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 single-particle Hamiltonian, $\langle \epsilon \rangle = 6 \frac{1}{2} kT = 3kT$, 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) N 3-D QSHOs $\Rightarrow$ 3N 1-D QSHOs

$\Rightarrow$ act as if there are 3N particles w/ energy $\epsilon = \hbar\omega(n+\frac{1}{2})$

non-interacting, nondistinguishable $\Rightarrow$ $Z = z^{3N}$

$$z = \sum_i e^{-\beta\epsilon_i} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})} = e^{-\alpha/2}\sum_n e^{-\alpha n} \quad \text{letting } \alpha \equiv \beta\hbar\omega = \frac{\hbar\omega}{kT}$$

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

$$\Rightarrow Z = [2\sinh\alpha/2]^{-3N} = \left[2\sinh\frac{\hbar\omega}{2kT}\right]^{-3N}$$

b) $$E = -\frac{\partial}{\partial\beta}\ln Z = -\hbar\omega\frac{\partial}{\partial\alpha}\ln Z = -\hbar\omega\,\partial_\alpha\left[-3N\ln(2\sinh\alpha/2)\right]$$

$$= 3N\hbar\omega\,\partial_\alpha\left[\ln 2 + \ln(\sinh\alpha/2)\right] = 3N\hbar\omega\frac{\frac{1}{2}\cosh\alpha/2}{|\sinh\alpha/2|} = \frac{3}{2}N\hbar\omega\frac{\cosh\alpha/2}{\sinh\alpha/2}$$

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b) (continued)

$$= \frac{3}{2} N\hbar\omega \coth \alpha/2 \qquad \Rightarrow \qquad E = \frac{3}{2} N\hbar\omega \coth \frac{\hbar\omega}{2kT}$$

c) $$C = \frac{dE}{dT} = \frac{d\alpha}{dT}\frac{d}{d\alpha} E = \left(-\frac{\hbar\omega}{k}\frac{1}{T^2}\right)\partial_\alpha\left(\frac{3}{2}N\hbar\omega \coth \alpha/2\right)$$

$$= -\frac{\hbar\omega}{kT^2}\left[\frac{3}{2}N\hbar\omega \frac{\frac{1}{2}\sinh^2\alpha/2 - \frac{1}{2}\cosh^2\alpha/2}{\sinh^2\alpha/2}\right] = -\frac{\hbar\omega}{kT^2}\left[\frac{3}{4}N\hbar\omega\frac{-1}{\sinh^2\alpha/2}\right]$$

$$= \frac{3}{4}Nk\left(\frac{\hbar\omega}{kT}\right)^2 \operatorname{csch}^2 \alpha/2 = \frac{3}{4}Nk\left(\frac{\hbar\omega}{kT}\right)^2 \operatorname{csch}^2\frac{\hbar\omega}{2kT}$$

d) Low T $\Rightarrow$ High α

$$\Rightarrow \operatorname{csch}^2\alpha/2 = \frac{1}{\sinh^2\alpha/2} = \left(\frac{2}{e^{\alpha/2} - e^{-\alpha/2}}\right)^2 \rightarrow \frac{4}{e^{\alpha/2} - 0}$$

$$= 4e^{-\alpha/2}$$

$$\Rightarrow C \rightarrow \frac{3}{4}Nk\left(\frac{\hbar\omega}{kT}\right)^2 4e^{-\alpha/2} = 3Nk\left(\frac{\hbar\omega}{kT}\right)^2 e^{-\hbar\omega/2kT}$$

High T $\Rightarrow$ Low α

$$\Rightarrow \operatorname{csch}^2\alpha/2 = \frac{1}{\sinh^2\alpha/2} \rightarrow \frac{1}{(\alpha/2)^2} = \frac{4}{\alpha^2} = 4\left(\frac{kT}{\hbar\omega}\right)^2$$

$$\Rightarrow C \rightarrow \frac{3}{4}Nk\cancel{\left(\frac{\hbar\omega}{kT}\right)^2} 4\cancel{\left(\frac{kT}{\hbar\omega}\right)^2} = 3Nk \qquad \checkmark$$