School of Physics & Astronomy

THE UNIVERSITY *of* EDINBURGH

Statistical Physics

PHYS11024 (SCQF Level 11)

Friday 6th May, 2022 13:00 - 15:00
(May Diet)

Please read full instructions before commencing writing.

Examination Paper Information

Answer **TWO** questions

Special Instructions

- Only authorised Electronic Calculators may be used during this examination.
- Attach supplied anonymous barcodes to *each* script book used.

Special Items

- School supplied barcodes

Chairman of Examiners: Prof J Dunlop
External Examiner: Prof D Litim

Anonymity of the candidate will be maintained during the marking of this examination.

1. (a) Explain how the canonical and grand canonical ensembles are obtained by maximising the Gibbs entropy subject to certain constraints, which you should specify. **[5]**

(b) The grand potential is defined as

$$\Phi = F - \mu N$$

where F is the Helmholtz free energy, μ is the chemical potential and N is the particle number.

Use the combined 1st/2nd law of thermodynamics to explain in what sense T, V and μ are natural variables for Φ. Give expressions for the entropy S, the pressure P, and particle number N as derivatives of Φ. **[6]**

(c) The canonical partition function for an ideal gas of N particles of mass m in volume V is given by

$$Z_c = \frac{[V/\lambda^3]^N}{N!}$$

where $\lambda = h/(2\pi m k_B T)^{1/2}$ and k_B is Boltzmann's constant. (You are not required to show this.)

Using this expression for Z_c, show that the grand canonical partition function for the ideal gas is given by

$$\mathcal{Z}_{gc} = \exp\left[\frac{Vz}{\lambda^3}\right] ,$$

where

$$z = \mathrm{e}^{\mu/(k_B T)} .$$ **[2]**

(d) (i) Use the above expression for $\mathcal{Z}_{gc}$ to obtain an expression for the grand potential Φ. **[1]**

Hence, using your expressions from part (b), show that in the grand canonical ensemble:

(ii) the average number of particles is

$$\overline{N} = \frac{V\mathrm{e}^{\mu/(k_B T)}}{\lambda^3} ;$$ **[1]**

(iii) the entropy is given by

$$S = k_B \overline{N}\left[\frac{5}{2} - \ln\left(\rho\lambda^3\right)\right] ;$$ **[3]**

(iv) and the pressure is given by

$$P = \rho k_B T ,$$ **[1]**

where the density is $\rho = \overline{N}/V$.

(e) A certain non-ideal fluid has grand canonical partition function

$$\mathcal{Z}_{gc} = \exp\left[\frac{V}{\lambda^3}(z + cz^2)\right] ,$$

where c is a constant and z is as given in (c).

(i) Show that

$$\rho\lambda^3 = z + 2cz^2 \, .$$ **[2]**

(ii) By making an expansion of z in powers of the density,

$$z = a\rho + b\rho^2 + \dots \ ,$$

find the second virial coefficient B_2 for this fluid. **[4]**

2. An ionic solution with permittivity ϵ contains two freely moving ionic species with opposite charges $q_1 = +q$, $q_2 = -q$, but with the same overall number densities denoted by $n_1(\infty)$ and $n_2(\infty)$.

First consider a fixed point charge $-\theta$ at the origin.

(a) Derive the Poisson-Boltzmann equation for the electrostatic potential $\phi(\underline{r})$

$$\nabla^2\phi(\underline{r}) = -\sum_{i=1,2} \frac{n_i(\infty)q_i}{\epsilon} \mathrm{e}^{-\beta q_i \phi(\underline{r})} + \frac{\theta}{\epsilon}\delta(\underline{r}) \tag{1}$$

where $\beta = 1/(kT)$ and k is Boltzmann's constant. You should state clearly any assumptions required and explain why the theory is 'self-consistent' and in what sense it is a mean-field theory. **[7]**

(b) Show that equation (1) reduces to the Debye-Hückel equation

$$\nabla^2\phi(\underline{r}) = \frac{\phi(\underline{r})}{\lambda_D^2} + \frac{\theta}{\epsilon}\delta(\underline{r}) \,,$$

under conditions which you should state, and give an expression for λ_D. **[3]**

(c) (i) Explain why ϕ depends only on the radial distance r from the origin. **[1]**

(ii) Show that, away from the origin, the solution of the Debye-Hückel equation for the electrostatic potential is of the form

$$\phi(r) = \frac{A}{r}\mathrm{e}^{-r/\lambda_D} + \frac{B}{r}\mathrm{e}^{+r/\lambda_D} \,. \tag{2}$$

[4]

Hint: You may assume the form of the Laplacian operator acting on a spherically symmetric function $\phi(r)$, where r is the radial co-ordinate:

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

Now consider, instead of the point charge at the origin, a charged sphere of radius a, held fixed in the solution, with its centre at the origin. The sphere has surface charge density $-\sigma$, where $\sigma > 0$.

(d) Use the boundary conditions at the surface of the sphere and at infinity to determine the constants A and B in the expression (2) in part (c), and hence obtain an expression for $\phi(r)$. **[4]**

(e) Give an expression for the net charge density, $\rho(r)$, and make an annotated sketch of $\rho(r)$. **[3]**

(f) By taking the radius of the sphere to zero, obtain $\phi(r)$ for a point charge $-\theta$ at the origin. **[3]**

3. A particle of mass m falls under gravity in a viscous medium. The motion is governed by a Langevin equation of the form

$$m\frac{\mathrm{d}^2 z(t)}{\mathrm{d}t^2} + \gamma\frac{\mathrm{d}z(t)}{\mathrm{d}t} = f(t) + mg$$

where $z(t)$, the vertical co-ordinate of the particle, is measured downwards and $f(t)$ is a random variable.

(a) Explain the meaning of the terms in the above equation and explain why $f(t)$ can be taken to obey

$$\langle f(t)\rangle = 0 \quad \langle f(t)f(t')\rangle = \Gamma\delta(t-t')$$

where Γ is a constant and the angle brackets denote an average. **[4]**

(b) If the particle begins from rest at $z = 0$ at $t = 0$, show that the solution of the Langevin equation is

$$z(t) = \frac{1}{m}\int_0^t \mathrm{d}t' \int_0^{t'} \mathrm{d}t'' \mathrm{e}^{-(t'-t'')/\tau}\left[f(t'') + mg\right] ,$$

giving the expression for τ in terms of m and γ. **[6]**

(c) (i) Find an expression for $\langle z(t)\rangle$. **[3]**

(ii) Show that your solution for part (c)(i) behaves for 'early' times like that of a freely falling particle, and behaves for 'late' times like that of a particle falling with a terminal speed. You should specify the criteria that determine 'early' and 'late' times. **[3]**

(d) Defining $\Delta z(t) = z(t) - \langle z(t)\rangle$, show that

$$\langle(\Delta z(t))^2\rangle = \frac{\Gamma\tau^2}{m^2}\left[t - \tau(1-\mathrm{e}^{-t/\tau}) - \frac{\tau}{2}(1-\mathrm{e}^{-t/\tau})^2\right] .$$ **[5]**

(e) Compute the leading behaviour of $\dfrac{\langle(\Delta z(t))^2\rangle^{1/2}}{\langle z(t)\rangle}$ in the early and late time limits. **[4]**