7.D.3. Systems of Distinguishable Particles

For identical but distinguishable particles, there is no need to symmetrize the N-particles states. Thus, (7.51 & c) are replaced by

$$\mathrm{Tr}_N\,\hat{\rho} = \sum_{\boldsymbol{k}_1 \ldots \boldsymbol{k}_N} \left\langle \boldsymbol{k}_1 \;\ldots\; \boldsymbol{k}_N \mid \hat{\rho} \mid \boldsymbol{k}_1 \;\ldots\; \boldsymbol{k}_N \right\rangle = 1 \qquad (7.60)$$

$$Z_N = \sum_{\boldsymbol{k}_1 \ldots \boldsymbol{k}_N} \left\langle \boldsymbol{k}_1 \;\ldots\; \boldsymbol{k}_N \mid e^{-\beta \hat{H}_N} \mid \boldsymbol{k}_1 \;\ldots\; \boldsymbol{k}_N \right\rangle \qquad (7.60a)$$

Ex. 7.5.

Use the canonical ensemble to compute the entropy, internal energy, and heat capacity of the Einstein solid described in Ex.7.1 of §7.B.

Answer

Since the every particle (oscillator) is fixed to its own lattice site, they can always be identified and hence are distinguishable. In the number representation, the Hamiltonian takes the form

$$\hat{H}_N = \hbar\,\omega \sum_{i=1}^{3N} \left(\hat{n}_i + \frac{1}{2} \right) \qquad (1)$$

where $\hat{n}_i$ is the number operator with eigenstates $\mid n_i \rangle$ so that

$$\hat{n}_i \mid n_i \rangle = n_i \mid n_i \rangle \qquad n_i = 0, 1, 2, \;\ldots \qquad (1a)$$

(7.60a) becomes

$$\begin{aligned}
Z_N(T) &= \sum_{n_1=0}^{\infty} \cdots \sum_{n_{3N}=0}^{\infty} \left\langle n_1 \ldots n_{3N} \mid \exp\left[-\beta\,\hbar\,\omega \sum_{i=1}^{3N} \left(\hat{n}_i + \frac{1}{2} \right) \right] \mid n_1 \ldots n_{3N} \right\rangle \\
&= \sum_{n_1=0}^{\infty} \cdots \sum_{n_{3N}=0}^{\infty} \prod_{j=1}^{3N} \left\langle n_j \mid \exp\left[-\beta\,\hbar\,\omega \left(\hat{n}_j + \frac{1}{2} \right) \right] \mid n_j \right\rangle \\
&= \sum_{n_1=0}^{\infty} \cdots \sum_{n_{3N}=0}^{\infty} \prod_{j=1}^{3N} \exp\left[-\beta\,\hbar\,\omega \left(n_j + \frac{1}{2} \right) \right] \\
&= \prod_{j=1}^{3N} \left\{ \sum_{n_j=0}^{\infty} \exp\left[-\beta\,\hbar\,\omega \left(n_j + \frac{1}{2} \right) \right] \right\} \\
&= \prod_{j=1}^{3N} \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \\
&= \left(\frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \right)^{3N} \qquad (3)
\end{aligned}$$

$$\begin{aligned}
\rightarrow \quad A &= -k_B\,T \ln Z_N(T) \\
&= -3\,N\,k_B\,T \left[-\frac{1}{2}\beta\,\hbar\,\omega - \ln\left(1 - e^{-\beta\hbar\omega} \right) \right] \\
&= \frac{3}{2} N\,\hbar\,\omega + 3\,N\,k_B\,T \ln\left(1 - e^{-\beta\hbar\omega} \right) \qquad (4)
\end{aligned}$$

$$\begin{aligned}
S &= -\left(\frac{\partial A}{\partial T} \right)_N \\
&= -3\,N\,k_B \ln\left(1 - e^{-\beta\hbar\omega} \right) + 3\,N\,k_B\,T \frac{e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \left(\frac{\hbar\,\omega}{k_B\,T^2} \right)
\end{aligned}$$

$$= -3 N k_B \ln\left(1 - e^{-\beta \hbar \omega}\right) + 3 N k_B \beta \hbar \omega \frac{e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \quad (5)$$

where both terms are positive since $\ln\left(1 - e^{-\beta \hbar \omega}\right) < 0$.

$$U = A + T S$$

$$= \frac{3}{2} N \hbar \omega + 3 N \hbar \omega \frac{e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \quad (6)$$

$$= \frac{3}{2} N \hbar \omega \left(1 + \frac{2 e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}}\right)$$

$$= \frac{3}{2} N \hbar \omega \frac{1 + e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}}$$

$$= \frac{3}{2} N \hbar \omega \coth\left(\frac{1}{2} \beta \hbar \omega\right) \quad (6a)$$

$$C_N = \left(\frac{\partial U}{\partial T}\right)_N$$

$$= 3 N \hbar \omega \frac{\partial}{\partial T}\left(\frac{1}{e^{\beta \hbar \omega} - 1}\right) \quad \text{[(6) used.]}$$

$$= 3 N \hbar \omega \frac{-e^{\beta \hbar \omega}}{\left(e^{\beta \hbar \omega} - 1\right)^2}\left(-\frac{\hbar \omega}{k_B T^2}\right)$$

$$= 3 N k_B \left(\frac{\hbar \omega}{k_B T}\right)^2 \frac{e^{\beta \hbar \omega}}{\left(e^{\beta \hbar \omega} - 1\right)^2}$$

$$= 3 N k_B \left(\frac{\hbar \omega}{k_B T}\right)^2 \frac{e^{-\beta \hbar \omega}}{\left(1 - e^{-\beta \hbar \omega}\right)^2} \quad (7)$$