

Problem set 2 – Liquids

Problem 7

The classical configuration integral is given by

$$Z_N = \int \dots \int e^{-\beta U(\tau_1, \dots, \tau_N)} d\tau_1 \dots d\tau_N,$$

where $U(\tau_1, \dots, \tau_N)$ is the total potential energy and $\beta = 1/(k_B T)$.

- Explain what is meant by *pair-wise additivity* and give the corresponding expression for U in terms of the pair potential between particles i and j , $\phi(r_{ij}) = \phi_{ij}$.
- Use your above expression for U in terms of ϕ_{ij} within the pair-wise additivity approximation together with the definition of the Mayer f -function, $f_{ij} \equiv e^{-\beta\phi_{ij}} - 1$, to show that Z_N can be written as

$$Z_N = \int \dots \int \prod_{i>j}^N (1 + f_{ij}) d\tau_1 \dots d\tau_N.$$

- Explain the significance of the Mayer f -function in performing the integrals in Z_N . Include in your answer a sketch of a realistic/reasonable pair potential ϕ_{ij} and the corresponding Mayer f -function f_{ij} .

Problem 8

For a monatomic system the second virial coefficient is given explicitly by

$$B_2(T) = -2\pi \int_0^\infty (e^{-\beta\phi(r)} - 1) r^2 dr$$

where $U(r)$ is the intermolecular pair potential and $\beta = 1/(k_B T)$.

- Sketch the square well potential defined as follows:

$$\phi(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma \leq r \leq \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}$$

- Find an expression for the second virial coefficient for this potential.
- The properties of Ar gas can be described using the square well potential with $\sigma = 3.067 \text{ \AA}$, $\lambda = 1.70$ and $\epsilon/k_B = 93.3K$. Calculate the predicted value of the Boyle temperature.

Problem 9

The pair potential between molecules forming an imperfect gas can be described by the following interaction potential

$$\phi(r) = \begin{cases} \infty & r < \sigma \\ -\frac{A}{r^6} & r \geq \sigma \end{cases}$$

where $A = 1.11 \times 10^{-78} \text{ J m}^6$ is an interaction parameter and $\sigma = 0.356 \text{ nm}$ is the hard sphere diameter.

- a) Sketch the interaction potential $\phi(r)$ and calculate the depth of the potential energy at contact (i.e. at $r = \sigma$).
- b) Using that $\phi \ll k_B T$ for $r \geq \sigma$, show that the second virial coefficient $B_2(T)$ for this potential may be written as

$$B_2(T) = 2\pi \int_0^\sigma r^2 dr + 2\pi \int_\sigma^\infty \frac{\phi(r)}{k_B T} r^2 dr$$

- c) The imperfect gas under consideration obeys the Van der Waals equation of state, which can also be written in terms of a virial expansion

$$p = \frac{Nk_B T}{V - Nb} - a \left(\frac{N}{V} \right)^2 \approx k_B T \left[\rho + \left(b - \frac{a}{k_B T} \right) \rho^2 + \dots \right]$$

Combine the answer to (b) and the above virial expansion to show that the van der Waals parameters are given by

$$a = -2\pi \int_\sigma^\infty \phi(r) r^2 dr \quad b = 2\pi \int_0^\sigma r^2 dr$$

- d) Hence, calculate a and b and explain their physical significance.

Problem 10 – Extra

Consider a Lennard-Jones gas for which the pair potential is

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

with ϵ the depth of the potential well and σ the particle diameter.

- a) By transforming the integration variable from r to dimensionless distance $y = r/\sigma$ and defining the dimensionless temperature $T^* = k_B T/\epsilon$, show that

$$B_2(T)/\sigma^3 = -2\pi \int_0^\infty \left[\exp \left(-\frac{4}{T^*} [y^{-12} - y^{-6}] \right) - 1 \right] y^2 dy$$

Hence, the dimensionless second virial coefficient for a Lennard-Jones gas $B_2^*(T^*) = B_2(T)/\sigma^3$ is a function *solely* of the dimensionless temperature T^* .

- b) Now assume that the higher order virial coefficients for a Lennard-Jones gas $B_n^*(T^*) = B_n(T)/\sigma^{3(n-1)}$ are likewise functions solely of T^* , and define the dimensionless number density ρ^* and the dimensionless pressure p^* by:

$$\rho^* = \rho\sigma^3 \quad p^* = \frac{p\sigma^3}{\epsilon}$$

Show from the virial expansion $p = k_B T (\rho + B_2 \rho^2 + B_3 \rho^3 + \dots)$ that the equation of state of a Lennard-Jones gas is a universal function of (p^*, ρ^*, T^*) . In other words, *different Lennard-Jones systems with different parameters σ and ϵ all have the same equation of state expressed in the dimensionless quantities (p^*, ρ^*, T^*)* . This is an (other) example of the ‘law of corresponding states’.

Problem 11

In this problem we will obtain the expression for the radial distribution function $g(r)$ in terms of the configuration integral Z_N (derived in lecture 4) in a slightly different way.

- (a) Consider a one-component fluid. The probability that any particle is in $d\tau_1$ at \mathbf{r}_1 and any second particle in $d\tau_2$ at \mathbf{r}_2 , irrespective of the positions of the other $N - 2$ particles, can also be expressed in terms of the pair correlation function $g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$:

$$\rho^2 g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\tau_1 d\tau_2. \quad (\rho = N/V) \quad \text{Eq. 1}$$

What would the above probability be if all the particles were *independent* of each other? In other words, what would the value of $g^{(2)}$ be in this case and explain that the factor $g^{(2)}$ thus corrects for the “non-independence”, i.e. the *correlations* between the particles.

Note that for isotropic and homogeneous systems such as liquids and gases, $g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ only depends on the relative distance between particles 1 and 2: $g^{(2)}(|\mathbf{r}_1 - \mathbf{r}_2|) = g(r)$, which is of course the radial distribution function.

- b) As we have seen in lecture 4, the probability that particle 1 is in $d\tau_1$ at \mathbf{r}_1 and particle 2 is in $d\tau_2$ at \mathbf{r}_2 , irrespective of the positions of the other $N - 2$ particles, is:

$$\frac{\int d\tau_3 \cdots \int d\tau_N e^{-\beta U(\dots)} d\tau_1 d\tau_2}{Z_N}. \quad \text{Eq. 2}$$

Explain that the probability that *any* particle is in $d\tau_1$ and *any* second particle in $d\tau_2$, irrespective of the positions of the other $N - 2$ particles, is the above probability multiplied by $\frac{N!}{(N-2)!}$.

- c) Show that

$$\frac{N!}{\rho^2 (N-2)!} = V^2 \left[1 + \left(\frac{1}{N} \right) \right]. \quad \text{Eq. 3}$$

- d) Combine Eqs. 1 and 3 from parts a) and c) with your answer to part b) to obtain the expression for the radial distribution function $g(r)$ in terms of the configuration integral Z_N (which was also derived in lecture 4):

$$g(r) = \frac{V^2}{Z_N} \int d\tau_3 \cdots \int d\tau_N e^{-\beta U(\dots)}.$$

Problem 12

The compressibility equation is given by

$$1 + 4\pi\rho \int_0^\infty h(r)r^2 dr = \rho k_B T \kappa_T, \quad \text{Eq. 1}$$

where $\rho = \frac{N}{V}$ is the number density, $h(r) \equiv g(r) - 1$ the total correlation function and $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$ the isothermal compressibility.

- (a) Show that the isothermal compressibility can be rewritten as

$$\kappa_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_T.$$

The second virial coefficient is given by

$$B_2(T) = -2\pi \int_0^\infty (e^{-\beta\phi(r)} - 1) r^2 dr, \quad \text{Eq. 2}$$

where $\phi(r)$ is the interaction pair potential as a function of the separation r and $\beta = 1/(k_B T)$.

- (b) In the limit of small ρ we can assume that the radial distribution function $g(r) = \exp(-\phi(r)\beta)$. Use this to show that in the low density limit the compressibility equation can be written in terms of B_2 as

$$1 - 2\rho B_2 = k_B T \left(\frac{\partial \rho}{\partial p} \right)_T.$$

- (c) Show that for small ρ this can be approximated as

$$\left(\frac{\partial p}{\partial \rho} \right)_T = k_B T (1 + 2\rho B_2 + \dots).$$

and, hence, obtain an expression for the pressure. Comment on your answer.