Solved problems

Q1: Consider a small system with fixed volume and number of particles in thermal contact with a heat path at temperature T.

a) Show that the mean energy square of the system is given by: $\left\langle E^2 \right\rangle = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}$, where Z is the partition of the system.

$$\left\langle E \right\rangle = \sum_r p_r \varepsilon_r = \frac{1}{Z}\sum_r \varepsilon_r e^{-\beta\varepsilon_r} = \frac{1}{Z}\sum_r \left(-\frac{\partial}{\partial \beta}\right) e^{-\beta\varepsilon_r} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \underline{-\frac{\partial \log Z}{\partial \beta}}$$

$$\left\langle E^2 \right\rangle = \sum_r p_r {\varepsilon_r}^2 = \frac{1}{Z}\sum_r {\varepsilon_r}^2 e^{-\beta\varepsilon_r} = \frac{1}{Z}\sum_r \left(-\frac{\partial}{\partial \beta}\right)\left(-\frac{\partial}{\partial \beta}\right) e^{-\beta\varepsilon_r} = \underline{\frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}}$$

b) Show that the dispersion of the energy is given by: $(\Delta E)^2 = \left\langle E^2 \right\rangle - \left\langle E \right\rangle^2 = \frac{\partial^2 \log Z}{\partial \beta^2}$, where Z is the partition of the system.

$$(\Delta E)^2 = \left\langle \left(E - \left\langle E \right\rangle\right)^2 \right\rangle = \left\langle E^2 - 2E\left\langle E \right\rangle + \left\langle E \right\rangle^2 \right\rangle = \left\langle E^2 \right\rangle - 2\left\langle E \right\rangle\left\langle E \right\rangle + \left\langle E \right\rangle^2$$

$$= \left\langle E^2 \right\rangle - \left\langle E \right\rangle^2$$

$$= \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2}\left(\frac{\partial \ln Z}{\partial \beta}\right)^2 = \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) = \frac{\partial}{\partial \beta}\frac{\partial}{\partial \beta}\log Z = \underline{\frac{\partial^2 \log Z}{\partial \beta^2}}$$

c) prove that $(\Delta E) = kT^2 C_v$

where C_v is the specific heat of the system, at constant volume

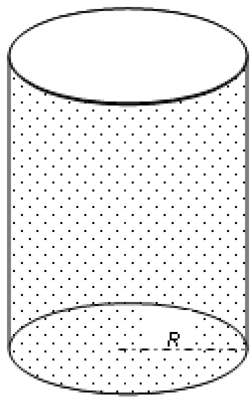
Answer:

$$(\Delta E)^2 = \frac{\partial^2 \log Z}{\partial \beta^2} = -\frac{\partial}{\partial \beta}\left(\frac{\partial \log Z}{\partial \beta^2}\right) = -\frac{\partial}{\partial \beta}\left\langle E \right\rangle = -\frac{\partial T}{\partial \beta}\frac{\partial}{\partial T}\left\langle E \right\rangle = \frac{1}{k\beta^2}\frac{\partial}{\partial T}\left\langle E \right\rangle = kT^2 C_v$$

Thus, we see that energy fluctuations are intimately related to the specific heat of the system.

d) prove that $\frac{\Delta E}{\left\langle E \right\rangle} \propto \lim_{N\to\infty}\frac{1}{\sqrt{N}} = 0$. What is this means?

So, in the limit of number of particles being very large, the fluctuations are negligible, and the energy remains practically constant.



Q2: An ideal gas, which consists of *N* indistinguishable atoms of mass *m* is located inside an infinitely high cylinder of radius R. In the presence of uniform downward gravitational field, find the

a. partition function,
b. free energy and
c. Specific heat of this system.

Answer:

a. For the cylinder, the volume integral $\int d^3 r = \underbrace{\int dxdy}_{\pi R^2} \int dz = \pi R^2 \int dz$

$$Z_{sp}=\frac{1}{h^3}\int d^3r\,d^3p\,e^{-\beta\frac{p^2}{2m}-\beta mgz}$$

$$=\frac{\pi R^2}{h^3}\underbrace{\left(\int_0^{\infty}dz\,e^{-\beta mgz}\right)}_{\frac{1}{\beta mg}}\underbrace{\left(\int_{-\infty}^{\infty}dp_x\,e^{-\beta\frac{p_x^2}{2m}}\right)^3}_{\left(\frac{2\pi m}{\beta}\right)^{3/2}}=\frac{R^2}{h^3}\frac{\sqrt{m}}{2g}\left(\frac{2\pi}{\beta}\right)^{5/2}$$

Where R is the radius of the cylinder. The full partition function of the N indistinguishable atoms is $Z_N=\frac{1}{N!}\left(Z_{sp}\right)^N$. The free energy is

b.

$$F=-k_BT\ln Z_N\approx Nk_BT\left[\ln N-1-\ln Z_{sp}\right]$$

c. And the specific heat is:

$$C_V=-T\left(\frac{\partial^2F}{\partial T^2}\right)_V=\frac{5}{2}N$$

Q5- A gas of N identical classical non-interacting atoms is held in a potential $V(r)=a\,r$, where $r=\sqrt{x^2+y^2+z^2}$. The gas is in thermal equilibrium at temperature T.

(a) Find the **single particle partition function** Z_1 of an atom in the gas. Express your answer in the form $Z_1=AT^{\alpha}a^{-\eta}$ and provide an expression for the following:

i- prefactor $A=8\pi k^3\left(\frac{2\pi mk}{h^2}\right)^{3/2}$

ii- $\alpha=$ 9/2

iii- $\eta=$ 3

Note:

$Z_1=\int\exp[-E/kT]$ where $E=p^2/2m+V(r)$.

$$Z_1=\frac{1}{h^3}\left(\int_{-\infty}^{\infty}\exp[-p_x^2/2mkT]dp_x\right)\left(\int_{-\infty}^{\infty}\exp[-p_y^2/2mkT]dp_y\right)\left(\int_{-\infty}^{\infty}\exp[-p_z^2/2mkT]dp_z\right)$$

$$\times\int_0^{\pi}d\theta\int_0^{2\pi}d\phi\int_0^{\infty}dr\exp[-ar/kT]r^2\sin\theta$$

Using equation sheet values for integrals leads to

$$Z_1=\left(\frac{2\pi mkT}{h^2}\right)^{3/2}(4\pi)2\left(\frac{kT}{a}\right)^3=8\pi k^3\left(\frac{2\pi mk}{h^2}\right)^{3/2}T^{9/2}a^{-3}=AT^{\alpha}a^{-\eta}$$

(b) For this classical gas with N-particles, find an expression for

i- $$F=-kT\ln Z=-kT\ln\frac{Z_1^N}{N!}=-kT\left[-\ln N!+N\ln Z_1\right]$$

$$\approx-NkT\left[-\ln N+1+\ln Z_1\right]$$

ii- $$S=-\left(\frac{\partial F}{\partial T}\right)_{V,N}=-k\left[-N\ln N+N+N\ln Z_1\right]+kTN\left(\frac{\partial Z_1}{\partial T}\right)_{V,N},$$

$$\left(\frac{\partial Z_1}{\partial T}\right)_{V,N}=\frac{9}{2T}$$

$$\therefore \quad S = kN\left[\frac{11}{2} + N\ln\left(\frac{Z_1}{N}\right)\right]$$

Q3: A system is composed of a large number N of one-dimensional quantum harmonic oscillators whose angular frequencies are distributed over the range $\omega_a \le \omega \le \omega_b$ with a frequency distribution function $f(\omega) = A/\omega$. Calculate the following:

a) The constant A.

b) The partition function of the system. [Hint: use the formula $E_n = (n + \frac{1}{2})\hbar\omega$]

c) The average energy, and find the limit in the high temperature case, i.e. $2k_B T > \hbar\omega$.

d) The specific heat in above limit.

Answer:

(a).

$$N = \int_{w_a}^{w_b} f(w)dw = A\int_{w_a}^{w_b} \frac{dw}{w} = A\ln\left(\frac{w_a}{w_b}\right) \Rightarrow A = \frac{N}{\ln\left(\frac{w_a}{w_b}\right)}$$

(b) In quantum mechanics, since the energy levels is $\epsilon_n = (n + \frac{1}{2})h\nu$, the part function is given by

$$Z_1 = \sum_{n=0}^{\infty} e^{-\beta\epsilon_n} = e^{-a}\sum_{n=0}^{\infty}\left\{e^{-2a}\right\}^n$$

$$= \frac{e^{-a}}{1 - e^{-2a}} = \frac{1}{e^{a} - e^{-a}} = (2\sinh a)^{-1}$$

where $a = \frac{\hbar w}{2kT}$.

(c).

$$E_w = -\frac{\partial \ln Z_1}{\partial \beta} = \frac{\hbar w}{2}\coth(a)$$

$$E = \int_{w_a}^{w_b} f(w)E_w dw = \frac{A\hbar}{2}\int_{w_a}^{w_b} \coth\left(\frac{\beta\hbar w}{2}\right)dw = \frac{A}{\beta}\ln\left[\frac{\sinh\left(\frac{\beta\hbar w_a}{2}\right)}{\sinh\left(\frac{\beta\hbar w_b}{2}\right)}\right]$$

$$\bar{E} = \frac{E}{N} = \frac{1}{\beta\ln\left(\frac{w_a}{w_b}\right)}\ln\left[\frac{\sinh\left(\frac{\beta\hbar w_a}{2}\right)}{\sinh\left(\frac{\beta\hbar w_b}{2}\right)}\right]$$

$$\cong kT \qquad (2kT \gg \hbar w)$$

(d).

$$C_v = k$$

Q4: A system consists of N noninteracting, distinguishable two-level atoms. Each atom can exist in one of two states, $E_0 = 0$, and $E_1 = \varepsilon$. The number of atoms in energy level E_i is n_i. The internal energy of the system is $U = n_0 E_0 + n_1 E_i$.

a) Write down the expression of the number of microstates.

b) Compute the entropy of the system as a function of internal energy.

c) Use $\frac{1}{T} = \frac{\partial S}{\partial U}$, to calculate the internal energy of the system as a function of temperature.

d) Compute the heat capacity of a fixed number of atoms, N.

Answer:

a)

$$W = \frac{N!}{n_1!(N-n_1)!}$$

Note that: $E_0 = 0 \Rightarrow \quad U = n_1\varepsilon$

b)

Consequently

$$\frac{S}{k_B} = \ln W \approx \ln\left(\frac{N!}{n_1!(N-n_1)!}\right) = N\ln N - N - n_1\ln n_1 - (N-n_1)\ln(N-n_1) + (N-n_1)$$

Finaly

$$\frac{S}{k_B} \approx N\ln N - \frac{U}{\varepsilon}\ln\frac{U}{\varepsilon} - \left(N - \frac{U}{\varepsilon}\right)\ln\left(N - \frac{U}{\varepsilon}\right)$$

c) To find the temperature, we do the usual procedure:

$$\frac{1}{T} = \frac{\partial S}{\partial U} \approx \frac{k_B}{\varepsilon}\ln\left(\frac{N\varepsilon - U}{U}\right)$$

As result

$$U = \frac{N\varepsilon}{e^{\beta\varepsilon}+1}, \qquad \beta = \frac{1}{k_B T}$$

d) The specific heat will be

$$C_v = \left(\frac{\partial U}{\partial T}\right)_{N,V} = Nk_B(\beta\varepsilon)^2\frac{e^{\beta\varepsilon}}{\left(e^{\beta\varepsilon}+1\right)^2}$$

H.W. Plot U and Cv as a function of T.

Glossary

- **Adiabatic** Of processes: occurring without heat transfer. Of walls: insulating. Reversible adiabatic processes are isentropic.
- **Equation of State** A relationship between the state variables of the system. Simple systems in equilibrium are fully specified by two properties such as temperature and volume; all the other functions of state are functions of these. For an ideal gas, the equation of state is $PV = nRT$; for an ideal paramagnet it is $m = cB/\mu_0 T$ where c is a constant.
- **Equilibrium** A system is in equilibrium when its macroscopic properties (temperature, pressure) are uniform and not changing with time.
- **Extensive** Some thermodynamic functions of state are extensive: if the intensive variables (T, P, B) are kept constant, the extensive variables are proportional to the amount of substance present. Energy, volume, entropy, total magnetisation, enthalpy, Gibbs and Helmholtz free energies and heat capacities are all extensive. Extensive properties expressed per unit mass or per mole are then intensive, and are called **specific**: eg. specific heat capacity. All functions of state are either extensive or intensive.
- **Function of state** A property of a system which only depends of the current state of the system and not on its history. Examples are temperature, pressure, volume, internal energy, entropy, magnetisation for a paramagnet (but not for a ferromagnet). Also called a **state variable** or a **macroscopic variable**.