

Problems - Imperfect gases

- (a) Explain briefly what is meant by a canonical ensemble, and why it is a useful concept in statistical mechanics.
(b) State how the internal energy (E) and the Helmholtz free energy (A) are related to the canonical partition function $Q \equiv Q(N, V, T)$.
(c) The canonical partition function for an interacting gas is given approximately by

$$Q = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} (V - Nb)^N \exp \left[\frac{aN^2}{V k_B T} \right]$$

where a and b are positive constants.

Show that $p = k_B T (\partial \ln Q / \partial V)_{N,T}$ and, hence, obtain an expression for the pressure of the gas. Comment on your result.

- (d) Show that the internal energy per atom is given by

$$\frac{E}{N} = \frac{3}{2} k_B T - a \frac{N}{V}.$$

and comment on the physical interpretation of the fact that this result does not depend upon b .

(Part IA 2007)

- A perfect monatomic gas in thermal equilibrium occupies a vertical cylinder of height h and cross-sectional area A , in a uniform gravitational field with characteristic acceleration g .
 - (a) Find an expression for the classical molecular partition function of the gas. Note that the potential energy for a gas molecule equals mgz .
 - (b) Show that in the limit of $mg h / k_B T$ becoming very small (i.e. in the limit of no gravity), the classical molecular partition function of a perfect gas is recovered. Estimate the height h at which this simplification breaks down for xenon.

Note that

$$\int_{-\infty}^{\infty} \exp(-\alpha x^2) dx = \sqrt{\frac{\pi}{\alpha}}$$

3. The classical canonical partition function Q_{class} is given by

$$Q_{class} = \frac{1}{N!h^{3N}} \int \dots \int e^{-\beta H_N(p,\tau)} dp d\tau$$

where $H_N(p, \tau)$ is the classical N -body Hamiltonian for interacting particles.

- (a) Show that for an imperfect gas Q_{class} can be written as

$$Q_{class} = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} Z_N$$

where $Z_N = \int \dots \int e^{-\beta U(x_1, \dots, x_N)} d\tau$ is the classical configuration integral and $\beta = 1/(k_B T)$.

- (b) Evaluate Z_N to find the classical canonical partition function for a perfect gas and comment on your answer.

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

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

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

- (a) Sketch the square well potential defined as follows:

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

- (b) Find an expression for the second virial coefficient for this potential.
 (c) 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.

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

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

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 $U(r)$ and calculate the depth of the potential energy at contact (i.e. at $r = \sigma$).

- (b) Using that $U \ll k_B T$ for $r \geq \sigma$, show that the second virial coefficient $B_2(T)$ for this potential may be written as

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

- (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

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

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

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

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

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

- (a) By transforming the integration variable from r to $y = r/\sigma$ 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 $B_2(T)/\sigma^3$ is a function *solely* of the dimensionless temperature T^* .

- (b) Now assume (as is readily shown) 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^* . 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 example of the ‘law of corresponding states’.