

Physics 127b: Statistical Mechanics

Lecture 2: Dense Gas and the Liquid State

Mayer Cluster Expansion

This is a method to calculate the higher order terms in the virial expansion. It introduces some general features of perturbation theory in many body systems, for example the use of diagrams to represent terms in the series, and the topology of diagrams to understand which ones have the correct extensive behavior that are therefore are the ones to be retained. The Mayer cluster expansion also illustrates the intricacy of such methods, and I will only sketch the results. *Pathria* has a fairly terse discussion. The best reference for a sufficiently detailed account to be understandable, but not so dry as to be indigestible, is chapter 4 in *States of Matter* by *Goodstein*. Other references are chapter 12 of *Statistical Mechanics* by Mayer and Mayer (on reserve), and a pedagogical paper by *Salpeter* in *Annals of Physics* **5**, 185 (1958)—the first part of this paper is available as a [handout](#) on the website.

The configuration integral is written

$$Z_N = \int \dots \int d^{3N} r e^{-\beta \sum_{i < j} u(|\vec{r}_i - \vec{r}_j|)} = \int \dots \int \prod_{i < j} (1 + f_{ij}) d^{3N} r \quad (1)$$

with $f_{ij} = e^{-\beta u(r_{ij})} - 1$ with the idea that the effect of f_{ij} is *small*, either because the potential is small, or because a large potential only acts over a small volume, as in the previous lecture. In this case we can expand the product in Z_N

$$Z_N = \int \dots \int \left[1 + \sum_{i < j} f_{ij} + \sum_{\substack{i < j, k < l \\ i, j \neq k, l}} f_{ij} f_{kl} + \dots \right] d^{3N} r, \quad (2)$$

where you can see what terms are in the multiple sums by thinking of all, unrepeated, interactions (e.g. 1 – 2 and 1 – 3 is included, but 1 – 2 and 1 – 2 is not). We then want to take logs to get thermodynamic quantities, e.g. in the canonical ensemble

$$A = -k_B T \ln \left[\frac{1}{N!} \frac{1}{\lambda^{3N}} Z_N \right], \quad (3)$$

and in the microcanonical ensemble

$$\frac{PV}{k_B T} = \ln Q = \ln \left[\sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{z}{\lambda^3} \right)^N Z_N \right]. \quad (4)$$

Note that the latter expression gives a convenient derivation of the virial expansion, since small density corresponds to small z . We will have to expand $\ln(1 + a_1 z + a_2 z^2 \dots)$ in small z and then relate ρ to z via

$$\rho = \frac{z}{V} \frac{\partial \ln Q}{\partial z}. \quad (5)$$

The key idea is to represent the terms diagrammatically. This is generally a very useful approach in complicated perturbation expansions. Often simplifications of the results can be expressed in terms of the topology of the diagrams, such as the *linked cluster expansion* below. In the Mayer cluster expansion, each particle index is denoted by a dot or small circle, and each f_{ij} by a link between the dots i and j (see Fig. (1)). Each diagram corresponds to a contribution to the expansion of Z_N (with each term in the sums in Eq. (2) considered as a separate contribution), and there is an algebraic expression that can be associated with each diagram, as listed in the caption. The configuration integral Z_N is given by the sum of all distinct N -dot

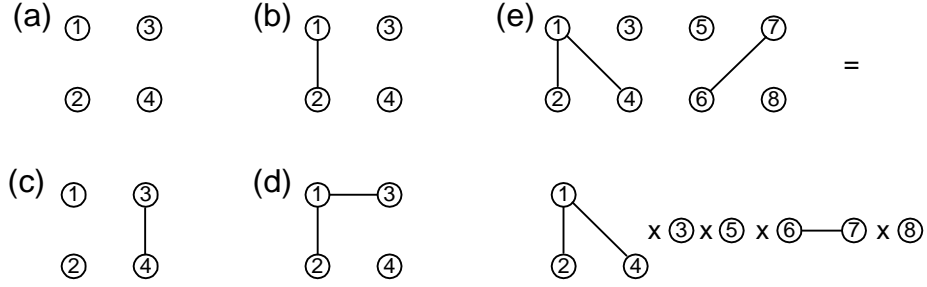


Figure 1: Some diagrams in the Mayer cluster expansion at fourth order representing: (a) $\int 1 d^{12}r$; (b) $\int f_{12} d^{12}r$; (c) $\int f_{34} d^{12}r$; and (d) $\int f_{12} f_{13} d^{12}r$ (with $d^{12}r$ meaning $d^3r_1 d^3r_2 d^3r_3 d^3r_4$). Note that (b) and (c) lead to the same values of the integral, and so are equivalent (but must be counted separately). Panel (e) shows an eighth order diagram demonstrating the factorization property: the value represented is the product of the terms $\int f_{12} f_{14} d^3r_1 d^3r_2 d^3r_4$, $\int d^3r_3$, $\int d^3r_5$, $\int f_{67} d^3r_6 d^3r_7$, and $\int d^3r_8$.

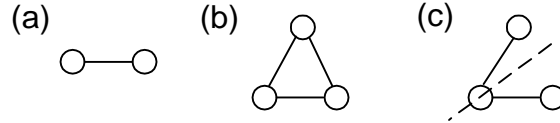


Figure 2: Linked clusters: (a) and (b) show the only irreducible, second and third order diagrams; (c) is a reducible third order diagram.

graphs. Note that in the counting, relabelled, similar-looking graphs such as in Fig. (1b,c) are counted as distinct, although they will give the same expressions once the integrals are done. Since the integrals over the coordinates i, j for dots linked by f_{ij} gain contributions only from small r_{ij} , we think of the linked dots as particle clusters—there is a contribution to the configuration integral from all the various clusters that can form in the gas. Note the factorization property of unlinked clusters, Fig. (1e). Furthermore, each cluster has one free integration variable, giving a factor of V , with the remaining integrations over difference coordinates involving f giving factors of atomic volumes, so that the volume dependence of the whole graph is V^L with L the number of linked clusters.

The diagrams are useful even for direct evaluation of low order expansions: as an example you will investigate the direct expansion up to third order in the homework. However the full power of the method comes because the complications introduced by the logarithm in forming the thermodynamic quantities can actually be eliminated by a general result that is most easily stated in terms of the diagrams, and in fact the expansions for the thermodynamic quantities are actually easier than for Z_N . This is the *linked cluster expansion*.

The linked cluster results take the form, for example for the grand canonical potential,

$$\ln Q = \sum_{\text{linked clusters}} (\text{counting factor}) \times (\text{cluster integral}) \quad (6)$$

where the summation is restricted to linked cluster, where a linked cluster is one with at least one f_{ij} line

connecting each part of the diagram. The *counting factor* takes into account topologically similar diagrams that give the same integral, and numerical factors depending on the order of the term. Notice that we would guess that only linked clusters occur in the thermodynamic quantities, since other terms do not give the right extensive scaling with V . Finding out what the counting factor is, however, involves considerable careful work, which the references describe.

From this the virial expansion can be formed, and introduces a new topological property (irreducibility) of retained diagrams:

$$P = \rho k_B T \left[1 - \sum_{l=1}^{\infty} \frac{l}{l+1} \beta_l \rho^l \right] \quad (7)$$

with

$$\beta_l = \frac{1}{l!} \times (\text{sum over all } \textit{irreducible} \textit{ } l+1 \textit{ clusters}), \quad (8)$$

where an *irreducible cluster* is one that cannot be cut into two pieces by cutting at a single dot. Reducible diagrams factor into simpler ones, since the integrals only depend on difference coordinates, e.g. for the diagram in Fig. (2c)

$$\int \int f(r_{12}) f(r_{13}) dr_{12} dr_{13} = \int f(r_{12}) dr_{12} \int f(r_{13}) dr_{13}. \quad (9)$$

(The particular form of Eq. (7) comes from developing the expansion for $\ln \gamma_N$ with $\gamma_N = Z_{N-1}/Z_N$.) The $l = 1$ term in the virial expansion (Fig. (2a)) is what we have found before; the $l = 2$ term in Eq. (7) depicted in Fig. (2b) is

$$l = 2 : \quad -\frac{2\rho^2}{3} \frac{1}{2!} \int (e^{\beta u(r_{12})} - 1)(e^{\beta u(r_{13})} - 1)(e^{\beta u(r_{23})} - 1) d^3 r_{12} d^3 r_{23} \quad (10)$$

The Liquid State

The *classical* liquid state is one of the most difficult states of matter to understand quantitatively, since there are no small parameters to use as a crutch (temperature, kinetic, and potential energies are all comparable). Quantum liquids are actually easier to understand, based on expansions in the number of thermal excitations at low temperatures (and the fact that the noninteracting gases already have interesting properties). A low order truncation of the virial expansion is not much use in understanding the strongly interacting classical liquid. There are two general classes of methods that are used to go beyond this. Neither of these methods are controlled approximations in general (nor are they particularly imaginative), but rather represent a last-ditch hope in the absence of really good methods. In some cases, e.g. with a long range Coulomb interaction, these methods may become exact in some limits.

It is hard to say much about this topic without spending more time on it than the successes warrant. I will just mention a few of the ideas. The best discussion I know of is §4.5 of *Goodstein's States of Matter*.

If we focus on the deriving the equation of state, the calculation can be reduced to finding the radial distribution function $g_N(r)$. Remember that for the nearly ideal gas the radial distribution function is

$$g_N(r) \simeq e^{-\beta u(r)}. \quad (11)$$

We can phrase the calculation in terms of calculating $W(r)$ defined by the correction to this

$$g_N(r) = e^{-\beta u(r)} e^{W(r)} \quad (12)$$

or

$$\ln g_N(r) + \beta u(r) = W(r). \quad (13)$$

Usually, approximate expressions for $W(r)$ are derived as functions or functionals of $g_N(r)$ leaving algebraic or integral equations to be solved for g_N .

Infinite summation

If the low order Mayer (virial) expansion is of no use, we might try summing an *infinite* number of diagrams. The diagrammatic expansion for W is given by

$$e^{W(r)} = e^{\beta u(r)} g_N(r) = \frac{V^2}{Z_N} \int \cdots \int \prod_{\substack{i < j \\ i, j \neq 1, 2}} (1 + f_{ij}) d^3 r_3 \dots d^3 r_N \quad (14)$$

where the product on the right hand side does not include $(1 + f_{12})$ which gives the term $e^{\beta u(r)}$ on the right hand side. The diagrammatic expansion is similar to the Mayer expansion, except there are now two fixed points \vec{r}_1, \vec{r}_2 that we do not integrate over and provide “anchors” for the diagrams. It is not possible to sum *all* the diagrams, so various infinite classes are summed, chosen by some simplicity of topological form, or intuition of important physical content. The diagrams left out are in principle just as large as the ones retained, and so getting a good answer (for a particular result) is more an art than a science. Two examples are the “hypernetted chain” and the “Percus-Yevick” approximations (see *Goodstein* §4.5b for more details). The details are quite intricate, and I leave you to consult that reference if you are interested.

Truncated Hierarchies

In this method a differential equation for $g_N(r)$ is derived. This equation depends on the next higher order density correlation functions. These in turn can be related to higher ones, and an *exact* hierarchy of equations can be derived. This is then truncated at some order, by making a simple factorization *approximation* of a high order correlation function, i.e. supposing that it factorizes into products of lower order ones. The hope is that high-order correlation functions do not have much physical content. Unfortunately, in most cases it seems that they do contain important physics, but this is now obscured in the complexity.

We define an effective “potential of mean force” ϕ_N (cf. the nearly ideal gas expression) in terms of the exact (unknown) g_N

$$\phi_N(r) = -k_B T \ln g_N(r) \quad (15)$$

and try to calculate the effective mean force

$$-\frac{\partial \phi_N(\vec{r}_1, \vec{r}_2)}{\partial \vec{r}_1} = \frac{k_B T}{g_N} \frac{\partial g_N(\vec{r}_1, \vec{r}_2)}{\partial \vec{r}_1}. \quad (16)$$

(Although ϕ and g only depend on the difference $\vec{r}_1 - \vec{r}_2$ the notation in terms of individual position is convenient here.) This can be interpreted as the force on the particle 1 at \vec{r}_1 holding particle 2 fixed at \vec{r}_2 , but averaging over all positions of the other particles in the potentials of these two and their own interactions. Using

$$g_N(\vec{r}, \vec{r}') = \frac{V^2}{N(N-1)} \frac{\int d^{3N} r \sum_{i \neq j} \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) e^{-\beta U}}{\int d^{3N} r e^{-\beta U}} \quad (17)$$

gives

$$-\frac{\partial \phi_N(\vec{r}_1, \vec{r}_2)}{\partial \vec{r}_1} = \frac{\int d^3 r_3 \dots d^3 r_N \partial U / \partial \vec{r}_1 e^{-\beta U}}{\int d^3 r_3 \dots d^3 r_N e^{-\beta U}}. \quad (18)$$

The potential energy derivative $\partial U / \partial \vec{r}_1$ contains the term $\partial u(r_{12}) / \partial \vec{r}_1$ involving the fixed particle and $N - 2$ terms of the form $\partial u(r_{1j}) / \partial \vec{r}_1$ with $j \neq 1, 2$. Equation (18) can then be written

$$\frac{\partial \phi_N(r_{12})}{\partial \vec{r}_1} = \frac{\partial u(r_{12})}{\partial \vec{r}_1} + \rho \frac{\int d^3 r_3 g_N^{(3)}(\vec{r}_{12}, \vec{r}_{13}) \partial u(r_{13}) / \partial \vec{r}_1}{g_N(\vec{r}_{12})} \quad (19)$$

where $g_N^{(3)}$ is the three-particle distribution function

$$g_N^{(3)}(\vec{r}, \vec{r}') = \frac{V^2}{N(N-1)(N-2)} \left\langle \sum_{i \neq j \neq k} \delta(\vec{r} + \vec{r}_i - \vec{r}_j) \delta(\vec{r}' + \vec{r}_i - \vec{r}_k) \right\rangle \quad (20)$$

which can be used to define a third order effective potential $\phi_N^{(3)} = -k_B T \ln g_N^{(3)}$. This procedure can be repeated to define the hierarchy. We can truncate the hierarchy at second order by making the *superposition* or *factorization* approximation

$$\phi_N^{(3)}(\vec{r}_{12}, \vec{r}_{13}) \simeq \phi_N(\vec{r}_{12}) + \phi_N(\vec{r}_{23}) + \phi_N(\vec{r}_{13}) \quad (21)$$

$$g_N^{(3)}(\vec{r}_{12}, \vec{r}_{13}) \simeq g_N(\vec{r}_{12}) g_N(\vec{r}_{23}) g_N(\vec{r}_{13}) \quad (22)$$

to give

$$\frac{\partial \phi_N(r_{12})}{\partial \vec{r}_1} = \frac{\partial u(r_{12})}{\partial \vec{r}_1} + \rho \int d^3 r_3 g_N(r_{23}) g_N(r_{13}) \frac{\partial u(r_{13})}{\partial \vec{r}_1}. \quad (23)$$

This equation is usually expressed in the integrated form. First introduce the function

$$E(r) = \int_{\infty}^r \frac{du(r')}{dr'} g_N(r') dr'. \quad (24)$$

Equation (23) reduces to

$$\frac{\partial \phi_N(r_{12})}{\partial \vec{r}_1} = \frac{\partial u(r_{12})}{\partial \vec{r}_1} + \rho \int d^3 r_3 g_N(r_{23}) \frac{\partial E(r_{13})}{\partial \vec{r}_1}. \quad (25)$$

The integral can then be expressed in the form

$$\phi_N(r_{12}) = u(r_{12}) + \rho \int d^3 r_3 g_N(r_{23}) E(r_{13}) + C. \quad (26)$$

The integration constant C is evaluated by taking particle 2 to infinity for fixed \vec{r}_1, \vec{r}_3 ($\phi_N(r_{12}) \rightarrow 0, u(r_{12}) \rightarrow 0, g_N(r_{23}) \rightarrow 1$). The expression can then be written in the form known as the Yvon-Born-Green equation

$$\ln g_N(r) + \frac{u(r)}{k_B T} = -\frac{\rho}{k_B T} \int E(|\vec{r} - \vec{r}'|) [g_N(r') - 1] d^3 r'. \quad (27)$$

Notice this is an integral equation for g_N in the form of Eq. (13).

*Quantum Cluster Expansion

This is an advanced topic to show how cluster expansions can be done for a dilute quantum gas. You can read it or skip it as you like. The more interesting aspects of quantum systems, such as Bose-Einstein condensation cannot be treated using this formalism, and the methods introduced later in the term are more useful in general. You can read *Pathria* §9.4-6 for more details.

The starting point is

$$Q = \sum_{N=0}^{\infty} Q_N(V, T) z^N = \sum_{N=0}^{\infty} \frac{Z_N(V, T)}{N!} \left(\frac{z}{\lambda^3}\right)^N \quad (28)$$

with $z = e^{\beta\mu}$ the fugacity, and where the second expression just defines the quantity Z_N (which in the classical case is the configuration integral). In the $V \rightarrow \infty$ we get

$$\frac{P}{k_B T} = \frac{\ln Q}{V} = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} b_l z^l \quad (29)$$

with

$$b_1 = \frac{Z_1}{V} = 1 \quad (30)$$

$$b_2 = \frac{1}{2!\lambda^3 V} (Z_2 - Z_1^2) \quad (31)$$

$$\vdots \quad (32)$$

Note that Z_N scales as V^N , but the combination $Z_2 - Z_1^2$ appearing in b_2 must scale as V (cf. the linked cluster result), and similarly for higher order terms.

We can also calculate the density ρ

$$\rho = \frac{z}{V} \frac{\partial \ln Q}{\partial z} = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} l b_l z^l \quad (33)$$

which can be inverted to give a series for $z(\rho)$, and so with Eq. (29) the virial expansion

$$\frac{P}{\rho k_B T} = \sum_{l=1}^{\infty} a_l(T) (\rho \lambda^3)^{l-1} \quad (34)$$

with $a_1 = b_1 = 1$, $a_2 = -b_2$, $a_3 = 4b_2^2 - 2b_3 \dots$

The n th term in the virial expansion is given in terms of the partition functions for m particles with $m \leq n$. Classically, it is straightforward to write down expressions for Z_n and this is just reproducing the results of the Mayer expansion. Quantum mechanically, for Z_n we have to solve the n -body quantum mechanical problem, and this can only be done easily up to $l = 2$, i.e. the first nontrivial virial coefficient.

It is easiest to compare with the noninteracting system (note that even the noninteracting quantum system has nonzero higher terms in the virial expansion)

$$b_2 - b_2^{(0)} = \frac{1}{2\lambda^3 V} (Z_2 - Z_2^{(0)}) \quad (35)$$

$$= \frac{\lambda^3}{V} (Q_2 - Q_2^{(0)}) \quad (36)$$

$$= \frac{\lambda^3}{V} \text{Tr}(e^{-\beta H_2} - e^{-\beta H_2^{(0)}}) \quad (37)$$

with

$$H_2 = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) + u(r_{12}). \quad (38)$$

The eigenfunctions of the two body problem can be separated

$$\Psi = \frac{1}{V^{1/2}} e^{i\vec{P}\cdot\vec{R}/\hbar} \psi_n(\vec{r}_{12}) \quad (39)$$

where ψ_n satisfies

$$\left\{ -\frac{\hbar^2}{2\mu} + \nabla_{\vec{r}}^2 + u(r) \right\} \psi_n(\vec{r}) = \varepsilon_n \psi_n(\vec{r}), \quad (40)$$

with $\mu = m/2$ the reduced mass, and then

$$b_2 - b_2^{(0)} = \frac{\lambda^3}{V} \sum_j e^{-\beta P_j^2/4m} \sum_n \left(e^{-\beta \varepsilon_n} - e^{-\beta \varepsilon_n^{(0)}} \right) \quad (41)$$

$$= 8^{1/2} \sum_n \left(e^{-\beta \varepsilon_n} - e^{-\beta \varepsilon_n^{(0)}} \right) \quad (42)$$

where the sum over the center of mass momentum states is just $8^{1/2}V/\lambda^3$. The final sum over the energy eigenstates can be split into contributions from the bound states and from the continuum (scattering) states (e.g. see *Pathria* §9.5)

$$b_2 - b_2^{(0)} = 8^{1/2} \sum_B e^{-\beta \varepsilon_B} + \frac{8^{1/2}}{\pi} \sum_l (2l + 1) \int_0^\infty e^{-\beta \hbar^2 k^2 / 2m} \frac{\partial n_l(k)}{\partial k} dk \quad (43)$$

with η_l the phase shift. The l -sum is over l even for Bosons and l odd for Fermions.