

## 1. NOTES AND PROBLEM SET 1

### 1.1. Introduction (by Amir Erez, class of 2006)

This course deals with Complex Fluids. Complex Fluids are typically solutions of some large molecules (e.g. polymers) or supramolecular structures (e.g. micelles or bilayers, see below) in ordinary liquids.

Thus ordinary liquids are the basis of Complex Fluids, and we will start by describing the structure and dynamics of ordinary liquids. This already is complicated enough, since we can construct a good theory only when we have a small parameter and there is no such parameter for description of the structure of liquids. In solids e.g., free energy is dominated by the potential energy of interactions between molecules which favors symmetric (crystal) structures, while entropy contribution causes only minor distortions to the perfect symmetry (atom vibrations or phonons, vacancies etc). The behavior of gases, *vice versa* is dominated by the kinetic energy and the entropy contributions with interaction energy being a small parameter. However, in liquids none of the terms in the free energy is negligible in comparison to other and thus there is no free parameter and therefore no exact theory of liquids. There are ingenious guesses and we will get acquainted with some of them and learn the basics of liquid theory.

Further on in the course we will populate the ordinary liquids with polymers and other supramolecular structures and thus study the statistics and dynamics of Complex Fluids.

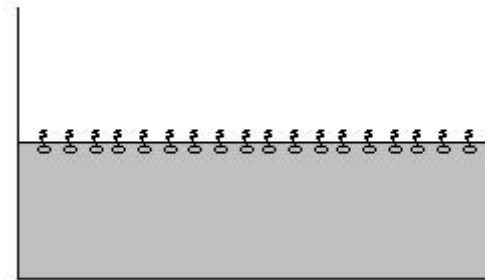
#### 1.1.1. Soap Molecules

Soap molecules can be described by a hydrophobic (oily) tail ( such as  $CH_2 - CH_2 - CH_2 -$  ) and a hydrophilic head. The head can be hydrophilic because of dissociation of two ions - the ionic bond electrostatic force is screened because of the water's high dielectric constant and this makes entropy gain the significant contribution to

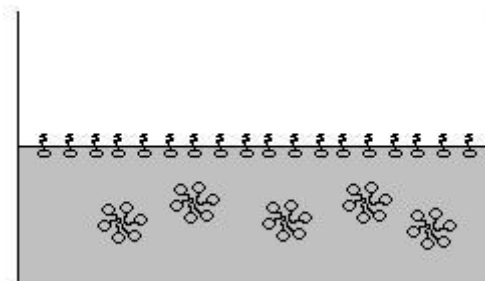
the free energy. (More on this below).

Therefore when we put soap molecules in water they will tend to fill the surface with tails outside and heads in the water. This is called a

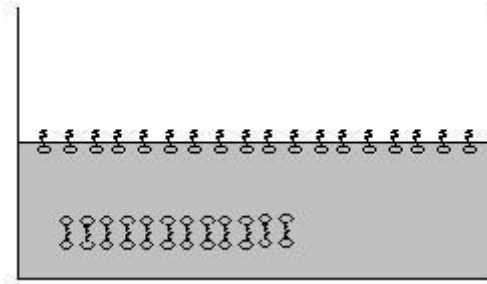
*monolayer*:



Adding more soap after the air-water interface is full will give self assembled structures, called *spherical micelles* where all the tails are inside (not touching the water) and the heads are outside (in contact with the water):



However the setup above is not always possible. When the 'tail' takes too much volume, such as when there is more than one 'tail', then the closed structures are not possible and instead we get *bilayers*:



These bilayers can be closed to form vesicles. Note that bilayers are self assembled, meaning that they are equilibrium structures. Vesicles are not. However, once formed, vesicles are very stable (the energy barriers to "open" the vesicles into bilayers are large).

## 1.2. Statistical Mechanics reminder (by Oleg)

### 1.2.1. Ensemble entropy definition

We imagine a large ensemble of  $\mathcal{N}$  similarly prepared systems. The probability  $p_j$  of any microscopic state  $j$  is defined as the ratio of the number of times  $\mathcal{N}_j$  this state appears in the ensemble to  $\mathcal{N}$ :  $p_j = \mathcal{N}_j/\mathcal{N}$ .

The ensemble average of any quantity  $A$  is defined as:  $\langle A \rangle = \sum_j p_j A_j$ , where  $A_j$  is the value of  $A$  in the microscopic state  $j$ .

The system entropy  $S$  is generally defined as

$$S = -\langle \ln p_j \rangle = -\sum_j p_j \ln p_j \quad (1.1)$$

Notice, that this definition does not require an *a priori* knowledge of the constraints put onto the ensemble (e.g. where the energy, temperature, pressure, volume or anything else is constant). This is essentially a recipe to measure the entropy of the statistical system under any conditions. One can rationalize this definition as a measure of disorder over the ensemble, i.e. of the number  $W$  of unique ways one can construct the ensemble for the given set of probabilities  $\{p_j\}$  (or  $\{\mathcal{N}_j\}$ ). Indeed,

$$W = \frac{\mathcal{N}!}{\mathcal{N}_1! \mathcal{N}_2! \dots \mathcal{N}_j! \dots} \quad (1.2)$$

Using Stirling approximation and  $\mathcal{N} = \sum_j \mathcal{N}_j$ , we can arrive at:

$$W = - \sum_j \mathcal{N}_j \ln \frac{\mathcal{N}_j}{\mathcal{N}} = -\mathcal{N} \sum_j p_j \ln p_j = \mathcal{N}S. \quad (1.3)$$

One can construct any ensemble by postulating that in thermodynamic equilibrium the system entropy reaches its maximal value under the given constraints.

### 1.2.2. Microcanonical ensemble

In *Microcanonical ensemble* one fixes the system energy  $E$ , its volume  $V$  and the number of particles  $N$ . We maximize  $S$  by the appropriate choice of  $\{p_j\}$  with the only constraint of  $\sum_j p_j = 1$ . Using Lagrange multiplier  $\alpha$  this leads us to:

$$\frac{\partial}{\partial p_j} \sum_i (-p_i \ln p_i - \alpha p_i) = -\ln p_j - 1 - \alpha = 0.$$

From here we get that the probabilities of every microstate are the same  $p_j = \exp(-1 - \alpha)$ . Instead of finding  $\alpha$  from normalization, we directly find the probabilities:  $p_j = 1/g$ , where  $g$  is the number of accessible microstates.

### 1.2.3. Canonical ensemble

The *Canonical ensemble* can be imagined as a large set of thermally connected similar systems of same volume  $V$  and number of particles  $N$ . The whole of the ensemble is isolated from the environment. For each of the systems the rest of the ensemble serves as a heat reservoir. The probabilities of the microstates are distributed under the constraints of constant total energy  $\mathcal{E}$  of the ensemble, i.e. of the average energy (called internal energy) per system  $E = \langle \epsilon \rangle = \mathcal{E}/\mathcal{N} = \sum_j \epsilon_j p_j$ . This constraint leads to a new Lagrange multiplier  $\beta$  and eventually to temperature  $T$  as a parameter(s) that fix(es) the average energy of the system. Thus we maximize  $S' = \sum_i (-p_i \ln p_i - \alpha p_i - \beta \epsilon_i p_i)$ :

$$\frac{\partial}{\partial p_j} \sum_i (-p_i \ln p_i - \alpha p_i - \beta \epsilon_i p_i) = -\ln p_j - 1 - \alpha - \beta \epsilon_j = 0.$$

From here we get the Boltzmann distribution

$$p_j = \frac{e^{-\beta \epsilon_j}}{Z}, \quad (1.4)$$

where we replace  $\alpha$ -dependent term that has to be found from the normalization condition, by the partition function  $Z$  that we find from the same condition:

$$Z = \sum_j e^{-\beta\epsilon_j}. \quad (1.5)$$

We also use this opportunity to define temperature  $T = \beta^{-1}$ . For a given temperature (or  $\beta$ ) one can find the internal energy

$$E = \sum_j \epsilon_j p_j = \frac{1}{Z} \sum_j \epsilon_j e^{-\beta\epsilon_j} = - \left( \frac{\partial \ln Z}{\partial \beta} \right)_{V,N}. \quad (1.6)$$

The change in energy  $dE = \sum_j \epsilon_j dp_j + \sum_j p_j d\epsilon_j$  consists of two terms. The first term is associated with the change in microstates probabilities while keeping their energies: this clearly is related to the change in the system entropy, and indeed, substituting Eq. 1.4 one can show that  $\sum_j \epsilon_j dp_j = TdS$  i.e. is heat. The second term does not involve change in the system entropy (since  $\{p_j\}$  remain the same) and depends on the change in microstates energies only: thereby this term is associated with the mechanical work, e.g.  $-PdV$ . Thus,

$$dE = TdS - pdV. \quad (1.7)$$

Instead of maximizing  $S'$ , traditionally we minimize free energy  $F$  defined as:

$$F = U - TS = \sum_j p_j (\epsilon_j + T \ln p_j) = \sum_j p_j T \ln (p_j e^{\epsilon_j/T}) = -T \ln Z, \quad (1.8)$$

where we used Eq. 1.4 and  $\sum_j p_j = 1$  normalization condition.

#### 1.2.4. Grand Canonical ensemble

Similarly we can define a *Grand Canonical ensemble* as a large set of systems of same volume  $V$  that can exchange heat and particles. As before the whole of the ensemble is isolated from the environment. We will be minimizing the free energy under the constraint of preserved total number of particles in ensemble, i.e. constant average number of particles per system  $\langle N \rangle = \sum_j N_j p_j$ . The preservation of the average energy per system is already taken care by  $F$ . Thus we come up with a new Lagrange multiplier - chemical potential  $\mu$  that fixes  $\langle N \rangle$  and a new thermodynamic potential (*Grand potential*) to minimize:  $\Omega = F - \mu \langle N \rangle$

or ( $\Omega = F - \mu N$  for a large system). An additional constraint, as before is  $\sum_j p_j = 1$ . Thus we get:

$$\frac{\partial}{\partial p_j} \sum_i (\epsilon_i p_i + T p_i \ln p_i - \mu N_i p_i - \gamma p_i) = \epsilon_j + T \ln p_j + T - \mu N_j - \gamma = 0.$$

From here we get the Gibbs distribution

$$p_j = \frac{1}{\zeta} \exp\left(\frac{\mu N_j - \epsilon_j}{T}\right), \quad (1.9)$$

with grand partition function as a normalization factor:

$$\zeta = \sum_j \exp\left(\frac{\mu N_j - \epsilon_j}{T}\right). \quad (1.10)$$

The grand potential can be found from (*derive*):

$$\Omega = -T \ln \zeta. \quad (1.11)$$

And the average number of particles from:

$$\langle N \rangle = \sum_j N_j p_j = \frac{1}{\zeta} \sum_j N_j \exp\left(\frac{\mu N_j - \epsilon_j}{T}\right) = T \left(\frac{\partial \ln \zeta}{\partial \mu}\right)_{T,V} = - \left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V}, \quad (1.12)$$

Combining now all of derivatives of different thermodynamic potentials we can write:

$$dE = TdS - pdV + \mu dN, \quad (1.13)$$

$$dF = -SdT - pdV + \mu dN, \quad (1.14)$$

$$d\Omega = -SdT - pdV - Nd\mu. \quad (1.15)$$

### 1.2.5. Application to classical systems

In the following we will consider classical systems only: those of  $N$  molecules in volume  $V$  with states defined by  $\{\vec{p}_i, \vec{r}_i\}_N$  couples (replacing microstate number  $j$ ) and the Hamiltonian (replacing the microstate energy  $\epsilon_j$ ):

$$H(\{\vec{p}_i, \vec{r}_i\}_N) = \sum_{i=1}^N \frac{p_i^2}{2m} + U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \quad (1.16)$$

We further assume pairwise, spherically symmetric interactions between molecules  $u(\vec{r}_1, \vec{r}_2) = u(|\vec{r}_2 - \vec{r}_1|) = u(r_{12})$ :

$$U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum_{i=1}^N \sum_{j=i+1}^N u(r_{ij}) = \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N u(r_{ij}) \quad (1.17)$$

Then the partition function of the Canonical ensemble is calculated as:

$$\begin{aligned} \mathcal{Z}_N(T, V, N) &= \sum_{\{\vec{p}_i, \vec{r}_i\}_N} e^{-\beta H(\{\vec{p}_i, \vec{r}_i\}_N)} = \frac{1}{N!(2\pi\hbar)^{3N}} \int e^{-\beta H(\{\vec{p}_i, \vec{r}_i\}_N)} d\vec{p}_1 d\vec{r}_1 \dots d\vec{p}_N d\vec{r}_N = \\ &= \frac{n_q^N}{N!} \underbrace{\int e^{-\beta U(\vec{r}_1, \dots, \vec{r}_N)} d\vec{r}_1 \dots d\vec{r}_N}_{Q_N} = \frac{n_q^N}{N!} Q_N, \end{aligned} \quad (1.18)$$

where Eq. 1.16 was substituted, integration over  $\{d\vec{p}_i\}$  was performed,  $n_q = (\frac{mT}{2\pi\hbar^2})^{3/2}$  is quantum density and  $Q_N$  is *configurational integral*. Probability density of a *microscopic* state  $\{\vec{p}_i, \vec{r}_i\}_N$  of the system is given by Boltzmann distribution:

$$p(\{\vec{p}_i, \vec{r}_i\}_N) = \frac{e^{-\beta H(\{\vec{p}_i, \vec{r}_i\}_N)}}{\mathcal{Z}_N} \quad (1.19)$$

The grand partition function of the Grand Canonical ensemble is:

$$\zeta(T, V, \mu) = \sum_{N, \{\vec{p}_i, \vec{r}_i\}_N} e^{\beta(\mu N - H(\{\vec{p}_i, \vec{r}_i\}_N))} = \sum_{N=0}^{\infty} e^{\beta\mu N} \mathcal{Z}_N \quad (1.20)$$

And the probability density of a *microscopic* state  $(N, \{\vec{p}_i, \vec{r}_i\}_N)$  of the system is given by Gibbs distribution:

$$p(N, \{\vec{p}_i, \vec{r}_i\}_N) = \frac{e^{\beta(\mu N - H(\{\vec{p}_i, \vec{r}_i\}_N))}}{\zeta} \quad (1.21)$$

### 1.3. Virial Expansion

The Virial expansion is essentially a Taylor expansion of thermodynamic functions in the powers of particle density  $n$ . As any such expansion it is valid at low densities when the particles occupy only a small fraction of the available volume. We will be interested in the virial expansion the free energy  $F$  and pressure  $P$ :

$$F = F^{id} + An^2 + Bn^3 + \dots, \quad (1.22)$$

$$P = nT + A_1 n^2 + B_1 n^3 + \dots, \quad (1.23)$$

where  $F^{id}$  and  $nT$  are the free energy and pressure in ideal gas. In fact we will limit ourselves here to the coefficients of the square terms ( $n^2$ ): the resulting coefficients are called the *second virial coefficients*.

For the virial expansion it is convenient to use the formalism of the Grand Canonical ensemble: for small particle density  $n \ll 1/(4\pi\sigma^3/3)$  (where  $\sigma$  is a diameter of one molecule) we can always choose the volume of the system small enough so that the average number of particles  $\langle N \rangle = nV \ll 1$  and can be used as a small parameter in expansion. Furthermore, we notice that for low densities different terms in the grand partition function  $\zeta$  are essentially the powers of  $\langle N \rangle$ . Indeed, for low densities the system properties should be close to those of ideal gas for which  $\mu = T \ln(n/n_q)$ . The configurational integral  $Q_N \approx V^N$  since over most of the space the interaction energy is close to 0. Thus the  $N$ -s term  $\zeta_N$  in the grand partition function can be estimated as  $\zeta_N = e^{\beta\mu N} \mathcal{Z}_N = e^{\beta\mu N} \frac{n_q^N}{N!} Q_N \approx \frac{(nV)^N}{N!} = O(nV)$ . Thus for the second order expansion we can keep terms up to  $N = 2$  in the grand partition function.

### 1.3.1. Calculation of the Second Virial Coefficient (by Shai Kinast, class of 2006)

In the proceeding discussion we shall expand the grand canonical partition function ( $\zeta$ ) up to second order ( $N = 2$ ), from which we will get directly the grand thermodynamic potential ( $\Omega = -\tau \ln \zeta$ ). From there we will find  $\langle N \rangle$  and therefore  $n$  for a given  $\mu$  and use this relation and  $F = \Omega + \mu N$  to calculate the dependence of  $F$  on  $n$  up to  $n^2$  terms. While we use the expansion up to second order only, the extension of this approach to higher order terms is straightforward, although mathematically more cumbersome.

Let us write the expression for Gibbs sum (grand canonical partition function) as:

$$\zeta = \zeta_0 + \zeta_1 + \zeta_2 + \dots,$$

where  $\zeta_0$  is the *zero order term*,  $\zeta_1$  is the *first order term* and so on. Each consecutive term represents higher order in the expansion over the small parameter  $nV$ , i.e.  $\zeta_N = O((nV)^N)$  (here is a good place to think a bit about the difference between  $N$  on one side and  $\langle N \rangle$ ,  $n$  on the other side). Since we are interested in the expansion up to  $(nV)^2$ , we will keep  $\zeta_0, \zeta_1, \zeta_2$  terms only.

In zero order ( $N = 0$ ) the hamiltonian is simply  $H_0 = 0$  and the zero order term of



the partition function is  $\zeta_0 = 1$ .

For the first order ( $N = 1$ ) the hamiltonain is  $H_1 = p^2/2m$  (momentum only) and  $\zeta_1 = n_q V \lambda$ , where  $\lambda \equiv e^{\mu/\tau}$  is called the *absolute activity*. It is worth mentioning that for the limit case (ideal gas) the chemical potential is simply  $\mu = \tau \ln(n/n_q)$ , so that  $\zeta_1 \approx nV = N$ . One can also note that the properties of ideal gas can be derived from these first two terms in the expansion  $\zeta_0$  and  $\zeta_1$ .

The second order terms ( $N = 2$ ) are somewhat more complicated, as for the first time we introduce the potential energy into the hamiltonian:

$$H_2 = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + u(\vec{r}_1 - \vec{r}_2)$$

and the second order term of the partition function is therefore:

$$\zeta_2 = \frac{1}{2} \lambda^2 n_q^2 \int d\vec{r}_1 d\vec{r}_2 e^{-u(\vec{r}_1 - \vec{r}_2)/\tau}$$

Note that since the interactions between molecules are short ranged,  $u(\vec{r}_1 - \vec{r}_2)/T \ll 1$  over most of the volume  $V$ . Thus integral over  $d\vec{r}_1 d\vec{r}_2$  is of the order of  $V^2$ . Together with  $\lambda \sim n/n_q$ , this gives us  $\zeta_2 \sim \langle N \rangle^2$  as expected. Change of variables from  $\vec{r}_2$  to  $\vec{r} \equiv \vec{r}_1 - \vec{r}_2$  transforms the integral into a simpler form:

$$\int d\vec{r}_1 d\vec{r}_2 e^{-u(\vec{r}_1 - \vec{r}_2)/\tau} \rightarrow \int d\vec{r}_1 \int d\vec{r} e^{-u(\vec{r})/\tau} = V \int d\vec{r} e^{-u(\vec{r})/\tau}$$

Substituting in the grand canonical potential one gets:

$$\Omega = -\tau \ln \left[ 1 + \lambda n_q V + \frac{1}{2} (\lambda n_q)^2 V \int d\vec{r} e^{-u(\vec{r})/\tau} \right]$$

We remember that for low densities  $\lambda n_q \approx n$  and  $nV \ll 1$ , allowing us to expand the above expression around  $\lambda n_q V$  (using Taylor expansion  $\ln(1+x) = x - x^2/2 + \mathcal{O}(x^3)$ ):

$$\Omega = -\tau \left[ \lambda n_q V + \frac{1}{2} (\lambda n_q)^2 V \int d\vec{r} e^{-u(\vec{r})/\tau} - \frac{1}{2} (\lambda n_q V)^2 + \mathcal{O}((\lambda n_q V)^3) \right]$$

$$\Omega \approx -\tau V \left[ \lambda n_q - \frac{1}{2} (\lambda n_q)^2 a \right],$$

where the second virial coefficient is defined as:

$$a = \int d\vec{r} (1 - e^{-u(\vec{r})/\tau}) \quad (1.24)$$

Going one step further, we get an expression for the density as a function of chemical potential:

$$n = \frac{N}{V} = -\frac{1}{V} \left( \frac{\partial \Omega}{\partial \mu} \right)_{\tau, V} = -\frac{1}{V} \left( \frac{\partial \Omega}{\partial \lambda} \right) / \left( \frac{\partial \mu}{\partial \lambda} \right) = \lambda n_q - (\lambda n_q)^2 a$$

or

$$\lambda n_q = n + (\lambda n_q)^2 a$$

where we use  $\mu = \tau \ln \lambda$ . Substituting  $\lambda n_q \approx n$  on the right, we can write:

$$\lambda n_q = n + n^2 a$$

Plugging this in the grand canonical potential one gets the expression for  $\Omega$  in terms of particle density:

$$\Omega = -\tau V \left[ n + \frac{n^2 a}{2} \right]$$

Having the grand canonical potential we can finally calculate the free energy:

$$F = \Omega + \mu N = -\tau V \left[ n + \frac{n^2 a}{2} \right] + n V \tau \ln \left( \frac{n + n^2 a}{n_q} \right)$$

$$F \approx F^{id} + \frac{\tau V a}{2} n^2$$

where we use  $\ln \left[ \frac{n}{n_q} (1 + na) \right] \approx \ln \frac{n}{n_q} + na$ , and the free energy of an ideal gas is  $F^{id} = n V \tau \left( \ln \frac{n}{n_q} - 1 \right)$ .

From here it is straightforward to get the pressure, by the relation  $P = -(\partial F / \partial V)_{\tau, N}$ :

$$P = \left( \frac{\partial F}{\partial V} \right)_{\tau, N} = n \tau + \frac{\tau a}{2} n^2.$$

Finally we conclude that the virial coefficients of the free energy and of the pressure are  $(\tau V a)/2$  and  $(\tau a)/2$  respectively.

Of particular interest is the case of spherically symmetric potential energy  $u = u(r)$ , in which the coefficient  $a$  is reduced to:

$$a = 4\pi \int_0^\infty r^2 dr (1 - e^{-u(r)/\tau})$$

Let us calculate  $a$  explicitly for the most simple case, where the potential energy contains only the hardcore interaction:

$$u(r) = \begin{cases} \infty & , r \leq \sigma \\ 0 & , r > \sigma \end{cases}$$

Substituting, we get:

$$a = 4\pi \int_0^\sigma r^2 dr = \frac{4\pi}{3} \sigma^3$$

This is just the volume of a sphere with diameter twice as large as a molecule diameter. This volume can be thought of as an *effective volume* of a molecule, inside which other molecule (with the same effective volume) can not penetrate, as one might expect from a hardcore interaction. Thus an increase in free energy due to hard core interactions can be interpreted as having free energy cost of  $T$  per each particle collision (since one can estimate that there are  $\langle N \rangle / 2 \cdot n \frac{4\pi}{3} \sigma^3 = n^2 V a / 2$  collisions at any time)

The hardcore interaction is a convenient model, from which we can elaborate our discussion introducing some more complicated interactions (under the very general name *softcore interactions*, meaning non-hardcore interactions). These interactions can often be divided into:

$$U = (\text{hardcore interaction}) + (\text{attractive and/or repulsive terms})$$

By its definition it can be easily shown that  $a$  decreases when attractive terms are added, while it increases when the additional terms are repulsive.

Within the second virial coefficient approximation the properties of any soft core system can be mapped onto the properties of hard core system with the same density of particles and particle diameter  $\sigma$  determined from  $a = \frac{4\pi}{3} \sigma^3$  where  $a$  is defined by Eq. 1.24.

#### 1.4. Molecular interactions (by Amir Erez)

##### 1.4.1. Short range repulsion

at the distances  $\sim$  molecular diameter  $\sigma$  due to the overlap of electron orbits of the two molecules. The repulsion can be approximated by the *hard core* potential:

$$u_{hc}(r) = \begin{cases} 0, & r > \sigma \\ \infty, & r < \sigma \end{cases} \quad (1.25)$$

##### 1.4.2. Long range attraction

decaying roughly as  $\propto r^{-6}$  stems from the dipole-induced dipole interactions, called Van der Waals (VdW) interactions:

The Van Der Waals interaction is the attraction between dipole and induced dipole. To understand it better we split considerations into three parts:

- 1) Energy of an induced dipole in an external electric field
- 2) Interaction energy of dipole-induced dipole pair
- 3) Two models for polarizability, for non-polar and polar molecules.

1) An induced dipole is subject to an electric force because of the difference in electric field at its "poles":

$$d_i = \alpha E = ql$$

$$F = q\Delta E \approx ql \frac{dE}{dr} = \alpha E \frac{dE}{dr}$$

Integrating this will give the energy of a dipole in an electric field:

$$U = - \int F dr = -\frac{1}{2} \alpha E^2$$

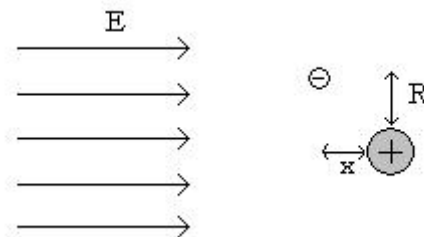
2) When the external field  $E$  is produced by a dipole we can say:

$$E \approx \frac{d}{4\pi\epsilon_0 r^3}$$

Thereby giving us:

$$U \approx -\frac{\alpha d^2}{(4\pi\epsilon_0)^2 r^6} \quad (1.26)$$

3) *Electronic polarizability* is common to all molecules, both polar and non-polar. To describe electronic polarizability we consider a model of an atom with the electron orbiting it in a plane (conservation of angular momentum). The atom is subject to an external electric field:



We can find the electron orbit displacement  $x$  from force equilibrium:

$$eE = \frac{e^2}{4\pi\epsilon_0 R^2} \cos \theta = \frac{e^2}{4\pi\epsilon_0 R^2} \frac{x}{R}$$

By denoting  $d_i = ex$  we get:

$$d_i = 4\pi\epsilon_0 R^3 E = \alpha E$$

$$\alpha = 4\pi\epsilon_0 R^3 \tag{1.27}$$

Note that we can extend this approach to heavy atoms and molecules since the outer electrons 'see' a screened nucleus electric charge that is very similar to the case of hydrogen atom.

Using Eqs. 1.26 and 1.27 we can express the Van der Waals energy of two nonpolar molecules as:

$$U_{vdw}(r) = \frac{-2\alpha^2 I}{(4\pi\epsilon_0)^2 r^6}, \tag{1.28}$$

where  $I = \frac{e^2}{8\pi\epsilon_0 R}$  is the ionization energy of a molecule. Typically,  $I \approx 2 \times 10^{-18} J$ , so that the VdW energy is of the order of magnitude of thermal energy.

Note that the quantum mechanical calculation will give instead of the '2' prefactor,  $\frac{3}{4}$ .

We can check whether the result we got for  $\alpha$  is reasonable by considering the *electric susceptibility* of a medium. The electric susceptibility  $\chi$  is proportional to the density of atoms  $n$ :

$$\chi = \epsilon - 1 = \frac{n\alpha}{\epsilon_0}$$

The atom density in liquids or solids is roughly  $1/(\text{atom volume})$  or:

$$n \approx \frac{1}{\frac{4}{3}\pi R^3}$$

Thereby giving us, for non metals,  $\chi \approx 3$  or  $\epsilon \approx 4$ . Indeed when the table values of dielectric constant for nonpolar media is nearly always  $2 < \epsilon < 6$ .

### 1.4.3. Mixing energy

When we have two different types of molecules:

$$U_{vdw}(r) = \frac{-2\alpha_1\alpha_2 I}{(4\pi\epsilon_0)^2 r^6}$$

We compare the energy of an unmixed state:

A A A B B B

with that of a mixed state:

A A B A B B

We can see that the change in energy is:

$$\Delta U = U_{AA} + U_{BB} - U_{AB} - U_{AB} = 2U_{mix}$$

$$U_{mix} = \frac{U_{AA} + U_{BB}}{2} - U_{AB}$$

This determines whether mixing is energetically favourable or not. In general  $U_{AA}$ ,  $U_{BB}$  and  $U_{AB}$  stem from Van Der Waals interactions we see that:

$$U_{mix} \propto \frac{-\alpha_A^2 - \alpha_B^2}{2} + \alpha_A \alpha_B = -\frac{1}{2}(\alpha_A - \alpha_B)^2 < 0$$

Therefore the mixed state energy is higher than the unmixed state. This means that from energy considerations alone, the molecules will not mix. Entropy considerations dictate maximal mixing so the balance is determined by the temperature of the solution. **From this we can conclude that different types of molecules will not mix in a low enough temperature.**

#### 1.4.4. Dipole Polarizability of Polar Molecules

For polar molecules (such as water molecules) there is an additional type of polarizability: *dipole polarizability*. Dipole polarizability is typically larger than electron polarizability and gives media a significantly higher dielectric constant. For example, for water a dielectric constant is  $\epsilon \approx 80$ . High polarizability determines many important properties of water. E.g. salts dissociate easily in water, since the ion bond energy decreases by a factor of 80 (as compared to air or vacuum). Therefore the energy price for breaking the ionic bond is small compared to the entropy gain and this is why at room temperature table salt (NaCl) will undergo a process of **disassociation** separating to the two ions.

We now proceed to derive the Van Der Waals interaction energy for polar molecules.

For the molecular dipole  $\vec{d}$ , without external electric field  $\langle \vec{d} \rangle = 0$  due to randomness

of orientation. With external electric field we get a preferred direction, meaning that on average the dipole will be in the direction of the external field:

$$\langle \vec{d} \rangle = \vec{d}_i$$

The field-dipole energy is  $U = -\vec{d}\vec{E}$  so using the Boltzmann factor we get the probability for the dipole to point in the direction  $\theta$  relative to the direction of the external electric field:

$$P(\theta) = \frac{1}{Z} e^{\beta \vec{d}\vec{E}}$$

$$Z = \int e^{\beta \vec{d}\vec{E}} d\Omega$$

$$\vec{d}_i = \langle \vec{d} \rangle = \frac{1}{Z} \int d_e \cos \theta e^{\beta d_e \cdot E \cdot \cos \theta} d\Omega$$

Taking  $\vec{d}_e \cdot \vec{E} \ll \tau$  where  $\beta = 1/\tau$  and Taylor expanding:

$$d_i = \frac{\int (d_e \cos \theta + \beta E d_e^2 \cos^2 \theta) d\Omega}{\int (1 + \beta d_e E \cos \theta) d\Omega} = \beta E d_e^2 \frac{\int \cos^2 \theta d\Omega}{\int d\Omega}$$

we get the induced dipole:

$$d_i = \frac{d_e^2}{3k_B T} E$$

Or

$$\alpha = \frac{d_e^2}{3k_B T}$$

For water, this calculation will give  $\epsilon \approx 105$  at room temp. whereas the empiric value is  $\epsilon \approx 80$ .

We can immediately see that this is a much higher polarizability than in non-polar molecules.

Plugging this into the general Van Der Waals formula:

$$U_{vdw} = \frac{-\alpha d_e^2}{(4\pi\epsilon_0)^2 r^6}$$

We get the interaction energy between two polar molecules:

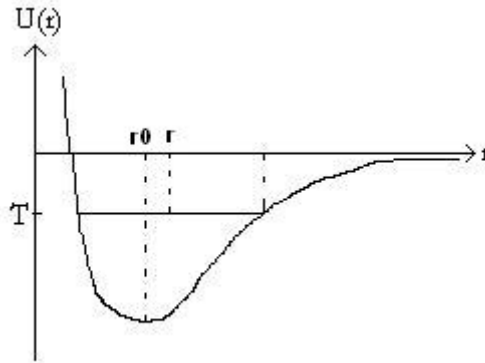
$$U_{vdw}^{pol} = \frac{-d_e^4}{(4\pi\epsilon_0)^2 \cdot 3k_B T \cdot r^6}$$

**Note:** For calculating the attractive forces between polar and non-polar molecules, such as oil and water, we assume that the field is created by the polar molecule (therefore using  $d_e$  for the water) and the non-polar molecule responds using  $\alpha = 4\pi\epsilon_0 R^3$  in the formula  $U = -\frac{\alpha d_e^2}{(4\pi\epsilon_0)^2 r^6}$ .

From this, and using mixing energy considerations, we can partially explain the very good separation between water and oil at room temperature. Later in the course we shall discuss the behaviour of the hydrophobic tails.

### 1.4.5. Thermal expansion

It is easily seen that, generally, the potential is not symmetric with respect to the minimum  $r_0$ :



An increase in temperature results in the system oscillating between two values of  $r$  which are not equidistant from the minimal state  $r = r_0$ . On average the radius  $r > r_0$ .

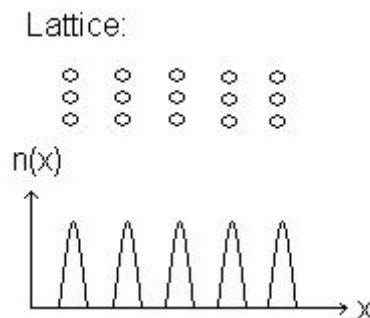
In general, total interaction potential between two molecules is the sum of short-range repulsion and long-range attraction. Since hard core potential is not smooth, for modeling it is often replaced by some other steep repulsive potential, e.g. Lennard-Jones interaction (repulsion + VdW attraction) is:

$$u(r) = 4\epsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right), \quad (1.29)$$

where  $\epsilon$  is the binding energy of two molecules in potential minimum.

## 1.5. The Radial Distribution Function

Let us consider a solid lattice, where the atoms' position is rigidly determined. We can now make a plot of the atom density as a function of  $x$  :





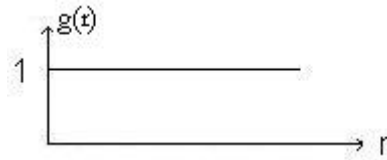


FIG. 1: Ideal gas distribution function

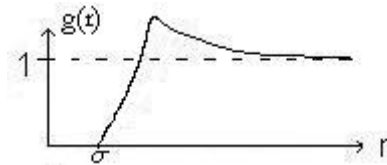
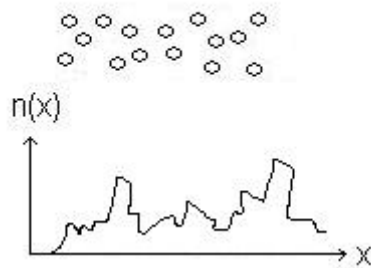


FIG. 2: Low density real gas distribution function

In fluids, we have a less ordered structure. In fact, our density function  $n(x)$  now depends on time:



On average,  $\langle n(\vec{r}) \rangle_t = n$  meaning that the fluid is homogenous.

Instead of using a fixed coordinate distribution function, we can "sit" on one molecule and measure the density of the molecules around it, thereby getting a radial distribution function. We normalize the distribution function by average density so that it gives 1 when the density is the average density, we can expect that as  $r \rightarrow \infty$  we get  $g(r) \rightarrow 1$ .

Let us examine a few examples of radial distribution functions: (we denote  $\sigma$  as the molecule diameter)

For a real gas, we have to consider short range repulsion and long range Van Der Waals attraction (more on this below) giving us a different distribution function:

Note that the repulsion accounts for the climb left of the maximum, whereas the attraction affects the descent to the right of the maximum.

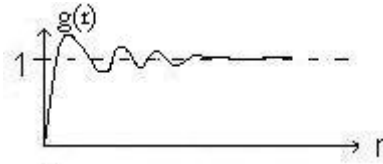
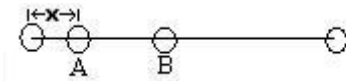


FIG. 3: Fluid distribution function

Fluids have a somewhat different distribution function:

The surprising fact is that attractive forces are not required to make the maxima/minima in the plot for liquids. We shall now examine the reason that the system exhibits a clear structure even in the absence of intermolecular attractive forces.

To simplify things, we shall examine the case where we have two molecules restricted to moving in one dimension, like two beads on a piece of string of length  $L$ :



We determine the position of A and sum over all the position for B. We can do the calculation in two ways: either the molecules can penetrate each other, or they cannot. We begin by assuming they can inter-penetrate.

Therefore A and B are identical, and we can look at either one of them. Following the micro-canonic formalism the probability that A is a certain distance from the left edge is proportional to the number of microscopic states of the system. ie. The probability for finding A at position X is the number of possible positions of B, when A is at X.

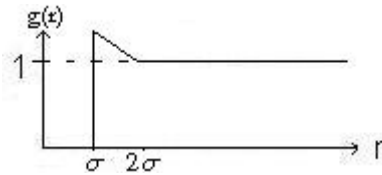
When  $\sigma < x < 2\sigma$  then B cannot penetrate the region between the left side and A and therefore the number of states of the system:

$$g(x) \propto (L - x - 2\sigma)$$

Whereas when  $2\sigma < x$  we can fit B inside the gap therefore:

$$g(x) \propto (L - x - 2\sigma) + (x - 2\sigma) = L - 4\sigma$$

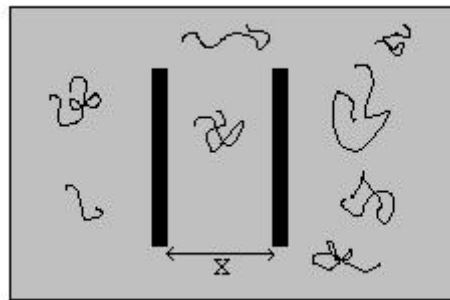
Giving us a plot of the radial distribution function that looks like this:



This demonstrates that we require only a repulsive (hardcore interaction) force to get a relevant  $g(r)$ .

## Depletion interaction

The depletion interaction force is a force in the sense of statistical physics - that is, as a derivative of the free energy. Based on the approach outlined above, let us consider a system composed of a fluid (with polymers) and two plates:



For as long as  $x >$  polymer length, then there is no depletion force. However, when the plates become close  $x \approx$  polymer length, then there are less states to arrange the system (this is because polymers cannot enter between the plates). This means the entropy is lower and the free energy is higher. As  $x \rightarrow 0$  we get maximal entropy and therefore there is an attractive force that makes the two plates stick together. This is the depletion interaction.

### 1.5.1. Tonks gas/Frenkel liquid

The considerations above applied to a few hard core beads (rods) on a line can be generalized to a large number  $N$  of beads (rods).

The problem of hard core interacting rods in 1D can be solved exactly (among a few problems that can be solved exactly in the field). The idea is to first consider the distribution

of  $N \ll 1$  points-like objects on a line of length  $L$ , so that their average density is  $\bar{n} = N/L$ . Let's consider the probability of finding  $k$ -th neighbour of object  $A$  in the distance range of  $[x, x + dx]$  from  $A$ :

$$dp = P(k, x)dx = Poisson(k - 1, \bar{n}x) \cdot \bar{n}dx, \quad (1.30)$$

where  $P(k, x)$  is the probability density, the term  $Poisson(k - 1, \bar{n}x)$  is the probability of having  $k - 1$  neighbours in  $[0, x]$  range given by the Poisson distribution:

$$Poisson(k, \lambda) = \frac{\lambda^k}{k!} e^{-\lambda} \quad (1.31)$$

for the average number of events  $\lambda = \bar{n}x$ .

The  $\bar{n}dx$  term in the Eq. 1.30 describes then the probability of having the last  $k$ -th neighbor in the range of  $[x, x+dx]$  given that we have already placed the first  $k-1$  neighbours up to  $x$ . Dividing  $dp$  by  $dx$  gives us the respective probability density  $P(k, x)$  that is the same as the simple number density of  $k$ -th neighbours.

$$P(k, x) = Poisson(k - 1, \bar{n}x) \cdot \bar{n} \quad (1.32)$$

To calculate the analog of the radial distribution function we need to sum up  $P(k, x)$  for all  $k$  as we do not care which neighbour is found at the distance  $x$  and divide the result by  $\bar{n}$  (average density) for proper normalization:

$$g(x) = \frac{P(x)}{\bar{n}} = \frac{1}{\bar{n}} \sum_{k=1}^{\infty} P(k, x) = \sum_{k=1}^{\infty} Poisson(k - 1, \bar{n}x) = \sum_{k=0}^{\infty} Poisson(k, \bar{n}x) = 1, \quad (1.33)$$

from the normalization of the Poisson distribution. This trivial result could be expected since there are no interactions between the point-like objects and therefore no correlations in their positions.

The next step is to consider  $N \ll 1$  rod-like objects of length  $d$  each on a line of length  $L$ . As before, the object density is  $\bar{n} = N/L$ . It is convenient also to define the line (analogue of volume) fraction of the rods, i.e. the part of the system length occupied by the rods  $\phi = Nd/L = \bar{n}d$ .

The trick now is that we can shrink rods to points (this reduces the system length to  $L' = L - Nd$  and increases the average density to  $\bar{n}' = N/L' = N/(L - Nd) = \bar{n}/(1 - \phi)$ ). This maps the rod-like object problem to the point-like objects one. Each arrangement of the rods is mapped to a single arrangement of the points and vice versa. This means that the

entropy of the system non-colliding rods is the same as that of points and all of statistical quantities can be obtained by the reverse mapping of the two systems (since for the non-colliding rods the interaction energy is zero, the system thermodynamics is determined solely by the entropy). In particular, the probability density  $P(k, x)$  of finding the  $k$ -th neighbours at the coordinate  $x$  can be expressed now as:

$$P(k, x) = \text{Poisson}(k - 1, \bar{n}'x') \cdot \bar{n}' \cdot \theta(x'), \quad (1.34)$$

where  $x' = x - kd$  is the result of "shrinking" of the original coordinate  $x$  by the  $k$  rod sizes (those of neighbors and of the particle at the origin).  $\theta$  is the Heaviside step function ( $\theta(x < 0) = 0$ ,  $\theta(x > 0) = 1$ ). It ensures that the probability density is defined only in the proper range (i.e. for  $x' > 0$ , since the  $k$ -th neighbor cannot be found closer than  $kd$  to the origin).

Then in analogy to the Eq. 1.33, the pair distribution function can be expressed as:

$$\begin{aligned} g(x) &= \frac{1}{1 - \phi} \sum_{k=1}^{\infty} \text{Poisson}(k - 1, \bar{n}'(x - kd)) \cdot \theta(x - kd) = \\ &= \frac{1}{1 - \phi} \sum_{k=1}^{\infty} \frac{1}{(k - 1)!} \left[ \frac{\bar{n}(x - kd)}{1 - \phi} \right]^{k-1} \exp\left(-\frac{\bar{n}(x - kd)}{1 - \phi}\right) \theta(x - kd) \end{aligned} \quad (1.35)$$

The Matlab files calculating this function are uploaded to the course site.

### 1.6. Particle distribution functions by Shai Kinast class of 2006

After defining the *radial* distribution function, we shall introduce the *l-particle* distribution function. Before we do that, let us recall that in the canonical ensemble (where  $\tau, V$  and  $N$  are constants) the partition function takes the form:

$$\begin{aligned} \mathcal{Z}_N(\tau, V, N) &= \sum_{\{\vec{p}_i, \vec{r}_i\}_N} e^{-\beta H(\{\vec{p}_i, \vec{r}_i\}_N)} = \frac{1}{N!(2\pi\hbar)^{3N}} \int e^{-\beta H(\{\vec{p}_i, \vec{r}_i\}_N)} d\vec{p}_1 d\vec{r}_1 \dots d\vec{p}_N d\vec{r}_N = \\ &= \frac{1}{N!(2\pi\hbar)^{3N}} \int e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}} d\vec{p}_1 \dots d\vec{p}_N \int e^{-\beta U(\vec{r}_1 \dots \vec{r}_N)} d\vec{r}_1 \dots d\vec{r}_N = \frac{n_q^N}{N!} Q_N \end{aligned}$$

where we use the definition of the quantum density ( $n_q$ ):

$$n_q^N = \frac{1}{(2\pi\hbar)^{3N}} \int e^{-\beta \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}} d\vec{p}_1 \dots d\vec{p}_N = \frac{1}{(2\pi\hbar)^{3N}} \prod_{i=1}^N \int e^{-\beta \frac{\vec{p}_i^2}{2m}} = \left( \frac{m}{2\pi\beta\hbar^2} \right)^{3N/2}$$

and the *configurational integral* is defined as:

$$Q_N = \int e^{-\beta U(\vec{r}_1 \dots \vec{r}_N)} d\vec{r}_1 \dots d\vec{r}_N$$

The probability density to find the system in a certain microscopic state  $\{\vec{p}_i, \vec{r}_i\}_N$  is hence:

$$P(\{\vec{p}_i, \vec{r}_i\}_N) = \frac{e^{-\beta H(\{\vec{p}_i, \vec{r}_i\}_N)}}{\mathcal{Z}_N}$$

The *l-particle distribution function*  $g_N^{(l)}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_l)$  is defined to be *proportional* to the probability to have any  $l$  molecules (in a system of  $N$  molecules) in the defined positions  $\vec{r}_1, \vec{r}_2, \dots, \vec{r}_l$  (the normalization is given further in this section).

Let us calculate this function step by step. We start with the probability to find  $N$  molecules in *any* position (within a given volume  $V$ ) and with *any* momentum. Using the above expression for the probability in the canonical ensemble we have:

$$g_N \sim \frac{e^{-\beta U(\vec{r}_1 \dots \vec{r}_N)}}{\mathcal{Z}_N} \int e^{-\beta \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}} d\vec{p}_1 \dots d\vec{p}_N = \frac{N! e^{-\beta U(\vec{r}_1 \dots \vec{r}_N)}}{Q_N},$$

where we integrate over momenta since we care only about positions and do not care about particle momenta and we substituted  $\mathcal{Z}_N = n_q^{3N} Q_N / N!$ .

Now imagine that we 'fix' the position of  $l$  out of  $N$  molecules, and 'do not care' about the position of the other  $N - l$  molecules (in other words, we allow them to have *any* position). Therefore we integrate over positions of  $N - l$  molecules  $[d\vec{r}_{l+1} d\vec{r}_{l+2}, \dots, d\vec{r}_N]$ . While integrating we should make sure that we do not count the same configuration twice. Thus we perform integration as usual and introduce factor  $(N - l)!$  to avoid counting the same configuration many times.

$$g_N^{(l)}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_l) \sim \frac{N!}{Q_N (N - l)!} \int d\vec{r}_{l+1} d\vec{r}_{l+2}, \dots, d\vec{r}_N e^{-\beta U(\vec{r}_1 \dots \vec{r}_N)}$$

Finally, we add a normalization factor  $n^l$  in order to have  $g_N^{(l)}$  dimensionless and to remove trivial dependency on density:

$$n^l g_N^{(l)}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_l) = \frac{N!}{(N - l)! Q_N} \int d\vec{r}_{l+1} d\vec{r}_{l+2}, \dots, d\vec{r}_N e^{-\beta U(\vec{r}_1 \dots \vec{r}_N)}$$

A function of particular interest to us (and also the simplest one) is the *pair distribution function* ( $l = 2$ ):

$$n^2 g_N^{(2)}(\vec{r}_1, \vec{r}_2) = \frac{N(N-1)}{Q_N} \int d\vec{r}_3 d\vec{r}_4, \dots, d\vec{r}_N e^{-\beta U(\vec{r}_1 \dots \vec{r}_N)}$$

In a uniform isotropic fluid the *pair* distribution function is equivalent to the *radial* distribution function:

$$g_N^{(2)}(\vec{r}_1, \vec{r}_2) = g_N^{(2)}(|\vec{r}_1 - \vec{r}_2|) = g(r_{12})$$

Let us explore this function a little further for low density fluid.

Under the condition of pair-wise interactions the potential energy can be written as:

$$U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N u(|\vec{r}_i - \vec{r}_j|)$$

Substituting in the above definition we get:

$$n^2 g_N^{(2)}(\vec{r}_1, \vec{r}_2) = \frac{N(N-1)}{Q_N} e^{-\beta u(|\vec{r}_1 - \vec{r}_2|)} \int \exp\left(-\frac{\beta}{2} \sum_{i=1}^N \sum_{j \neq i}^N u(|\vec{r}_i - \vec{r}_j|)\right) d\vec{r}_3 d\vec{r}_4, \dots, d\vec{r}_N$$

where the pairs ( $i = 1, j = 2$ ) and ( $i = 2, j = 1$ ) are excluded from the double sum.

Low density condition allow us to approximate  $Q_N \approx V^N$ ,  $N(N-1) \approx N^2$  and:

$$\int \exp\left(-\frac{\beta}{2} \sum_{i=1}^N \sum_{j \neq i}^N u(|\vec{r}_i - \vec{r}_j|)\right) d\vec{r}_3 d\vec{r}_4, \dots, d\vec{r}_N \approx V^{N-2}$$

Therefore the pair distribution function for low density is reduced to:

$$g_N^{(2)}(r) = e^{-\beta u(r)}$$

*Yvon-Born-Green* (YBG) hierarchy is a set of equations relating the  $l$ -particle distribution function to the  $(l+1)$ -particle distribution function, the potential energy and the density. The first equation in the hierarchy relates the *pair* distribution function to the *triplet* distribution function:

$$-\tau \frac{\partial}{\partial \vec{r}_1} g_N^{(2)}(\vec{r}_1, \vec{r}_2) = g_N^{(2)}(\vec{r}_1, \vec{r}_2) \frac{\partial}{\partial \vec{r}_1} u(\vec{r}_1, \vec{r}_2) + n \int g_N^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) \frac{\partial}{\partial \vec{r}_1} u(\vec{r}_1, \vec{r}_3) d\vec{r}_3$$

Such type of hierarchies are useless unless they are somehow closed. One of the frequent closures is *Kirkwood's superposition approximation*:

$$g_N^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = g_N^{(2)}(\vec{r}_1, \vec{r}_2)g_N^{(2)}(\vec{r}_1, \vec{r}_3)g_N^{(2)}(\vec{r}_2, \vec{r}_3)$$

which leads to a closed equation for  $g(r)$ .

### 1.7. Distribution functions by Oleg

*Radial distribution function*  $g(r)$  is defined as a ratio of an average density of molecules at a *distance*  $r$  from a certain (can be any) molecule in the system to the average density of molecules  $n = N/V$ . In general,  $g(r \rightarrow \infty) = 1$ ,  $g(r < \sigma) \approx 0$ . In liquids,  $g(r)$  oscillates up to the distances of several  $\sigma$ .

*l-particle distribution function*  $g_N^{(l)}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_l)$  is proportional to the probability density to have any  $l$  molecules (in the system of  $N$  molecules) in the defined positions  $\vec{r}_1, \vec{r}_2, \dots, \vec{r}_l$ . In the canonical ensemble:

$$n^l g_N^{(l)}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_l) = \frac{N!}{(N-l)!Q_N} \int d\vec{r}_{l+1} d\vec{r}_{l+2}, \dots, d\vec{r}_N e^{-\beta U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)}, \quad (1.36)$$

where the normalization factor  $n^l$  is added to have  $g_N^{(l)}$  dimensionless and to remove trivial dependence on density.

The simplest distribution function is *pair distribution function*:

$$n^2 g_N^{(2)}(\vec{r}_1, \vec{r}_2) = \frac{N(N-1)}{Q_N} \int d\vec{r}_3 d\vec{r}_4, \dots, d\vec{r}_N e^{-\beta U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)} \quad (1.37)$$

In uniform isotropic fluid the pair distribution function is equivalent to the radial distribution function:

$$g_N^{(2)}(\vec{r}_1, \vec{r}_2) = g_N^{(2)}(|\vec{r}_1 - \vec{r}_2|) = g(r_{12}) \quad (1.38)$$

*Yvon-Born-Green* (YBG) hierarchy is a set of *exact* equations relating  $g_N^{(l)}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_l)$  distribution to  $g_N^{(l+1)}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{l+1})$ , molecular interaction potential and density. The first equation in the hierarchy relates the pair distribution function to the triplet distribution function:

$$-T \frac{\partial}{\partial \vec{r}_1} g_N^{(2)}(\vec{r}_1, \vec{r}_2) = g_N^{(2)}(\vec{r}_1, \vec{r}_2) \frac{\partial}{\partial \vec{r}_1} u(\vec{r}_1, \vec{r}_2) + n \int g_N^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) \frac{\partial}{\partial \vec{r}_1} u(\vec{r}_1, \vec{r}_3) d\vec{r}_3 \quad (1.39)$$



In order to solve the YBG hierarchy approximations (closures) are required. Kirkwood's *superposition approximation* is:

$$g_N^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = g_N^{(2)}(\vec{r}_1, \vec{r}_2)g_N^{(2)}(\vec{r}_1, \vec{r}_3)g_N^{(2)}(\vec{r}_2, \vec{r}_3) \quad (1.40)$$

This together with Eq. 1.39 leads to a closed equation for  $g(r)$ .

### 1.8. Density-Density correlation function and Structure factor

Some other functions closely related to the radial distribution/pair distribution functions:

1. Pair correlation function, simply defined to decay to zero at large distances:

$$h(r) = g(r) - 1 \quad (1.41)$$

2. Density-density correlation function, defined either as:

$$G(r) = \frac{\langle n(0)n(r) \rangle}{\bar{n}} = \delta(r) + \bar{n}g(r) \quad (1.42)$$

or

$$G(r) = \frac{\langle \delta n(0)\delta n(r) \rangle}{\bar{n}} = \delta(r) + \bar{n}h(r) \quad (1.43)$$

3. Structure factor is what is measured in different scattering experiments and is a Fourier transform of the density-density correlation function:

$$S(\vec{q}) = \frac{\langle n(\vec{q})n(-\vec{q}) \rangle}{N}, \quad (1.44)$$

where  $\vec{q} = \vec{k}_i - \vec{k}_f$  is so-called scattering angle, the difference between the incident and the measurement wave vectors. For isotropic system the structure factor depends only on  $q = |\vec{q}| = (4\pi/\lambda) \sin(\theta/2)$ , where  $\theta$  is the angle between the incident and measurement (scattered) directions.

The idea in deriving the Eq. 1.44 is to look at the scattering in the direction  $\vec{k}_f$  of the incident wave (electromagnetic, electrons, neutrons or any other) travelling in the direction  $\vec{k}_i$ :

$$\vec{E}_i = \vec{A}_1 e^{i(\vec{k}_i \vec{r} - \omega t)} \quad (1.45)$$

by the molecule  $j$  at the location  $\vec{r}_j$ :

$$\vec{E}_f = \vec{A}_2 e^{i(\vec{k}_f \vec{r} - \omega t + \varphi_j)} \quad (1.46)$$

$\varphi_j$  can be found from matching the phases of the two waves at the molecule:

$$\varphi_j = (\vec{k}_i - \vec{k}_f) \vec{r}_j = \vec{q} \vec{r}_j \quad (1.47)$$

Now assuming many molecules we sum up their scattering fields:

$$\vec{E}_f = \vec{A}_2 e^{i(\vec{k}_f \vec{r} - \omega t)} \sum_{j=1}^N e^{i\vec{q} \vec{r}_j} \quad (1.48)$$

As it can be easily seen the sum is just a Fourier transform  $n(\vec{q})$  of the molecular density  $n(\vec{r}) = \sum_{j=1}^N \delta(\vec{r} - \vec{r}_j)$ .

In a static scattering experiment we measure time/ensemble averaged intensity (not the field) that is proportional to the square of the field amplitude, thus:

$$S(\vec{q}) \propto \langle E_f E_f^* \rangle \propto \langle n(\vec{q}) n(-\vec{q}) \rangle. \quad (1.49)$$

In order to show that this is essentially a Fourier transform of the density-density correlation function, let's, well, Fourier transform the Eq. 1.42:

$$\begin{aligned} G(\vec{q}) &= \frac{1}{(2\pi)^{3/2} \bar{n}} \int d\vec{r} \langle n(0) n(\vec{r}) \rangle e^{-i\vec{q} \vec{r}} = \\ &= \frac{1}{(2\pi)^{3/2} \bar{n} V} \int d\vec{r}^j \int d\vec{r} \langle n(\vec{r}^j) n(\vec{r}^j + \vec{r}) \rangle e^{-i\vec{q} \vec{r}}, \end{aligned} \quad (1.50)$$

where we assumed that the system is homogeneous and so  $G(\vec{r})$  cannot depend on the reference point 0. Thus we shifted the reference point to  $\vec{r}^j$  and averaged over all such locations in the volume  $V$ .

Now changing the variables from  $\vec{r}^j$  and  $\vec{r}$  to  $\vec{r}^j$  and  $\vec{r}^j = \vec{r}^j + \vec{r}$ , we have:

$$\begin{aligned} G(\vec{q}) &= \frac{1}{(2\pi)^{3/2} N} \int d\vec{r}^j \int d\vec{r}^j \langle n(\vec{r}^j) n(\vec{r}^j) \rangle e^{-i\vec{q}(\vec{r}^j - \vec{r}^j)} = \\ &= \frac{1}{(2\pi)^{3/2} N} \int d\vec{r}^j \int d\vec{r}^j \langle n(\vec{r}^j) n(\vec{r}^j) \rangle e^{-i\vec{q}(\vec{r}^j - \vec{r}^j)} \\ &= \frac{1}{(2\pi)^{3/2} N} \left\langle \int d\vec{r}^j n(\vec{r}^j) e^{i\vec{q} \vec{r}^j} \int d\vec{r}^j n(\vec{r}^j) e^{-i\vec{q} \vec{r}^j} \right\rangle = \\ &= \frac{(2\pi)^{3/2}}{N} \langle n(\vec{q}) n(-\vec{q}) \rangle, \end{aligned} \quad (1.51)$$

i.e. up to a numeric coefficient (dependent on the choice of the definition of the Fourier transform) it is just the structure factor defined in the Eq. 1.44.

**Problem set 1**

1. Find the excluded volume (second virial coefficient) of hard rods of length  $b$  and diameter  $d$ , such that  $b \gg d$ , in 3D in the following situations:
  - when the angle  $\theta$  between the rods directions is fixed;
  - for random orientations of the rods

This problem due to Onsager is important in the context of liquid crystals: one generally finds that the excluded volume is smaller when the angle between the rods is small. At high densities of the rods (i.e. elongated molecules) they can prefer to orient in the same direction gaining translational entropy at the expense of losing some orientational entropy. This means that the material becomes liquid crystalline.

The problem is also important to understand excluded volume interactions in semi-flexible polymers, such as DNA.

2. Two hard spheres (with diameters  $\sigma$ ) are fixed at the distance  $L$ . Other 3 similar spheres are free to move along the line connecting the first two spheres. Determine the dependence of average density of the spheres on the distance from the leftmost sphere (similar system with 4 spheres in total and a general problem of many spheres were considered in the class).
3. Consider a real gas with the following interaction potential between the molecules:

$$u_{hc}(r) = \begin{cases} -\psi(r), & r > \sigma \\ \infty, & r < \sigma \end{cases} \quad (1.52)$$

Assume  $\psi(r)$  positive and much smaller than  $T$  and decaying to 0 at  $\infty$ . Obtain the expression for the second virial coefficient for this case. Show that it crosses 0 at a certain temperature.

4. Use the formal definitions of canonical ensemble averaging of any quantity  $A$

$$\langle A \rangle = \frac{1}{N!(2\pi\hbar)^{3N}} \int A(\{\vec{p}_i, \vec{r}_i\}_N) P(\{\vec{p}_i, \vec{r}_i\}_N) d\vec{p}_1 \dots d\vec{p}_N d\vec{r}_1 \dots d\vec{r}_N$$

and of  $g(r)$  (Eq. 1.37 and Eq. 1.38) to show that in a homogeneous system with pairwise interactions Eq. 1.17: the average total energy of interactions per molecule is

equal to:

$$\frac{\langle U \rangle}{N} = \frac{n}{2} \int u(r)g(r)dr = 2\pi n \int u(r)g(r)r^2 dr \quad (1.53)$$

Explain the result.

5. *Use of Virial Theorem in Statistical Mechanics:* Virial of a system of  $N$  bodies (particles) is defined in the Classical Mechanics as:

$$\mathcal{V} = \sum_{i=1}^N \vec{r}_i \cdot \vec{F}_i, \quad (1.54)$$

where  $\vec{r}_i$  and  $\vec{F}_i$  are respectively the position and the total force acting on the  $i^{\text{th}}$  body (particle). The *virial theorem* of Classical Mechanics states that (under very general assumptions - consult any class. mech. textbook) the time averaged values of the virial and of the kinetic energy  $K$  of the system are related by:

$$\bar{\mathcal{V}} = -2\bar{K} \quad (1.55)$$

The proof of virial theorem is rather straightforward and goes roughly like that:

$$\begin{aligned} \bar{\mathcal{V}} &= \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t dt' \sum_{i=1}^N \vec{r}_i(t') \cdot \vec{F}_i(t') = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t dt' \sum_{i=1}^N \vec{r}_i(t') m_i \ddot{\vec{r}}_i(t') = \\ &= [\text{integrate by parts}] = - \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t dt' \sum_{i=1}^N m_i |\dot{\vec{r}}_i(t')|^2 = -2\bar{K} \end{aligned}$$

- Show that in the context of Statistical Mechanics, for a system with volume  $V$ , pressure  $p$  and temperature  $T$  the virial theorem can be restated as:

$$\frac{pV}{NT} = 1 - \frac{1}{3NT} \left\langle \sum_{i=1}^N \vec{r}_i \frac{d}{d\vec{r}_i} U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \right\rangle, \quad (1.56)$$

where as before  $U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$  is the internal potential energy of interactions between particles.

*Hint:* Split forces on particles into external and internal to the system; assume that the external forces enter through the outside pressure on the system surface only (i.e. that there are no bulk external forces, such as gravity); use equipartition theorem and common sense.

- Show that in a homogeneous system with pair-wise interactions:

$$\frac{p}{nT} = 1 - \frac{2\pi n}{3T} \int_0^\infty g(r) \frac{du}{dr} r^3 dr \quad (1.57)$$

The notation is the same as in the Problem 4.

- *Another derivation of second virial coefficient:* Use the previous equation and the definition of  $g(r)$  to show that low density expansion of pressure in any system is:

$$\frac{p}{nT} = 1 + \frac{1}{2}an, \quad (1.58)$$

where  $a$  is already defined second virial coefficient Eq. ???. Why are second virial coefficients of free energy expansion and pressure expansion are related at all? (recall Thermo II)

- Use virial theorem to show that for *any* density, the pressure of a system of particles interacting though hard core repulsion only can be expressed through:

$$\frac{p}{nT} = 1 + \frac{2\pi}{3}n\sigma^3 g(\sigma) = 1 + 4\phi g(\sigma), \quad (1.59)$$

where  $\sigma$  is particle core diameter and  $g(\sigma)$  is the value of radial distribution function at the separation equal to  $\sigma$ .  $\phi = (1/6)\pi n\sigma^3$  is the fraction of total volume occupied by particles (called volume fraction). Show that for low densities this and the previous expressions give equivalent results up to a second virial coefficients (included).

*Hint:* You can overcome some mathematical difficulties of differentiating sharp functions by introducing a new function  $y(r) = g(r) \exp(\beta u(r))$ . This function is expected to be "smoother" than  $g(r)$ . Why?

6. Prove that crystalline structure is not possible in the 1D system of hard rods (Frenkel's problem discussed in the class). You can prove that by showing that fluctuations in the distance between molecules diverge with increasing distance between them (for any filling fraction smaller than 1). Why does this mean that the crystalline structure is not possible?
7. Find the structure factor of a uniformly filled sphere. Assume the uniform density

within the sphere of

$$n(r) = \begin{cases} N / \left(\frac{4\pi}{3} R^3\right), & r < R \\ 0, & r > R \end{cases} \quad (1.60)$$

and do the respective Fourier transforms. Notice the Fourier transform is in 3D although it takes into account that  $n$  is isotropic. Look at the angular dependences of  $S$  for  $R \ll \lambda$  (Rayleigh scattering) and for some  $R \sim \lambda$  (Mie scattering; plot it for, say, for  $R = 3\lambda$  in Matlab).