• **Problem 3.29** Consider a system of non-interacting, identical but distinguishable particles. Using both the canonical and the grand canonical ensembles, find the partition function and the thermodynamic functions $U(T, V, N)$, $S(T, V, N)$ and $F(T, V, N)$, where T is the temperature, V the volume and N the number of particles, in terms of the single-particle partition function $Z_1(T, V)$. Verify that $U_G = U_C$, where the subscripts C and G denote the canonical and grand canonical ensembles respectively. If s and f are the entropy and the Helmholtz free energy per particle respectively, show that, when N is large, $(s_G - s_C)/k = -(f_G - f_C)/kT \simeq (\ln N)/N$.

• **Problem 3.30** Consider a system of identical but distinguishable particles, each of which has two states, with energies ε and $-\varepsilon$ available to it. Use the microcanonical, canonical and grand canonical ensembles to calculate the mean entropy per particle as a function of the mean energy per particle in the limit of a very large system. Verify that all three ensembles yield identical results in this limit.

• **Problem 3.29** The canonical partition function for N non-interacting particles is

$$Z(T, V, N) = [Z_1(T, V)]^N.$$

From it, we immediately obtain

$$\begin{aligned}
U_C(T, V, N) &= -\left(\frac{\partial(\ln Z)}{\partial\beta}\right)_{V,N} = NkT^2\frac{Z_1'}{Z_1} \\
F_C(T, V, N) &= -kT\ln Z = -NkT\ln Z_1 \\
S_C(T, V, N) &= \frac{U_C - F_C}{T} = Nk\left(T\frac{Z_1'}{Z_1} + \ln Z_1\right)
\end{aligned}$$

where $Z_1' = (\partial Z_1/\partial T)_V$.

The grand canonical partition function is

$$\begin{aligned}
\mathcal{Z}(T, V, \mu) &= \sum_{N=0}^{\infty} e^{\beta\mu N} Z(T, V, N) = \sum_{N=0}^{\infty}[e^{\beta\mu} Z_1(T, V)]^N \\
&= \frac{1}{1 - e^{\beta\mu} Z_1(T, V)}.
\end{aligned}$$

To obtain thermodynamic quantities as functions of N, we must adjust the chemical potential μ so that

$$N = \langle N \rangle_{\mathrm{G}} = \left(\frac{\partial(\ln \mathcal{Z})}{\partial(\beta\mu)} \right)_{T,V} = \frac{\mathrm{e}^{\beta\mu} Z_1}{1 - \mathrm{e}^{\beta\mu} Z_1}$$

which implies that

$$\mathrm{e}^{\beta\mu} Z_1 = \frac{N}{N+1} \qquad \mu = -kT \ln\left(\frac{(N+1)Z_1}{N} \right).$$

We then find

$$\begin{aligned}
\Omega_{\mathrm{G}}(T, V, N) &= kT \ln \mathcal{Z} = kT \ln(N+1) \\
F_{\mathrm{G}}(T, V, N) &= \mu N - \Omega_{\mathrm{G}} = kT[N \ln N - (N+1)\ln(N+1) - N \ln Z_1] \\
U_{\mathrm{G}}(T, V, N) &= -\left(\frac{\partial(\ln \mathcal{Z})}{\partial \beta} \right)_{\beta\mu, V} = NkT^2 \frac{Z_1'}{Z_1} \\
S_{\mathrm{G}}(T, V, N) &= \frac{U_{\mathrm{G}} - F_{\mathrm{G}}}{T} \\
&= NkT \frac{Z_1'}{Z_1} - k[N \ln N - (N+1)\ln(N+1) - N \ln Z_1].
\end{aligned}$$

Clearly, we have $U_{\mathrm{G}}(T, V, N) = U_{\mathrm{C}}(T, V, N)$ and

$$\begin{aligned}
(S_{\mathrm{G}} - S_{\mathrm{C}})/k &= -\frac{(F_{\mathrm{G}} - F_{\mathrm{C}})}{kT} \\
&= (N+1)\ln(N+1) - N \ln N \\
&= \ln N + 1 + \frac{1}{2N} + \cdots.
\end{aligned}$$

On dividing this last result by N and taking N to be large, we get

$$\frac{s_{\mathrm{G}} - s_{\mathrm{C}}}{k} = -\frac{f_{\mathrm{G}} - f_{\mathrm{C}}}{kT} \simeq \frac{\ln N}{N}.$$

(c) *Grand canonical ensemble*. This ensemble describes a system in equilibrium with a reservoir, with which it can exchange both energy and particles, so both the energy and the number of particles fluctuate. The reservoir is characterized by a definite temperature $T = 1/k\beta$ and chemical potential μ or fugacity $z = e^{\beta\mu}$. The partition function is

$$\mathcal{Z}(T, \mu) = \sum_{N=0}^{\infty} z^N Z(T, N) = \frac{1}{1 - z(e^{\beta\varepsilon} + e^{-\beta\varepsilon})}$$

and the thermodynamic interpretation is through the grand potential $\Omega_G(T, \mu) = kT \ln[\mathcal{Z}(T, \mu)]$. The entropy will be obtained through the thermodynamic relation $\Omega = TS - U + \mu N$, where the particle number and internal energy are identified as the mean values

$$N_G = \langle N \rangle_G = z \left(\frac{\partial(\ln \mathcal{Z})}{\partial z} \right)_\beta = \frac{z(e^{\beta\varepsilon} + e^{-\beta\varepsilon})}{1 - z(e^{\beta\varepsilon} + e^{-\beta\varepsilon})}$$

$$U_G = \langle E \rangle_G = -\left(\frac{\partial(\ln \mathcal{Z})}{\partial \beta} \right)_z = -\varepsilon \frac{z(e^{\beta\varepsilon} - e^{-\beta\varepsilon})}{1 - z(e^{\beta\varepsilon} + e^{-\beta\varepsilon})} = -N_G \varepsilon \tanh(\beta\varepsilon).$$

As above, we would like to express thermodynamic functions in terms of the parameter $x = U_G/N_G\varepsilon = -\tanh(\beta\varepsilon)$ and N_G, rather than T and μ, so we first solve the above equations to obtain

$$\beta\varepsilon = \tfrac{1}{2}[\ln(1-x) - \ln(1+x)]$$

$$\beta\mu = \ln\left(\frac{N_G}{N_G+1}\right) - \ln 2 + \tfrac{1}{2}[\ln(1+x) + \ln(1-x)].$$

With these results in hand, we can calculate

$$\begin{aligned}
U_G &= N_G \varepsilon x \\
\Omega_G &= kT \ln \mathcal{Z} = kT \ln(N_G + 1) \\
S_G &= \frac{1}{T}(\Omega_G + U_G - \mu N_G) \\
&= k N_G \left[\frac{\ln(N_G+1)}{N_G} + \ln\left(1 + \frac{1}{N_G}\right) \right. \\
&\qquad \left. + \ln 2 - \tfrac{1}{2}(1+x)\ln(1+x) - \tfrac{1}{2}(1-x)\ln(1-x) \right].
\end{aligned}$$

On taking the limit that N_G is very large, we find for the entropy per particle that

$$s = \lim_{N_G \to \infty} \left(\frac{S_G}{N_G} \right) = k[\ln 2 - \tfrac{1}{2}(1+x)\ln(1+x) - \tfrac{1}{2}(1-x)\ln(1-x)]$$