Simple harmonic oscillator

The SHO has non-degenerate levels with $\epsilon_n = (n + \frac{1}{2})\hbar\omega$ for $n = 0, 1, 2, \ldots$.

a. The internal partition function is

$$\begin{aligned} \zeta(T) &= \sum_{n=0}^{\infty} e^{-\beta\epsilon_n} \\ &= \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega} \\ &= e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n}, \end{aligned}$$

but

$$\frac{1}{1-x} = 1 + x + x^2 + \cdots \qquad \text{for} \qquad 0 \le x < 1,$$

so

$$\zeta(T) = e^{-\beta\hbar\omega/2}\left(\frac{1}{1 - e^{-\beta\hbar\omega}}\right).$$

Thus

$$\ln\zeta(T) = -\beta\hbar\omega/2 - \ln\left(1 - e^{-\beta\hbar\omega}\right)$$

and

$$\begin{aligned} e^{\text{int}}(T) &= -\frac{\partial \ln\zeta}{\partial\beta} \\ &= \frac{1}{2}\hbar\omega + \frac{\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \\ &= \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}. \end{aligned}$$

b. The internal heat capacity is

$$\begin{aligned} c_V^{\text{int}}(T) &= \frac{\partial e^{\text{int}}}{\partial T} = \frac{\partial\beta}{\partial T}\frac{\partial e^{\text{int}}}{\partial\beta} \\ &= \left(-\frac{1}{k_B T^2}\right)(\hbar\omega)\left(-\frac{\hbar\omega e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}\right) \\ &= k_B\left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{-\hbar\omega/k_B T}}{(1 - e^{-\hbar\omega/k_B T})^2}. \end{aligned}$$

c. As is often the case, it is easier to derive this result than to interpret it.

Low temperature behavior: $k_B T \ll \hbar\omega$; $\beta\hbar\omega \gg 1$; $e^{-\beta\hbar\omega} \approx 0$, so

$$c_V^{\text{int}}(T) \approx k_B\left(\frac{\hbar\omega}{k_B T}\right)^2 e^{-\hbar\omega/k_B T}.$$

As in the Schottky case, this is very flat at $T = 0$.

High temperature behavior: $k_B T \gg \hbar\omega$; $\beta\hbar\omega \ll 1$; $e^{-\beta\hbar\omega} \approx 1$. But if we just leave it like this, we get $c_V^{\text{int}}(T) \approx 0(1/0)$, which is not helpful. We need a better approximation for $e^{-\beta\hbar\omega}$.

Let

$$x \equiv \frac{\hbar\omega}{k_B T} \longrightarrow 0.$$

Then

$$e^{-x} = 1 - x + \tfrac{1}{2}x^2 - \tfrac{1}{6}x^3 + \mathcal{O}(x^4)$$

so

$$\begin{aligned}
c_V^{\text{int}}(T) &= k_B x^2 \frac{e^{-x}}{(1-e^{-x})^2} \\
&= k_B x^2 \frac{\left[1 - x + \frac{1}{2}x^2 - \frac{1}{6}x^3 + \mathcal{O}(x^4)\right]}{\left[1 - \left(1 - x + \frac{1}{2}x^2 - \frac{1}{6}x^3 + \mathcal{O}(x^4)\right)\right]^2} \\
&= k_B x^2 \frac{\left[1 - x + \frac{1}{2}x^2 - \frac{1}{6}x^3 + \mathcal{O}(x^4)\right]}{x^2\left[1 - \frac{1}{2}x + \frac{1}{6}x^2 + \mathcal{O}(x^3)\right]^2} \\
&= k_B \frac{\left[1 - x + \frac{1}{2}x^2 + \mathcal{O}(x^3)\right]}{\left[1 - \frac{1}{2}x + \frac{1}{6}x^2 + \mathcal{O}(x^3)\right]^2}.
\end{aligned}$$

This result is good enough to tell us that

$$\text{when} \quad T \longrightarrow \infty, \quad x \longrightarrow 0, \quad \text{so} \quad c_V^{\text{int}} \longrightarrow k_B,$$

the classical equipartition result.

d. But we can also go on to get the leading order quantal corrections to equipartition:

$$c_V^{\text{int}}(T) = k_B \frac{\left[1 - x + \frac{1}{2}x^2 + \mathcal{O}(x^3)\right]}{\left[1 - \frac{1}{2}x + \frac{1}{6}x^2 + \mathcal{O}(x^3)\right]^2}.$$

But

$$\frac{1}{(1+z)^2} = 1 - 2z + 3z^2 - 4z^3 + \mathcal{O}(z^4),$$

where in our case

$$z = -\tfrac{1}{2}x + \tfrac{1}{6}x^2 + \mathcal{O}(x^3).$$

So

$$\begin{aligned}
c_V^{\text{int}}(T) &= k_B \left[1 - x + \tfrac{1}{2}x^2 + \mathcal{O}(x^3)\right] \left[1 - 2\left(-\tfrac{1}{2}x + \tfrac{1}{6}x^2 + \mathcal{O}(x^3)\right) + 3\left(-\tfrac{1}{2}x + \tfrac{1}{6}x^2 + \mathcal{O}(x^3)\right)^2 + \mathcal{O}(x^3)\right] \\
&= k_B \left[1 - x + \tfrac{1}{2}x^2 + \mathcal{O}(x^3)\right] \left[1 + x - \tfrac{1}{3}x^2 + 3\left(\tfrac{1}{4}x^2 + \mathcal{O}(x^3)\right) + \mathcal{O}(x^3)\right] \\
&= k_B \left[1 - x + \tfrac{1}{2}x^2 + \mathcal{O}(x^3)\right] \left[1 + x + \tfrac{5}{12}x^2 + \mathcal{O}(x^3)\right] \\
&= k_B \left[1 + (x - x) + (\tfrac{5}{12}x^2 + \tfrac{1}{2}x^2 - x^2) + \mathcal{O}(x^3)\right] \\
&= k_B \left[1 - \tfrac{1}{12}x^2 + \mathcal{O}(x^3)\right].
\end{aligned}$$

The leading order correction is negative, so as the temperature goes down, the heat capacity will start off by falling below the equipartition line $c_V^{\text{int}}(T) = k_B$.

e. So the graph is