Phys. 807 — Statistical Mechanics

HW3 Solution

Problem 1:
Show that the relations

$$p = \alpha\sqrt{2p'}\cos q' \quad ; \quad q = \frac{1}{\alpha}\sqrt{2p'}\sin q'$$

represent a canonical transformation $(p, q) \leftrightarrow (p', q')$. Expressing the hamiltonian $H = p^2/2m + m\omega^2 q^2/2$ as a function of p' and q', show that it can be made independent of q' by suitable choice of α, and use this form of the hamiltonian to determine its mean value E at the temperature T according to classical statistical mechanics.

Solution

The inverse formulas are

$$p' = \frac{1}{2}\Big(\frac{p^2}{\alpha^2} + \alpha^2 q^2\Big), \qquad \cos q' = \frac{p}{\sqrt{p^2 + \alpha^4 q^2}}, \qquad \sin q' = \frac{\alpha^2 q}{\sqrt{p^2 + \alpha^4 q^2}}$$

and therefore

$$\begin{aligned}
\dot{p}' &= \frac{1}{2}\Big(\frac{p^2}{\alpha^2} + \alpha^2 q^2\Big) = \frac{p\dot{p}}{\alpha^2} + \alpha^2 q\dot{q} = \frac{pq\alpha^2}{m}\Big(1 - \frac{m^2\omega^2}{\alpha^4}\Big) \\
\dot{q}' &= -\frac{\dot{p}}{\alpha^2 q} + \frac{p^2\dot{p} + \alpha^4 pq\dot{q}}{\alpha^2 q(p^2 + \alpha^4 q^2)} = \frac{\alpha^2(p^2 + m^2\omega^2 q^2)}{m(p^2 + \alpha^4 q^2)}
\end{aligned}$$

The Hamiltonian in new variables is

$$H' = \frac{\alpha^2}{m} p'\big(\cos^2 q' + \frac{m^2\omega^2}{\alpha^4}\sin^2 q'\big)$$

so

$$\begin{aligned}
\frac{\partial H'}{\partial p'} &= \frac{\alpha^2}{m}\big(\cos^2 q' + \frac{m^2\omega^2}{\alpha^4}\sin^2 q'\big) = \frac{\alpha^2}{m}\frac{p^2 + m^2\omega^2 q^2}{p^2 + \alpha^4 q^2} \\
\frac{\partial H'}{\partial q'} &= 2\frac{\alpha^2}{m}\Big(\frac{m^2\omega^2}{\alpha^4} - 1\Big)p'\sin q'\cos q' = -\frac{\alpha^2}{m}\Big(1 - \frac{m^2\omega^2}{\alpha^4}\Big)qp
\end{aligned}$$

We see that

$$\frac{\partial H'}{\partial p'} = \dot{q}' \qquad \text{and} \qquad \frac{\partial H'}{\partial q'} = -\dot{p}'$$

so the transformation is canonical.

If we now take $\alpha^2 = m\omega$

$$H' = \omega p'$$

The mean energy is

$$E = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}$$

where

$$\mathcal{Z} \;=\; \frac{1}{2\pi\hbar}\int_0^{2\pi} dq' \int_0^\infty dp'\; e^{-\beta\omega p'} \;=\; \frac{1}{\hbar\omega\beta}$$

so we get

$$E \;=\; \frac{\partial \ln\beta}{\partial\beta} \;=\; \frac{1}{\beta} \;=\; k_B T$$

Problem 2

For an ideal gas of particles with rest mass m_0 and kinetic energy $c\sqrt{p^2+(m_0c)^2} - m_0c^2$ determine the energy ϵ and the specific heat c_v per mole

a) For $\delta \equiv k_BT/m_0c^2 \ll 1$, including terms linear in δ

b) For $\gamma \equiv m_0c^2/k_BT \ll 1$, including linear and quadratic terms in γ.

Solution

The partition function for 1 molecule is

$$z \;=\; \int \frac{d^3p d^3x}{(2\pi\hbar)^3} e^{-\beta m_0 c^2\left(\sqrt{1+\frac{p^2}{m_0^2c^2}}-1\right)} \;=\; \frac{4\pi V}{(2\pi\hbar)^3}\int_0^\infty dp\; p^2 e^{-\beta m_0 c^2\left(\sqrt{1+\frac{p^2}{m_0^2c^2}}-1\right)}$$

Part (a)

In the first $\delta = \frac{k_BT}{m_0c^2} \ll 1$ case we get the one-molecule statistical sum in the form

$$z \;=\; \frac{4\pi V}{(2\pi\hbar)^3}\int_0^\infty dp\; p^2 e^{-\frac{1}{\delta}\left(\sqrt{1+\frac{p^2}{m_0^2c^2}}-1\right)} \;\simeq\; \frac{4\pi V}{(2\pi\hbar)^3}\int_0^\infty dp\; p^2 e^{-\frac{p^2}{2m_0^2c^2\delta}}\left(1+\frac{p^4}{8m_0^4c^4\delta}\right)$$
$$=\; \frac{\pi^{3/2}V(2\delta)^{3/2}m_0^3c^3}{(2\pi\hbar)^3}\left(1+\frac{15}{8}\delta\right) \;=\; \frac{V(2m_0\pi)^{3/2}}{(2\pi\hbar)^3\beta^{3/2}}\left(1+\frac{15}{8m_0c^2\beta}\right)$$

For an ideal gas of such molecules

$$\mathcal{Z} \;=\; \frac{1}{N!}\left(\frac{V(2m_0\pi)^{3/2}}{(2\pi\hbar)^3\beta^{3/2}}\left(1+\frac{15}{8m_0c^2\beta}\right)\right)^N$$

so

$$E \;=\; -\frac{\partial \ln\mathcal{Z}}{\partial\beta} \;=\; \frac{3N}{2\beta} - N\frac{\partial}{\partial\beta}\ln\left(1+\frac{15}{8m_0c^2\beta}\right) \;\simeq\; \frac{3N}{2\beta}\left(1-\frac{5}{4m_0c^2\beta}\right) \;=\; \frac{3N}{2}k_BT\left(1-\frac{5}{4}\delta\right)$$

and the specific heat is

$$c_V \;=\; \frac{3}{2}R\left(1-\frac{5}{4}\delta\right)$$

Part (b)

In the second $\gamma = \frac{m_0c^2}{k_BT} \ll 1$ case we get

$$z \;=\; \frac{4\pi V}{(2\pi\hbar)^3}\int_0^\infty dp\; p^2 e^{-\gamma\left(\sqrt{1+\frac{p^2}{m_0^2c^2}}-1\right)} \;\simeq\; \frac{4\pi V}{(2\pi\hbar)^3}\int_0^\infty dp\; p^2 e^{-\gamma\left(\frac{p}{m_0c}-1+\frac{m_0c}{2p}\right)}$$
$$=\; \frac{8\pi V m_0^3c^3}{(2\pi\hbar)^3\gamma^3}e^{\gamma}\left(1-\frac{\gamma^2}{4}\right) \;=\; \frac{8\pi V}{(2\pi\hbar)^3c^2\beta^3}e^{m_0c^2\beta}\left(1-\frac{m_0^2c^4\beta^2}{4}\right)$$

For the ideal gas of N molecules

$$\mathcal{Z} \;=\; \frac{1}{N!}\Big(\frac{8\pi V}{(2\pi\hbar)^3 c^2\beta^3} e^{m_0c^2\beta}\big(1-\frac{m_0^2c^4\beta^2}{4}\big)\Big)^N$$

so

$$\begin{aligned} E \;&=\; -\frac{\partial \ln \mathcal{Z}}{\partial\beta} \;=\; \frac{3N}{\beta} - Nm_0c^2 - N\frac{\partial}{\partial\beta}\ln\big(1-\frac{m_0^2c^4\beta^2}{4}\big) \\ &\simeq\; \frac{3N}{\beta} - Nm_0c^2 + \frac{N}{2}m_0^2c^4\beta \;=\; 3Nk_BT\big(1-\frac{\gamma}{3}+\frac{\gamma^2}{6}\big) \end{aligned}$$

and the specific heat is

$$c_V \;=\; 3RT\big(1-\frac{\gamma}{3}+\frac{\gamma^2}{6}\big)$$

Problem 3

What is the probability density and specific heat of a mole of an ideal gas at temperature T contained in a volume V if each molecule is subject to the same constant force in the x-direction?

Solution

The general formula for the probability density is given by Eq. (4.1) from the lecture notes

$$\rho(q_i,p_i) = \frac{1}{\mathcal{Z}}\, e^{-\beta H(q_i,p_i)}\;, \qquad\qquad \mathcal{Z} = \int\prod_{i=1}^n dq_i\, dp_i\, e^{-\beta H(q_i,p_i)}\;,$$

The Hamiltonian for a particle subject to force in x direction is

$$H \;=\; \frac{p^2}{2m} + \kappa x$$

where κ is the corresponding "Hooks law" coefficient $F = \kappa x$. We get

$$\rho(q,p) = \frac{1}{\mathcal{Z}}\; e^{-\beta(\frac{p^2}{2m}+\kappa x)}$$

where $\beta \;=\; \frac{1}{k_BT}$. For N particles

$$\rho(q,p) = \frac{1}{\mathcal{Z}}\; e^{-\beta\sum(\frac{p_i^2}{2m}+\kappa x_i)}$$

To get the partition function we need to integrate density over the phase space. The integration yields

$$\mathcal{Z}_{\rm one-particle} \;=\; \int\frac{dpdq}{2\pi\hbar}\; e^{-\beta(\frac{p^2}{2m}+\kappa q)} \;=\; \Big(\frac{2\pi m}{\beta}\Big)^{3/2}\int dxdydz\; e^{-\beta\kappa x}$$

Let us assume that the mole of an ideal gas occupies cubic volume $V \;=\; L^3$ with the origin $(0,0,0)$ being the corner of the cube, then

$$\int_V dq\; e^{-\beta\kappa q} \;=\; L^2\frac{1}{\kappa\beta}\Big(1-e^{-\beta\kappa L}\Big)$$

and

$$\mathcal{Z}_{\rm one-particle} \;=\; \int \frac{dpdq}{2\pi\hbar}\, e^{-\beta(\frac{p^2}{2m}+\kappa q)} \;=\; \Big(\frac{2\pi m}{\beta}\Big)^{3/2} L^2 \frac{1}{\kappa\beta}\Big(1-e^{-\beta\kappa L}\Big) \;=\; \Big(\frac{2\pi m}{\beta}\Big)^{3/2} V \frac{1}{\kappa\beta L}\Big(1-e^{-\beta\kappa L}\Big)$$

For N particles we get

$$\mathcal{Z} \;=\; \Big(\frac{2\pi m}{\beta}\Big)^{3N/2} V^N \Big(\frac{1-e^{-\beta\kappa L}}{\kappa\beta L}\Big)^N$$

The energy is given by Eq. (4.52) from the lecture notes so

$$E \;=\; -\frac{\partial}{\partial\beta}\ln\mathcal{Z}(\beta) \;=\; \frac{3N}{2\beta} - N\frac{\partial}{\partial\beta}\ln\Big(\frac{1-e^{-\beta\kappa L}}{\beta}\Big) \;=\; \frac{5N}{2\beta} - N\frac{\kappa L e^{-\beta\kappa L}}{1-e^{-\beta\kappa L}}$$

If we assume that κ is not negligible (and in microscopic terms L is very large) we can neglect the second term so

$$E \;=\; \frac{5N}{2\beta} \;=\; \frac{5N}{2}k_BT$$

and the specific heat is

$$C_V \;=\; \Big(\frac{\partial E}{\partial T}\Big)_V \;=\; \frac{5}{2}R$$