

Statistical Physics

Section 8: Reduced Density Distributions and Dense Liquids

In this section we treat classical fluids from the point of view of the two-point reduced density distribution and develop non-perturbative approaches for the case of dense fluids.

8. 1. Distribution functions

Since, as we saw in section 7, the partition function factorises:

$$Z_c = Z_{\text{ideal}}Q$$

positions and momenta are *independent* of each other. Let us be explicit and recall that the probability of the assembly being in a small volume of phase space at $(\{\underline{r}\}, \{\underline{p}\})$ is

$$p(\{\underline{r}\}, \{\underline{p}\}) \prod_i d^3r_i d^3p_i = \frac{e^{-\beta \sum_i p_i^2/2m} e^{-\beta U(\{\underline{r}\})}}{Z_{\text{ideal}} Q} \prod_i d^3r_i d^3p_i \quad (1)$$

(In the lecture we used \underline{q}_i rather than \underline{r}_i for the position vector, but this is unimportant.) So we can write a probability density in a $3N$ -dimensional *configuration space* for the position coordinates alone by integrating out the momenta:

$$p(\{\underline{r}\}) \prod_i d^3r_i = \frac{e^{-\beta U(\{\underline{r}\})}}{V^N Q} \prod_i d^3r_i \quad (2)$$

This is the probability of finding the system in some small volume of configuration space, that is, the probability density for finding particles $\{1\dots N\}$ at position $\{\underline{r}_1\dots\underline{r}_N\}$. Note the factor V^{-N} which arises from our definition of Q .

By integrating out a subset of the coordinates, we can define a family of *reduced distribution functions*,

$$p_m(\underline{r}_1, \dots, \underline{r}_m) = \int p(\{\underline{r}\}) \prod_{i=m+1}^N d^3r_i \quad (3)$$

where the integral is over the remaining $N - m$ coordinates. The reduced quantity is the probability density of finding particles $1, 2, 3\dots m$ in the stated positions. Bearing in mind that the particles are indistinguishable, it is better to define

$$\rho_m(\underline{r}_1, \dots, \underline{r}_m) = \frac{N!}{(N - m)!} p_m(\underline{r}_1, \dots, \underline{r}_m) \quad (4)$$

Which is the probability of *any* set of m particles occupying the stated positions. Clearly, ρ_1 is just the usual density:

$$\rho_1(\underline{r}) = \rho = N/V \quad (5)$$

The two-particle reduced density $\rho_2(\underline{r}_1, \underline{r}_2)$ is the probability of finding a pair of particles at given positions $\underline{r}_1, \underline{r}_2$. In a homogeneous, isotropic fluid this can only depend on the distance between the chosen positions, and can be written

$$\rho_2(\underline{r}_1, \underline{r}_2) = \rho^2 g(|\underline{r}_1 - \underline{r}_2|) \quad (6)$$

The quantity $\rho g(r)d^3\underline{r}$ is the conditional probability that a particle is present in the volume element d^3r at \underline{r} , given that a particle is already present at the origin and the overall density is ρ

Here $g(r)$ is called the *radial distribution function* sometimes referred to as the pair distribution or pair correlation function. Note the limits: $g = 1$ means that the events of particles at \underline{r}_1 and \underline{r}_2 are uncorrelated, whereas $g = 0$ means that it is impossible to have particles at both \underline{r}_1 and \underline{r}_2 . Thus $g > 1$ means the events of particles at \underline{r}_1 and \underline{r}_2 are correlated and $g < 1$ means the events are anticorrelated.

For a typical dense fluid it looks like this: The radial distribution function contains useful

Figure 1: Sketch of $g(\underline{r})$ for a crystalline solid, and $g(r)$ for an ideal gas and a dense gas

information about how the particles in the fluid are correlated, and can be measured rather directly by diffraction experiments (recall P2 Properties of Matter course, and see e.g. the book by Chandler, Ch.7).

8. 2. The virial theorem

As before we assume that the interaction energy $U(\{\underline{r}\})$ is pairwise additive: $U = \frac{1}{2} \sum_{i \neq j} \phi_{ij}$. In this case a very useful formula for the pressure P can be found:

$$P = P_{ideal} + P_{conf} = \rho kT - \frac{\rho^2}{6} \int_0^\infty \left(r \frac{d\phi}{dr} \right) g(r) 4\pi r^2 dr \quad (7)$$

This is called the *virial equation of state*.

A proof is as follows: introduce coordinates $\tilde{\underline{r}} = \underline{r}/L$, where $L = V^{1/3}$. Then

$$Q = \int \prod_i d^3\tilde{r}_i e^{-\beta U(\{\underline{r}\})} = \int \prod_i d^3\tilde{r}_i \exp \left[-\beta \frac{1}{2} \sum_{i \neq j} \phi(L\tilde{r}_{ij}) \right]$$

where the limits of integration for each coordinate are now L -independent. (Before they were all from 0 to L .) We have $F_{conf} = -kT \ln Q$ and so

$$\begin{aligned} P_{conf} &= - \left(\frac{\partial F_{conf}}{\partial V} \right)_{T,N} = - \frac{L}{3V} \left(\frac{\partial F_{conf}}{\partial L} \right)_{T,N} \\ \Rightarrow P_{conf} &= \frac{kTL}{3VQ} \int \prod_i d^3\tilde{r}_i \left(-\frac{1}{2} \sum_{i \neq j} \beta \tilde{r}_{ij} \phi'_{ij} \right) e^{-\beta U(\{\underline{r}\})} \end{aligned}$$

where $\phi' = d\phi/dr$. Since each term in the sum depends only on one pair of relative positions, the rhs can (after restoring $\underline{r} = L\tilde{r}$) be written in terms of the two-particle reduced distribution function ρ_2 defined earlier:

$$P_{conf} = -\frac{1}{6V} \int \rho_2(\underline{r}_1, \underline{r}_2) r_{12} \frac{d\phi}{dr_{12}} d^3r_1 d^3r_2 = -\frac{\rho^2}{6} \int_0^\infty \phi'(r) r g(r) 4\pi r^2 dr$$

which proves the result.

Tutorial Exercise: Check the argument and complete any missing steps.

The virial equation of state shows that for pairwise interactions, the same information resides in the equation of state as in the pair distribution function. In practice neither can be calculated exactly and one must resort to various approximation schemes.

Let us check how we recover our perturbation (virial expansion) from the virial equation of state

The leading correction to the pressure can be obtained by setting $g(r) = e^{-\beta\phi(r)}$ in the virial equation of state. This seems reasonable as $g(r)$ then has the form of a Boltzmann weight and has the correct limits $g(\infty) = 1$ and $g(0) = 0$. Actually what we are doing is to just use the two particle potential ϕ to construct $g(r)$ thus the approximation is just to think of the interaction of the two particles at the origin and r , and ignore all others.

Using this approximation for $g(r)$ in P_{conf} gives

$$\begin{aligned} P_{conf} &= -\frac{\rho^2}{6} \int_0^\infty 4\pi r^3 \phi' e^{-\beta\phi(r)} dr \\ &= +\frac{\rho^2}{6\beta} \int_0^\infty 4\pi r^3 \frac{d}{dr} [e^{-\beta\phi} - 1] dr \\ &= +\frac{\rho^2 kT}{2} \int_0^\infty 4\pi r^2 [e^{-\beta\phi} - 1] dr = B_2 \rho^2 \end{aligned} \quad (8)$$

after integrating by parts and noting that $e^{-\beta\phi(r)} - 1$ vanishes at large r . This recovers an expression for $B_2(T)$ that you are invited to develop in the tutorial.

Thus the approximation $g(r) = e^{-\beta\phi(r)}$ gives the same result as the approximation $Q = \prod_{i<j} \langle F_{ij} \rangle$ of Section 7. In other words, if we want P to order ρ^2 , we need only find $g(r)$ to zeroth order in density; and this is just the Boltzmann factor for a particle to be at r (given that there is one at the origin) evaluated as if all the others were not there.

8. 3. Debye- Hückel Theory

A fluid of charged particles is called a **plasma**. Even for low concentrations, the long-range Coulomb forces ensure that interactions are strong: in fact the integral for B_2 (see section 7.3) diverges (as you are invited to show in the tutorial) so the virial expansion *never* makes sense. We study the plasma now, as an example of how *nonperturbative* reasoning can be developed.

For simplicity we consider the “one-component” plasma, in which a gas of point particles of charge q at average number density n_∞ resides in a ‘smeared out’ background of charge density $-qn_\infty$. This is a good model for classical electrons in a semiconductor, where the

background is the fixed ionic charges, and the electron density is low enough for the classical limit to hold.

Very similar calculations can be carried out for a plasma where both positive and negative charges are mobile; this situation arises, for example, in interstellar gases or in a salt solution. The results differ only slightly from those given below (see tutorial).

Poisson Boltzmann equation We want to know the radial distribution function $g(r)$, which was defined so that $n_\infty g(r)$ is the mean density of particles at radius r *given that there is a particle at the origin*. Using the Boltzmann factor we can write this as

$$n(r) = n_\infty g(r) = n_\infty e^{-q\phi(r)/kT} \quad (9)$$

where n_∞ is the density far away (a constant equal to the overall density) and $\phi(r)$ is the electrostatic potential at distance r from the particle at the origin.

N.B. Here we use $n(r)$ to denote *particle* density at r (given a particle is present at the origin) rather than the usual $\rho(r)$ which we use here to denote *charge* density.

The potential ϕ obeys Poisson's equation

$$\nabla^2 \phi(r) = -\rho(r)/\epsilon \quad (10)$$

where ϵ is the dielectric constant of the vacuum (or other surrounding medium). The charge density $\rho(r)$ consists of three contributions:

(i) That of the point charge q at the origin

$$\rho_0 = q\delta(0) , \quad (11)$$

(ii) That of the fixed background charge density

$$\rho_{fixed}(r) = -n_\infty q \quad (12)$$

(iii) That of all the other free charges in the plasma.

We now assume that these free charges are themselves arranged around the central charge according to the radial distribution function $g(r)$, as yet unknown:

$$\rho_{free}(r) = qn_\infty g(r) \quad (13)$$

Surrounding our point charge at the origin, we therefore have $\rho = \rho_{free} + \rho_{fixed}$ and hence

$$\nabla^2 \phi = -\frac{n_\infty q}{\epsilon} [g(r) - 1] - \frac{q}{\epsilon} \delta(0) = -\frac{n_\infty q}{\epsilon} [e^{-\beta q \phi} - 1] - \frac{q}{\epsilon} \delta(0) \quad (14)$$

This has ϕ on both sides of the equation: we have developed a nonperturbative *self-consistent* equation for $\phi(r)$ (or equivalently $g(r)$). Though plausible, the argument is not exact because it ignores various higher-order correlations (between triplets, quadruplets etc..) – you may like to ponder *where* exactly the argument leaves these out.

The Poisson-Boltzmann equation is nonlinear but can be solved numerically to give $g(r)$ and $\phi(r)$. To see what sort of physics is involved, we consider only the limit where $\phi \ll kT$ (this requires low charge densities and/or high temperatures) so that

$$ng(r) = n_\infty e^{-\beta q \phi(r)} \simeq n_\infty [1 - \beta q \phi]$$

In that case, the Poisson Boltzmann equation becomes *linearised* to

$$\begin{aligned}\nabla^2\phi &= \frac{n_\infty q^2}{\epsilon}\beta\phi - \frac{q}{\epsilon}\delta(0) \\ \Rightarrow \nabla^2\phi - \frac{\phi}{\lambda_D^2} &= -\frac{q}{\epsilon}\delta(0)\end{aligned}\tag{15}$$

which is called the Debye Hueckel equation; the constant

$$\lambda_D = \left(\frac{kT\epsilon}{q^2 n_\infty}\right)^{1/2}\tag{16}$$

has dimensions of length and is called the *Debye screening length*.

Actually the Debye Hueckel equation (15) has the form of an equation for a Green function and can be solved using techniques such as Fourier transform (we do not do this here but see *Methods of Mathematical Physics*).

You can check, recalling that for isotropic systems (no angular dependence)

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right),$$

that a solution of the Debye Hueckel equation is

$$\phi = \text{const.} \frac{e^{-r/\lambda_D}}{r} = \frac{q}{4\pi\epsilon} \frac{e^{-r/\lambda_D}}{r}\tag{17}$$

where in the second equality we have chosen the prefactor to make sure that Gauss's law is obeyed for a small volume enclosing the origin (where we know there is a point charge q). This is called the *screened Coulomb potential*, and is the net potential around a point charge, once the other charges have arranged themselves so as to minimize their free energy.

Figure 2: Sketch of the potential $\phi(r)$ and the density $n_\infty g(r)$, given a charge (of same sign) at the origin. Note in the first sketch how the Coulomb potential is screened out at distances of order λ_D and in the second sketch how there is a depletion zone size of order λ_D .

At distances large compared to λ_D , the charge at the centre is “screened out”: it gives only an exponentially small contribution to the electrostatic potential. The screened coulomb potential is sometimes called the Yukawa potential, after Yukawa who first proposed this form for the strong force mediated by exchange of (massive) pi-mesons. Indeed, the result is the same as you would predict if the photon (which mediates the coulomb force) were a

massive particle. Accordingly it is sometimes said that, because of the many-body interactions between charges, photons in a plasma “acquire mass”. See the book by McComb for discussion of how the bare charge has been ‘renormalised’

Debye-Hueckel theory is an example of a ‘mean field’ theory. What this term generally means is that correlations are ignored at some level — in Debye Hueckel theory we have ignored correlations except two point correlations. We shall explore the meaning of mean field theories more fully in later sections. We also note that Debye-Hueckel theory is a self consistent approximation i.e. the density $n(r)$ depends on the potential $\phi(r)$ which is itself determined from the density.

8. 4. *Fluids at High Density

For ordinary (uncharged) dense fluids the main problem is short range, rather than long range, forces. For a fluid of one species, there are several approaches; we give only a brief tour.

It is possible, starting from the pair correlation function $g(r) = \rho_2(r)/n_\infty^2$ to write down an expression for this quantity in terms of the (unknown) three-particle distribution ρ_3 . Likewise ρ_3 can be expressed in terms of ρ_4 etc.. Since the higher order distribution functions are more and more complicated, this seems rather unpromising. However, in practice one truncates things at some finite order with a “closure” equation, such as

$$\rho_3(r_1, r_2, r_3) = \rho_2(r_1, r_2)\rho_2(r_1, r_3)\rho_2(r_2, r_3) \quad (18)$$

This scheme is known as Kirkwood hierarchy or closure. Having made this assumption, one has a *closed* system of equations from which $g(r)$, and hence the equation of state, can be worked out.

This is obviously guesswork, and there are many choices of closure, all giving somewhat different results. (Names include the Percus-Yevick closure, the hypernetted chain closure, etc..) Qualitatively the predictions are often fairly good, and many of these theories show a gas-liquid phase transition when attractions are present. Again, closure schemes ignore or approximate correlation functions at some level and are therefore (refined) mean field theories.