involved in an interaction with a white circle, and every f_{kj} as a bond between two white circles. Particles which do not take part in any interaction are written either by non-connected circles or let away. Finally, if one type of cluster is present n times in the system, its diagram will be elevated to the n-th.

Our previous examples would become:



We immediately see the advantages of this approach. Equivalent clusters are represented exactly in the same way, and topologically different clusters are clearly distinguishable.

It remains only the problem of the contained indices. Here, we do not have indices at all, but it is not easy to determine how often a certain diagram will occur in the Mayer expansion. In principle it is all about counting and ordering diagrams, but in practice it is a formidable problem of combinatorics. The same difficulty is met in other branches of physics where diagrammatic perturbation theory is used, such as Path Integral Statistical Field Theory. Usually, some physical reason allows one to throw away all but a certain class of graphs, thus simplifying the combinatorics. But in the case of the Mayer expansion, no such approximation seems appropriate, because all cluster forms are equally important.

We are not really interested here in calculating the coefficients of the expansion up to high orders, but only in showing a proof of principle. So, in the following, numbers coming from the combinatorics will not be explained; they will just appear in the equations.

Second-order correction

The easiest terms in (18) are the ones with a single Mayer f-function. They represent a single pair of interacting particles in the whole system, and their graph is just ○—○. The reduced partition function up to second order becomes:

$$\begin{aligned}
Z_Q(T,V,N) &= \frac{1}{N!}\int_{V^N}\left\{1+\frac{1}{2}\frac{N!}{(N-2)!}\;\circ\!\!-\!\!\circ\right\}\,\mathrm{d}q\\
&= \frac{1}{N!}\left[V^N+\frac{N(N-1)}{2}V^{N-1}\int_V \circ\!\!-\!\!\circ\;\mathrm{d}r\right]\\
&=: \frac{1}{N!}\left[V^N+\frac{N(N-1)}{2}V^{N-1}\;\bullet\!\!-\!\!\bullet\right].
\end{aligned}$$

where the black diagram is the integrated counterpart of the white one, i.e.

$$\bullet\!\!-\!\!\bullet := \int_V \circ\!\!-\!\!\circ\;\mathrm{d}r\,.$$

Now we calculate the pressure from the Z_Q:

$$\begin{aligned}
P(T,V,N) &= kT\partial_V \log Z(T,V,N)\\
&= kT\partial_V \log Z_Q(T,V,N)\\
&= kT\partial_V\left[-\log N! + N\log V + \log\left\{1+\frac{N(N-1)}{2V}\;\bullet\!\!-\!\!\bullet\right\}\right]\\
&\approx kT\partial_V\left[-\log N! + N\log V + \frac{N(N-1)}{2V}\;\bullet\!\!-\!\!\bullet\right]\\
&\approx kT\frac{N}{V}-\frac{kT}{2}\left(\frac{N}{V}\right)^2\;\bullet\!\!-\!\!\bullet
\end{aligned}$$

where we used the approximations $\log(1+x)\approx x$ for small densities and $N(N-1)\approx N^2$ for large particle numbers.

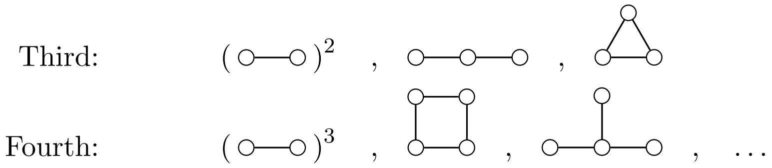
Written as a function of temperature and density, and assuming radial symmetry of the potential, we get the same result as before, i.e.:

$$P(T,\rho)=\rho kT-2\pi kT\rho^2\int_0^\infty\left(e^{-\frac{V_2(R)}{kT}}-1\right)R^2\,\mathrm{d}R\,. \tag{19}$$

One can easily check that the second virial coefficient is consistent with (6).

Higher-order corrections

Differently from the mechanical derivation, the cluster expansion gives us the full recipe (apart from combinatorics) for calculating higher-order corrections. They will be represented by graphs such as the following:



In these notes, we will not examine the details of the higher-order corrections, nor of their graphical representations in terms of graphs. The interested reader is referred to the cited literature.

Examples

In the following, we illustrate the virial expansion with classic examples.

Hard Sphere Potential

The hard sphere is one of the most frequently used model and reference system in soft matter research since it is very simple and takes into account only the excluded volume of the particles. The given interaction potential reads

$$V_{HS}(r) = \begin{cases} \infty & r < a \\ 0 & r \geq a \end{cases} \tag{20}$$

with the sphere diameter a. The infinite barrier at distances smaller than a models the strong electron-electron repulsion found when two particles come in contact.

Several thermodynamic quantities can be calculated analytically, *inter alia* the first coefficients of the virial expansion. Let us apply the virial formalism to calculate the first correction to the ideal gas EOS for excluded volume interaction of hard spheres from Eq. (6):

$$\begin{aligned} B_2 &= -2\pi \int_0^\infty \left(e^{-\frac{V_{HS}(r)}{kT}} - 1 \right) r^2 \, \mathrm{d}r & (21) \\ &= -2\pi \int_0^a (0-1) \; r^2 \, \mathrm{d}r & (22) \\ &= \frac{2}{3}\pi a^3 = 4 \cdot v_p & (23) \end{aligned}$$

with the particle volume $v_p = (4/3)\pi(a/2)^3$.

Thus, the second virial coefficient directly includes the excluded volume from the particles.

Square Well Potential

In most cases, hard core repulsion is not sufficient to describe fully the interparticle interaction, in particular in presence of attractions. In those cases, e.g. gaseous atomic species to aqueous protein solutions, the spherical square well potential is an easy and widely used model instead. It is mathematically written as follows:

$$V_{\mathrm{sw}}(r) = \begin{cases} +\infty & \text{if } r < a, \\ -\epsilon & \text{if } a < r < a(1+\delta), \text{ and} \\ 0 & \text{otherwise, i.e. if } r > a(1+\delta). \end{cases}$$

The potential is shown in Figure 1. The hard core ($r < a$) is given by

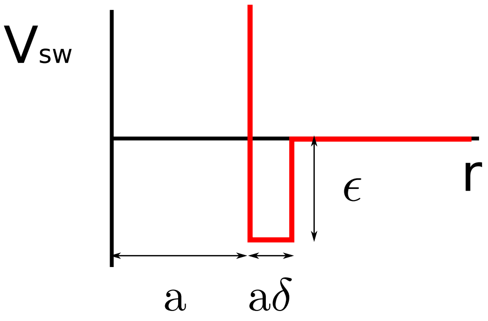


Figure 1: The square well potential as a function of inter-particle distance.

the hard sphere contribution. The square well in the region between a and $a(1+\delta)$ models the interaction between two particles. ϵ quantifies the interaction strength (and also the attractive or repulsive character), and δ the interaction range.

The second virial coefficient for the square well potential is given by Eq. (6), which in this case simplifies as follows:

$$\begin{aligned} B_2 &= -4v_p\left[-1+\left(e^{\frac{\epsilon}{kT}}-1\right)\cdot\left(\delta^3+3\delta^2+3\delta\right)\right] \\ &\approx -4v_p\cdot\left[-1+\frac{\epsilon}{kT}\left(\delta^3+3\delta^2+3\delta\right)\right] \quad . \end{aligned}$$

The last approximation holds if the interaction is reasonably weak, $\epsilon \ll kT$. The second-order virial EOS becomes:

$$P = kT\left\{\rho - 4v_p\cdot\left[-1+\frac{\epsilon}{kT}\left(\delta^3+3\delta^2+3\delta\right)\right]\cdot\rho^2\right\}$$

This EOS depends on the three material parameters a, ϵ, and δ, but the latter two appear in the EOS together. Therefore, we can reduce the number of independent parameters to two by introducing the quantity $\xi := 4\frac{\epsilon}{kT}\left(\delta^3+3\delta^2+3\delta\right)$. The EOS becomes then

$$P = kT\rho\left(1+4v_p\rho\right)-\xi\rho^2$$

where the first summand is the hard sphere contribution and the second specifies the additional interaction.

Van der Waals Equation of State (EOS)

In order to describe the gas-liquid phase transition, J.D. van der Waals suggested more than a century ago (when the virial expansion itself was not yet known) a special form of the EOS, the so-called **van der Waals EOS**:

$$\left(P + \frac{\xi}{v^2}\right) \cdot (v - \zeta) = kT \quad .$$

where $v = V/N$ is the specific volume. ζ has been introduced to account for the volume occupied by each particle, therefore reducing the total accessible volume for all particles. ξ accounts for additional interactions between the particles.

At that time, various alternatives had been proposed as improvements to the ideal EOS, and many others were thereafter. Nevertheless, this EOS kept been used for a very long time, since it provides reasonable thermodynamic consistency. Recasting the van der Waals EOS we obtain

$$\begin{aligned} P &= kT \frac{\rho}{1 - \zeta\rho} - \xi\rho^2 \\ &\approx kT\rho \left(1 + \zeta\rho + (\zeta\rho)^2 + \ldots\right) - \xi\rho^2 \\ &\approx kT \left[\rho + (\zeta - \xi)\rho^2 + \zeta^2\rho^3 + \ldots\right] \end{aligned}$$

where the series expansion is only valid for $\zeta\rho \ll 1$, corresponding to not too high particle densities.

The first summand is the ideal gas contribution. The second represents the correction due to the second virial coefficient, in particular consisting of the hard sphere virial coefficient (choose $\zeta = 4v_p$) and a contribution accounting for additional interaction, e.g. square-well attraction. The third and higher terms only account for excluded volume contributions, but are essential to yield phase separation, which cannot be described from the second virial coefficient alone. The correspondence up to second order with the virial expansion explains part of the success of the van der Waals EOS. At low particle densities the behavior is well described by the first correction via the second virial coefficient.

In conclusion, the virial expansion is a powerful tool in statistical mechanics, for it is able to link the macroscopic quantities of thermodynamics to the microscopic inter-particle potential.

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