Statistical Physics: Tutorial 7

John Peacock
Institute for Astronomy, Royal Observatory Edinburgh

Virial Expansion; Debye-Hückel theory

A: Core problems

1. **Second virial coefficient**

Review the argument in the lectures concerning the configurational integral, Q. Show that interactions perturb the free energy of a gas of interacting particles as

$$F = F_0 - kT \ln Q,$$

where Q can be approximated as follows, on the assumption that the interactions only have a weak effect on the independence of the gas particles:

$$Q \simeq \langle \exp[-\beta\phi] \rangle^{N^2/2} \equiv [Q(1)]^{N^2/2},$$

and the angle brackets denote a volume average over pairs. Changing to centre of mass coordinates gives

$$Q(1) = \frac{1}{V} \int 4\pi r^2 dr \, \exp[-\beta\phi(r)],$$

where the interactions are assumed to be a function of the separation of a pair, r, and the integration is over the macroscopic volume, V.

(a) Assume weak interactions, so that $\beta\phi \ll 1$. Show that a Taylor series approximation for $\ln[Q(1)]$ is $-(4\pi\beta/V) \int_0^\infty r^2 \phi \, dr$, and hence that the 2nd virial coefficient is $B_2 = 2\pi\beta \int_0^\infty r^2 \phi \, dr$.

(b) Assuming a Yukawa potential, $\phi = \epsilon \exp[-r/r_0](r_0/r)$, evaluate B_2 in this approximation.

(c) For a hard-sphere exclusion potential, $\phi \to \infty$ for $r < 2a$ (why not $r < a$, if the molecules are treated as spheres of radius a?). Show that the above Taylor series in ϕ yields a divergent value for $Q(1)$, but that the exact value for $Q(1)$ can nevertheless be close to unity; what is the condition on a for this to be so?. Thus give a better Taylor approximation for $\ln[Q(1)]$:

$$\ln[Q(1)] \simeq -(4\pi/V) \int_0^\infty r^2 (1 - \exp[-\beta\phi]) \, dr,$$

and evaluate B_2 in this case.

(d) Suppose that the interaction potential falls off like $r^{-\alpha}$ as $r \to \infty$. Show that B_2 diverges if $\alpha \leq 3$. What is the physical interpretation of this result?

2. **Virial expansion and Van der Waals**

   Assuming that $\phi(r)/kT$ is large and positive for $r < r_0$ and small for $r > r_0$, show that the second virial coefficient may be written as

   $$B_2(T) = b_0 - \frac{a_0}{kT}$$

   where you should obtain expressions for a_0 and b_0.

   Show that this form of B_2 recovers the one implied by the Van der Waals equation of state, $(P + \rho^2 a_0) = NkT/(V - Nb_0)$.

   Calculate the entropy and show that $S = S_{\text{Ideal}} - Nkb_0\rho$. Comment on why the entropy is reduced from the standpoint of information theory.

3. **Debye screening length**

   In the Debye Hückel theory we approximate the density of free charges by a continuous distribution $n(r)$. This 'continuum approximation' ignores the granularity of charges; show that it is is valid provided that

   $$q^3 n^{\frac{1}{2}} \left(\frac{\beta}{\epsilon}\right)^{\frac{3}{2}} \ll 1,$$

   where $\beta = 1/kT$ and n is the density of particles. Give a physical interpretation of this result.

   Hint: compare the microscopic length (typical separation between charges) ignored in the continuum approximation to the lengthscale predicted by the theory (Debye screening length).

B: Further problems

1. **Multi-species plasma** Consider a plasma containing more than one species of mobile ion, with no fixed charges but overall charge neutrality (for example, an ionized gas). By considering the distribution of ions around a point charge (of arbitrary sign) show that the Debye screening length λ_{D} obeys

   $$\lambda_{\text{D}}^{-2} = \frac{\sum_i q_i^2 n_i}{\epsilon kT}$$

   where q_i is the charge of species i and n_i is the particle density (at infinity) of species i.

2. **Radial distribution function** For a plasma containing two ionic species with opposite charges but the same density $n(\infty)$, calculate the radial distribution functions $g_{++}(r)$, $g_{-+}(r)$, where $n(\infty)g_{ij}(r)$ is the conditional probability density for finding a particle of type i in a small volume at distance r from one of type j. You may assume Debye-Hückel theory is valid and should use the results of the previous question.

3. **Semi-infinite plasma** A semi-infinite sample of a one-component plasma ends at a flat wall which carries a positive surface charge density σ. The one-component plasma is made up of free positive charges of far concentration $n(\infty)$ and a fixed background concentration $n(\infty)$ of negative charges. Assuming the Debye-Hückel equation applies, calculate and sketch the potential ϕ as a function of z, the distance from the wall. Sketch also, on the same horizontal axis, the density of free charges in the plasma.