School of Physics & Astronomy

THE UNIVERSITY *of* EDINBURGH

Statistical Physics

PHYS11024 (SCQF Level 11)

Wednesday 9th May, 2018 14:30 - 16:30
(May Diet)

Please read full instructions before commencing writing.

Examination Paper Information

Answer **TWO** questions

Special Instructions

- Electronic Calculators must **not** be used during this examination.
- Attach supplied anonymous bar codes to *each* script book.

Special Items

- School supplied barcodes

Chairman of Examiners: Prof A Trew
External Examiner: Prof E Copeland

ANONYMITY OF THE CANDIDATE WILL BE MAINTAINED DURING THE MARKING OF THIS EXAMINATION.

1. (a) Define the Gibbs entropy for an assembly which may be found in microstate i with probability p_i. Explain, without detailed calculation, how maximising this entropy subject to certain constraints, which you should specify, leads to the microcanonical, canonical and grand canonical distributions. (Note that you are not asked for the explicit forms of these distributions.) **[7]**

(b) Consider an assembly of N particles, which has microstates labelled by i, α each having energy $E_{i,\alpha}$ and volume V_α. The mean values $\overline{E}$ and $\overline{V}$ of the assembly in equilibrium are fixed.

By using the method of Lagrange multipliers derive the following expression for probabilities for the microstates of the equilibrium assembly:

$$p_{i,\alpha} = \frac{1}{Z} \exp\left[-\frac{\lambda_E}{k} E_{i,\alpha} - \frac{\lambda_V}{k} V_\alpha\right] ,$$

where k is the Boltzmann constant, λ_E and λ_V are Lagrange multipliers and you should define Z. **[7]**

(c) Use the combined first and second laws of thermodynamics to identify λ_E and λ_V in terms of the temperature, T, and the pressure, P. **[6]**

(d) Show that

$$-kT \frac{\partial \ln Z}{\partial P} = \overline{V}$$

and

$$-kT \frac{\partial \overline{V}}{\partial P} = \overline{(\Delta V)^2} \, .$$ **[5]**

2. The energy function for a classical statistical mechanical system comprised of N identical particles of mass m in volume V is given by

$$E(\{\vec{q}\},\{\vec{p}\}) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \sum_{i<j} U_{ij} \,,$$

where $\vec{q}_i$ and $\vec{p}_i$ are the position and momentum of particle i respectively, $U_{ij} = U(|\vec{q}_i - \vec{q}_j|)$ is a two-body interaction and $\beta = 1/(kT)$, with k the Boltzmann constant.

(a) Explain why the classical partition function is given by

$$Z = \frac{1}{N!\,h^{3N}} \int \prod_{i=1}^{N} d^3q_i\, d^3p_i\, e^{-\beta E(\{\vec{q}\},\{\vec{p}\})} \,,$$

with particular reference to the factors $N!$ and h^{3N}. **[3]**

(b) Show that Z from part (a) can be written as

$$Z = Z_{\text{ideal}}\, Q \,,$$

where Z_{ideal} is the partition function for an ideal gas and Q is a correction factor, which you should define, due to the two-body interactions. **[3]**

(c) Hence show that the pressure is given by

$$P = P_{\text{ideal}} + kT \frac{\partial \ln Q}{\partial V}$$

where P_{ideal} is the pressure of an ideal gas. You may use the thermodynamic relation $P = -\left.\dfrac{\partial F}{\partial V}\right|_N$, where F is the Helmholtz free energy. **[4]**

(d) Show that one can write

$$Q = \langle \prod_{i<j} F_{ij} \rangle \,,$$

where $F_{ij} = \exp[-\beta U_{ij}]$ and the angle brackets imply a spatial average. **[2]**

(e) Explain how Q may be approximated by

$$Q = \left(1 - \frac{2}{V} B_2\right)^{N(N-1)/2} \,,$$

where B_2, the second virial coefficient, is given by

$$B_2 = \tfrac{1}{2} \int d^3r \,[1 - e^{-\beta U(r)}] \,.$$ **[3]**

(f) For the potential

$$U(r) = \begin{cases} \infty & 0 < r < a \\ \epsilon & a \le r \le b \\ 0 & r > b \end{cases} \,,$$

compute $B_2(T)$. **[6]**

(g) Interpret the behaviour of $B_2(T)$ in the limits $T \to 0$ both for $\epsilon > 0$ and $\epsilon < 0$. You may refer to the virial expansion

$$\frac{P}{KT} = \rho + B_2 \rho^2 \,,$$

which you do not need to prove. **[4]**

3. (a) Discuss the issue of reconciling the second law of thermodynamics with physics at the microscopic level. You should clearly state the problem with regard to the Gibbs entropy and how it may be resolved by coarse-graining. Explain how the Langevin approach provides a realisation of such a procedure. **[7]**

(b) A Langevin equation for an *overdamped* Brownian particle in an harmonic potential is

$$\dot{x}(t) = -\mu\kappa x(t) + \mu f(t)$$

where $x(t)$ is the position, μ and κ are constants and $f(t)$ is a random force.

Explain how this equation may be obtained from Newton's law; explain the meaning of $f(t)$ and why it can be taken to obey

$$\begin{aligned} \langle f(t) \rangle &= 0 \\ \langle f(t) f(t') \rangle &= \Gamma \delta(t - t') \end{aligned}$$

where Γ is a constant and the angle brackets denote an average over the random force. **[3]**

(c) If the particle begins at the origin at $t = 0$, show that the solution of the Langevin equation is

$$x(t) = \mu \int_0^t f(t') \exp\left[-\mu\kappa(t - t')\right] \mathrm{d}t' \; .$$

Show further that

$$\langle x^2(t) \rangle = \frac{\mu\Gamma}{2\kappa} \left(1 - \exp(-2\mu\kappa t)\right) \; .$$ **[7]**

(d) Make an annotated sketch of this function explaining the short and long time limits. **[3]**

(e) Now consider the same particle subject to the same random force $f(t)$ and an additional constant force

$$\dot{x}_F(t) = -\mu\kappa x_F(t) + \mu F + \mu f(t) \; ,$$

where the position in the presence of a constant force of value F is denoted $x_F(t)$.

For a particle beginning at the origin at $t = 0$, show that

$$x_F(t) = \frac{F}{\kappa} \left[1 - \exp(-\mu\kappa t)\right] + x(t)$$

where $x(t)$ is the solution for zero force determined in part (c). Hence show that

$$\langle x_F^2(t) \rangle - \langle x_F(t) \rangle^2 = \langle x^2(t) \rangle \; .$$ **[5]**