Statistical Physics
Section 7: Interactions in Classical Fluids: Perturbation about the Ideal Gas

In this section we treat a classical fluid which comprises an assembly with N particles each of mass m, in a volume V. We assume that the density

$$\rho = \frac{N}{V} \tag{1}$$

is low enough that we can

- treat interactions as perturbations about the Ideal Gas
- neglect quantum indistinguishability and use Classical Statistical Mechanics

7. 1. Classical Statistical Mechanics

The classical Hamiltonian (which is, for our purposes, the energy) is

$$H = E = \sum_i \frac{\underline{p}_i^2}{2m} + U\left(\left\{\underline{q}_i\right\}\right) \tag{2}$$

where i labels the particles, $\underline{p}_i$ is the momentum and $\underline{q}_i$ is the position vector of particle i. We use this notation to emphasise that $\underline{p}_i$ and $\underline{q}_i$ are examples of *conjugate* or canonical coordinates such as you may have met in the formalism of Lagrangian or Hamiltonian dynamics.

Thus, classically the state of a particle i is specified by two coordinates $\underline{q}$ and $\underline{p}$. So in 3d each particle has 6 coordinates p_x,p_y,p_z,q_x,q_y,q_z and we can think of the state of the particle corresponding to a point in 6d space.

For N particles the dimension of the phase space of the N-particle system is $6N$ i.e. we can think of the state of the whole assembly as a point in the $6N$ dimensional known the **phase space** of the assembly.

Problem: Since $\underline{q}$ and $\underline{p}$ are continuous coordinates we have an infinity of possible states. This poses problems, for example, in using the Boltzmann definition of the entropy as proportional to the logarithm of the weight of a macrostate since the weight will always be infinite!

Solution: Divide phase space up into cells if side δp δq *etc*—see figure 1. Call the 'volume' of a cell (in the 6d space)

$$h^3 = (\delta p)^3(\delta q)^3$$

What is the meaning of this construction?

- In quantum mechanics the uncertainty principle would furnish a natural interpretation for the cell size.
- Classically one can interpret the cells as the uncertainty in any physical measurement (this was the view of Maxwell).

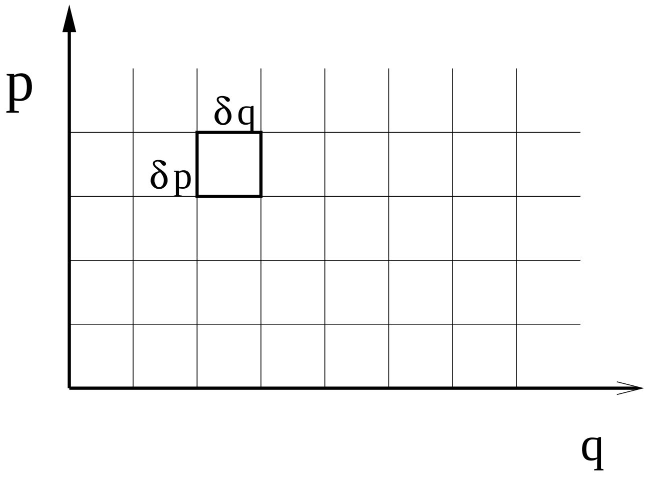

Figure 1: A 1d phase space divided into cells of side δq, δp.

- In the end the size of the cell turns out to be a 'book-keeping' device: it disappears from the final physical results.
- We can identify a cell in phase space with a state $\rightarrow$ controlled number of states.

Having identified cells in phase space with states, we can write down an expression for the classical partition function

$$Z_c = \frac{1}{N!} \sum_{\text{cells}} \exp -\beta H \tag{3}$$

If we take the cells small enough that the value of the energy varies very slowly between cells then we can replace the sum by an integral

$$\sum_{\text{cells}} \longrightarrow \frac{1}{h^3} \int dp_x \, dp_y \, dp_z \int dq_x \, dq_y \, dq_z$$

The sum over cells becomes a 'volume' integral over the 6d phase space; we divide by the volume of a cell so that, for example, the number of cells equals the phase space volume divided by the cell volume.

$$\boxed{Z_c(T,V,N) = \frac{1}{N! \, h^{3N}} \int \left[\prod_i d^3p_i \, d^3q_i \right] e^{-\beta H(\{\underline{q}\},\{\underline{p}\})}} \tag{4}$$

Thus the partition function is the integral of the Boltzmann factor over the $6N$ dimensional phase space. The limits of integration on momentum components are $p_i = \pm\infty$ and on positions $q_i = 0, L$.

In a purely classical approach, the factor h^{-3N} introduced by hand above as the cell size, also serves to make the integral dimensionless; so h is some constant with the units of momentum $\times$ length. But by comparing this Z_c with the classical limit of an ideal gas, one finds that h is in fact Planck's constant. Hence, as discussed previously quantum mechanics is involved, even in the so called "classical" limit, in an inescapable way. The indistinguishability factor $1/N!$ is also not obvious from a purely classical viewpoint, but must be there to ensure the entropy works out correctly. Basically we are employing the semi-classical 'quick fix'.

Alternatively we can consider (4) as the fundamental postulate of classical statistical mechanics.

Recovery of Classical Ideal Gas

For the classical ideal gas a particle's energy is simply its kinetic energy

$$\epsilon_i(\underline{q}_i, \underline{p}_i) = \frac{p_i^2}{2m}$$

and the assembly energy is just the sum of the particle energies.

Therefore the spatial integrals in (4) give V^N and

$$\begin{aligned} Z_c(T,V,N) &= \frac{V^N}{N!\,h^{3N}} \prod_{i=1}^{N} \left[\int \mathrm{d}^3 p_i \, e^{-\beta p_i^2/2m} \right] \\ &= \frac{V^N}{N!\,h^{3N}} \left[\int \mathrm{d}p \, e^{-\beta p^2/2m} \right]^{3N} \\ &= \frac{V^N}{N!\,h^{3N}} \left[\left(\frac{2m\pi}{\beta} \right)^{1/2} \right]^{3N} \\ &= \frac{1}{N!} \left[\frac{V}{\lambda_T^3} \right]^N \end{aligned}$$

We have used the formula for the gaussian integral that should be memorised

$$\boxed{\int_{-\infty}^{\infty} \mathrm{d}z \exp -\alpha z^2 = \left(\frac{\pi}{\alpha} \right)^{1/2}}$$

and the definition of the thermal de Broglie wavelength

$$\lambda_T = \left(\frac{h^2}{2\pi m k_B T} \right)^{1/2} \tag{5}$$

Note that h is present in Z_c via λ_T. Thus, quantities stemming from $\ln Z_c$ such as the free energy $F = -kT \ln Z_c$ or entropy S will apparently retain a dependence on h, as an additive constant.

However it should be noted that it is only free energy and entropy *differences* that can be measured experimentally (absolute values of free energy are not defined) and in the expression for e.g. a free energy difference the h dependence cancels.

Thus in the end h indeed plays no role in the results as we would expect for a classical assembly.

Explicitly we have

$$F_{\text{ideal}} = -kT \ln Z_c = kTN\left[1 - \ln N - \ln V + 3 \ln \lambda_T\right] \tag{6}$$

$$P_{\text{ideal}} = -\frac{\partial F_{\text{ideal}}}{\partial V} = \frac{NkT}{V} \tag{7}$$

where we have used Stirling's approximation in obtaining (6) from (5)

7. 2. Configurational Integral

In the interacting case an important simplification arises from the fact that the interaction potential $U(\{\underline{q}\})$ does not depend on the particle momenta. Then

$$H(\{\underline{q}\},\{\underline{p}\}) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U(\{\underline{q}\})$$

(where $p_i = |\underline{p}_i|$) and Z_c factors into two pieces:

$$Z_c(T,V,N) = \frac{1}{N!h^{3N}} \int \prod_i d^3p_i\, e^{-\beta \sum p_i^2/2m} \int \prod_i d^3q_i\, e^{-\beta U(\{\underline{q}\})} \tag{8}$$

corresponding to integrals over positions, and integrals over momenta. These factors can conveniently be separated (in dimensionless form) as follows:

$$Z_c(T,V,N) = Z_{\text{ideal}}\, Q \tag{9}$$

where the first factor is the partition function for the noninteracting case (the ideal gas)

$$Z_{ideal} = \frac{V^N}{N!h^{3N}} \prod_i \left[\int e^{-\beta p_i^2/2m} d^3p_i \right] = \frac{[V/\lambda_T]^N}{N!} \tag{10}$$

and the second is a correction factor (unity for ideal gases)

$$\boxed{Q = V^{-N} \int \prod_{i=1}^{N} d^3q_i\, e^{-\beta U(\underline{q}_1, \ldots \underline{q}_N)}} \tag{11}$$

which is known as the *configurational integral*. Accordingly, the interactions between our particles enter only via Q, and if we can evaluate this we have all we need to compute $Z_c(T,V,N)$.

From the factorization of Z_c there follows the decomposition of the free energy

$$F(T,V,N) = F_{\text{ideal}}(T,V,N) - kT \ln Q \tag{12}$$

and of the equation of state,

$$\boxed{P(T,V,N) = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{NkT}{V} + P_{\text{conf}}} \tag{13}$$

Thus the "configurational pressure"

$$P_{\text{conf}} = kT \frac{\partial \ln Q}{\partial V} \tag{14}$$

gives the correction to the ideal gas equation of state, i.e. the correction to the pressure due to interactions.

7. 3. Virial Expansion

In the following we take the interaction potential to be of the form

$$U(\{\underline{q}\}) = \frac{1}{2}\sum_{i\neq j}\phi(|\underline{q}_i - \underline{q}_j|) = \sum_{i<j}\phi_{ij}(r_{ij}) \tag{15}$$

Note that this implies

- 2 body interactions
- a central potential (depends only on distance between particles)

Examples of interatomic potentials are:

- The hardcore potential

$$\phi_{ij}(r) = \begin{array}{cc} \infty & r \leq a \\ 0 & > a \end{array} \tag{16}$$

- the Lennard Jones potential

$$\phi_{ij}(r) = 4\epsilon[(r_0/r)^{12} - (r_0/r)^6] \tag{17}$$

  Here ϵ is the depth of the attractive well and r_0 the hard core radius.

Figure 2: Sketch of the hard core potential and the Lennard Jones potential

For the Lennard Jones case note the *generic features* of repulsion at short distance, attraction at intermediate distance and interaction $\rightarrow 0$ at long range. In the generic case, there is no intrinsic limit to the number of particles that can be interacting simultaneously with each other. Consequently new *collective phenomena*, such as the phase transition from a vapour to a liquid, become possible. The hard core case, on the other hand, is not generic and is a very special case.

Our task is to calculate the configurational integral (11) which we write in the form

$$Q = \frac{1}{V^N}\int\left[\prod_i d^3q_i\right]\prod_{i<j}F_{ij} \tag{18}$$

where

$$F_{ij} = \exp -\beta\phi_{ij} \tag{19}$$

Just to be clear, let us write out the products

$$Q = \frac{1}{V^N} \int d^3q_1 \ldots d^3q_N F_{12} F_{13} \ldots F_{1N} F_{23} \ldots F_{2N} \ldots F_{N-1\,N}$$

note that there $N(N-1)/2$ F_{ij}s in the product: this is just the number of ways of choosing 2 sites from N.

We can think of Q as being a spatial average i.e. it is the integral of something (the product of F_{ij}) over the spatial co-ordinates divided by the volume V^N. Therefore we can write

$$Q = \langle \prod_{i<j} F_{ij} \rangle \tag{20}$$

where the angle brackets indicate the spatial average. Now this is very difficult to calculate because, for example F_{ij} is correlated with F_{ik}.

However a first approximation is

$$\begin{aligned} Q &= \prod_{i<j} \langle F_{ij} \rangle \\ &= \langle F \rangle^{N(N-1)/2} \end{aligned} \tag{21}$$

i.e. we replace the average of the product by the product of the averages. This amounts to the approximation that F_{ij} are in fact *uncorrelated.* Note that $\langle F_{ij} \rangle = \langle F \rangle$ does not depend on the indices i,j (as long as $i \neq j$).

We let

$$F_{ij} = 1 + f_{ij} \tag{22}$$

note that

$$f_{ij} = \exp(-\beta\phi_{ij}) - 1 \quad \to \quad \begin{array}{rcl} 0 & \text{as} & r \to \infty \\ -1 & \text{as} & r \to 0 \end{array} \tag{23}$$

so in a dilute gas, where the interparticle separations are large, f_{ij} is typically small. Let us take i,j = 1,2 as representative:

$$\langle F_{12} \rangle = 1 + \frac{1}{V^N} \int d^3q_1 \ldots d^3q_N f_{12} = 1 + \frac{1}{V^2} \int d^3q_1 d^3q_2 f_{12}$$

where we have integrated out the coordinates not involved in f_{12} and used $\int \mathrm{d}^3q = V$.

Now we change variables to centre of mass and relative coordinates

$$\underline{r} = \underline{q}_1 - \underline{q}_2 \qquad \underline{R} = \frac{1}{2}(\underline{q_1} + \underline{q_2}) \tag{24}$$

Noting that there is only dependence on the relative coordinate $\underline{r}$ so that $\int \mathrm{d}^3R = V$, we obtain

$$\langle F_{12} \rangle = 1 + \frac{1}{V} \int d^3r \, [\exp -\beta\phi(r) - 1] \tag{25}$$

which we write as

$$\langle F_{12} \rangle = 1 - \frac{2B_2}{V} \tag{26}$$

where

$$\boxed{B_2 = -\frac{1}{2}\int \mathrm{d}^3r\,[\exp -\beta\phi(r) - 1]} \tag{27}$$

The constant B_2 is known as the *second virial coefficient.*

So within our crude approximation we have

$$Q = \left(1 - \frac{2B_2}{V}\right)^{N(N-1)/2} \tag{28}$$

and following (12) we find

$$F = F_{\text{ideal}} - kT\ln Q \simeq F_{\text{ideal}} + \frac{N^2kT}{V}B_2$$

where we have approximated $N(N-1) \simeq N^2$ and $\ln(1 - 2B_2/V) \simeq -2B_2/V$ when N, V are large.

Then, from (13,14) we obtain

$$\boxed{\frac{P}{kT} = \rho + B_2\rho^2} \tag{29}$$

where $\rho = N/V$. Finally we note

$$S = -\frac{\partial F}{\partial T} = S_{ideal} - Nk\rho\frac{\partial}{\partial T}(TB_2)$$

Notes

- (29) is the start of the **virial expansion**. This is a *perturbation expansion* in the density ρ about the ideal gas limit. That is, we see the start of

$$\boxed{\frac{P}{kT} = \rho + B_2\rho^2 + B_3\rho^3\cdots} \tag{30}$$

- The microscopic theory developed here relates the virial coefficients B_n to the atomic interaction potential ϕ_{ij}.

- In the tutorial you are invited to develop a simple approximation for a generic ϕ_{ij} which yields

$$B_2 = b_0 - a_0/kT \tag{31}$$

  where b_0 and a_0 are positive constants. This recovers (see tutorial) the expansion of the 'van der Waals equation of state' usually written

$$\left(P + \rho^2 a\right) = \frac{NkT}{V - Nb} \tag{32}$$

  Also within the approx (31) one can show the entropy is reduced below that of the ideal gas. This is to be expected from information theory: the attractive interactions should make the positions of the atoms correlated. Correlations in the positions then reduce the missing information about the microscopic state of the system.

*7. 4. *Extension to higher order*

To improve upon our crude approximation (21), and in order to calculate the higher order virial coefficients let us write

$$F_{ij} = \langle F \rangle + \lambda_{ij} \tag{33}$$

where λ_{ij} is the deviation of F_{ij} from its average spatial value and $\langle \lambda_{ij} \rangle = 0$.

Then

$$Q = \langle (\langle F \rangle + \lambda_{12})\,(\langle F \rangle + \lambda_{13}) \cdots \rangle \tag{34}$$

which we wish to expand in powers of λ_{ij}. We do not explicitly carry out this procedure here, but note that it results in

$$Q = \langle F \rangle^{N(N-1)/2} + \left(\begin{array}{c} N \\ 3 \end{array} \right) \langle F \rangle^{N(N-1)/2-3} \langle \lambda_{12}\lambda_{23}\lambda_{13} \rangle + \ldots$$

Notes

- It turns out that an average of a product of λs in which a subscript appears only once is zero. Therefore there are no linear or quadratic terms in the expansion (convince yourself).
- The first term is what we calculated as our crude approximation in the previous section. The second term involves a 'cluster' of three sites say 123 and $\langle \lambda_{12}\lambda_{23}\lambda_{13} \rangle$ is representative of such terms. The binomial coefficient comes from the number of ways of choosing three sites from N.
- Physically the first term, which involved averaging F_{ij}, represents the interaction of two particles i.e. a 'two particle molecular cluster'. The second term, as noted above, involves 'three particle particle clusters', hence () is known as a cluster expansion.
- To extend to higher orders diagrammatic methods are required to enumerate the various clusters. This was actually the first instance of diagrammatic methods see e.g. the books by Huang or Pathria for details.
- But at higher densities the expansion at best converges slowly and at least near the phase transition to the liquid phase the expansion fails to converge at all. This is because near the phase transition larger and larger clusters of particles become important. Also perturbation theory about the ideal gas can't be expected to quantitatively describe the (high density) liquid phase which is a different state of matter! We will understand this more fully when we study phase transitions in Section 9–12