6. *Statistical Mechanics and Thermodynamics* (Spring 2007)

Consider N noninteracting distinguishable particles of mass m in a three-dimensional harmonic oscillator with Hamiltonian

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^{\,2}}{2m} + \frac{m\omega^2}{2}\mathbf{r}_i^{\,2}$$

The particles are in contact with a heat bath of temperature T and are in thermal equilibrium.

(a) Calculate the partition function $Z(T, N)$ of the system.

(b) Calculate the internal energy $E(T, N)$ of the system.

(c) Calculate the heat capacity $c(T, N)$ of the system.

(d) Simplify the expression for the heat capacity for low and high temperature (with respect to $\hbar\omega/k_B$).

Since part (d) asks for a low-temperature limit, we suspect that we'll have to solve for these quantities quantum-mechanically. Furthermore, we know that by the equipartition theorem (which is valid in the classical, high temperature, high particle number (?) limit), since there are six quadratic terms in the Hamiltonian, $\langle \epsilon \rangle = 6\,\frac{1}{2}kT$ so $E = N\langle\epsilon\rangle = 3NkT$, and as $dE = đQ$ $(đW = 0)$, $C = \frac{đQ}{dT} = \frac{dE}{dT} = 3Nk$, which can't be simplified. Thus we must solve quantum-mechanically and expect $C = 3Nk$ in the high-temperature limit.

a) $Z = z^N \qquad z = \sum_i e^{-\beta\epsilon_i} \qquad \epsilon = \hbar\omega\left(n_x + n_y + n_z + \frac{3}{2}\right) = \hbar\omega\left(N + \frac{3}{2}\right)$

$N = n_x + n_y + n_z$; The energies are degenerate since several combinations of values for n_x, n_y, and n_z yield the same value of N. How many combinations? Given a particular value for n_z, $n_x + n_y = N - n_z$, and n_x may range from zero to $N - n_z$. $\Rightarrow$ $(N - n_z + 1)$ comb.s for n_x and n_y. And n_z may range from zero to N, so the number of comb.s, and thus the multiplicity of the energies, is

$$m(N) = \sum_{n_z=0}^{N} (N - n_z + 1) \overset{*}{=} \sum_{n=1}^{N+1} n = \frac{1}{2}(N+1)(N+2) \qquad * \left(\text{reversing the summation}\right)$$

$$\Rightarrow \quad z = \sum_{N=0}^{\infty} m(N)\, e^{-\beta\epsilon(N)} = \sum_N \frac{1}{2}(N+1)(N+2)\, e^{-\beta\hbar\omega(N+3/2)} \qquad \alpha \equiv \beta\hbar\omega$$

$$= \frac{1}{2} e^{-\beta\hbar\omega 3/2} \sum_N (N^2 + 3N + 2)\, e^{-\beta\hbar\omega N} = \frac{1}{2} e^{-\alpha 3/2} \sum_N (N^2 + 3N + 2)\, e^{-\alpha N}$$

$$= \frac{1}{2} e^{-\alpha 3/2} (\partial_\alpha^2 - 3\partial_\alpha + 2) \sum_N e^{-\alpha N} = \frac{1}{2} e^{-\alpha 3/2} (\partial_\alpha^2 - 3\partial_\alpha + 2)(1 - e^{-\alpha})^{-1}$$

$$= \frac{1}{2} e^{-\alpha 3/2} \left[\partial_\alpha\left\{-(1 - e^{-\alpha})^{-2}(e^{-\alpha})\right\} + 3(1 - e^{-\alpha})^{-2}(e^{-\alpha}) + 2(1 - e^{-\alpha})^{-1}\right]$$

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a) (continued)

$$= \frac{1}{2} e^{-\alpha 3/2}\Big[2(1-e^{-\alpha})^{-3}(e^{-\alpha})^2 + (1-e^{-\alpha})^{-2}(e^{-\alpha}) + 3(1-e^{-\alpha})^{-2}(e^{-\alpha}) + 2(1-e^{-\alpha})^{-1}\Big]$$

$$= \frac{1}{2} e^{-\alpha 3/2}(1-e^{-\alpha})^{-1}\Big[2e^{-2\alpha}(1-e^{-\alpha})^{-2} + 4e^{-\alpha}(1-e^{-\alpha})^{-1} + 2\Big]$$

$$= e^{-\alpha 3/2}(1-e^{-\alpha})^{-1}\Big[e^{-2\alpha}(1-e^{-\alpha})^{-2} + 2e^{-\alpha}(1-e^{-\alpha})^{-1} + 1\Big]$$

$$= z(T) \qquad \text{where} \quad \alpha = \beta\hbar\omega = \frac{\hbar\omega}{kT}$$

$$Z(T,N) = z^N$$

since $\beta = \frac{1}{\hbar\omega}\alpha$

b) $$E = -\frac{\partial}{\partial\beta}\ln Z = -\frac{\partial}{\partial\beta} N \ln z = -N\frac{1}{z}\frac{\partial z}{\partial\beta} = -N\hbar\omega\frac{1}{z}\frac{\partial z}{\partial\alpha}$$

$$= -N\hbar\omega\left[-\frac{3}{2} + \frac{e^{-\alpha\frac{3}{2}}}{z}\left\{\begin{matrix}-2e^{-2\alpha}(1-e^{-\alpha})^{-3} - 3e^{-2\alpha}(1-e^{-\alpha})^{-4}(e^{-\alpha}) \\ -2e^{-\alpha}(1-e^{-\alpha})^{-2} - 4e^{-\alpha}(1-e^{-\alpha})^{-3}(e^{-\alpha}) - (1-e^{-\alpha})^{-2}(e^{-\alpha})\end{matrix}\right\}\right]$$

$$= N\hbar\omega\left[\frac{3}{2} + \frac{3e^{-3\alpha}(1-e^{-\alpha})^{-4} + 6e^{-2\alpha}(1-e^{-\alpha})^{-3} + 3e^{-\alpha}(1-e^{-\alpha})^{-2}}{e^{-2\alpha}(1-e^{-\alpha})^{-3} + 2e^{-\alpha}(1-e^{-\alpha})^{-2} + (1-e^{-\alpha})^{-1}}\right]$$

$$\begin{cases}\text{numerator} \equiv H \\ \text{denominator} \equiv L\end{cases}$$

$$= E(T,N) \qquad \text{where} \quad \alpha = \frac{\hbar\omega}{kT}$$

c) $$C = \frac{dE}{dT} = \frac{d\alpha}{dT}\frac{dE}{d\alpha} = -\frac{\hbar\omega}{k}\frac{1}{T^2}\frac{dE}{d\alpha} \qquad \text{where} \quad E = N\hbar\omega\left(\frac{3}{2} + \frac{H}{L}\right)$$

$$= -\frac{\frac{N}{k}\left(\frac{\hbar\omega}{T}\right)^2}{L^2}\left[\begin{matrix}L\{-9e^{-3\alpha}(1-e^{-\alpha})^{-4} - 12e^{-3\alpha}(1-e^{-\alpha})^{-5}(e^{-\alpha}) - 12e^{-2\alpha}(1-e^{-\alpha})^{-3} \\ -18e^{-2\alpha}(1-e^{-\alpha})^{-4}(e^{-\alpha}) - 3e^{-\alpha}(1-e^{-\alpha})^{-2} - 6e^{-\alpha}(1-e^{-\alpha})^{-3}(e^{-\alpha})\} \\ -H\{\partial_\alpha L = -H\}\end{matrix}\right]$$

$$= \frac{N}{k}\left(\frac{\hbar\omega}{T}\right)^2\left[\begin{matrix}\frac{3}{L}\{4e^{-4\alpha}(1-e^{-\alpha})^{-5} + 9e^{-3\alpha}(1-e^{-\alpha})^{-4} + 6e^{-2\alpha}(1-e^{-\alpha})^{-3} + e^{-\alpha}(1-e^{-\alpha})^{-2}\} \\ -H^2/L^2\end{matrix}\right]$$

d) High $T \Rightarrow$ low $\alpha \Rightarrow e^{-\alpha} \to 1,\ (1-e^{-\alpha}) \to \alpha;\ H \to 3\alpha^{-4},\ L \to \alpha^{-3}$

$$\Rightarrow C \to \frac{N}{k}\left(\frac{\hbar\omega}{T}\right)^2\left[3\,\frac{4\alpha^{-5}}{\alpha^{-3}} - \left(3\frac{\alpha^{-4}}{\alpha^{-3}}\right)^2\right]$$ keeping leading terms only

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d) (continued)

$$= \frac{N}{k}\left(\frac{\hbar\omega}{T}\right)^2\left[12\alpha^{-2} - 9\alpha^{-2}\right] = 3\frac{N}{k}\left(\frac{\hbar\omega}{T}\right)^2\left(\frac{kT}{\hbar\omega}\right)^2$$

$$= 3Nk \quad \checkmark$$

Low $T \Rightarrow$ high $\alpha \Rightarrow$ $e^{-\alpha} \to 0, e^{-\alpha}$ $\quad (1-e^{-\alpha})^{-n} \to 1, 1+ne^{-\alpha}$

$H \to 3e^{-\alpha} \qquad L \to 1$

$$\Rightarrow C \to \frac{N}{k}\left(\frac{\hbar\omega}{T}\right)^2\left[3e^{-\alpha} - (3e^{-\alpha})^2\right]$$

$$\to 3Nk\left(\frac{\hbar\omega}{kT}\right)^2 e^{-(\hbar\omega/kT)}$$