2.16. Finite-N Behavior of Thermodynamic Quantities

Using [see (2.397)]

$$\sinh\left(\frac{\epsilon\,\tilde{\omega}_e}{2}\right) = \frac{1}{2}\epsilon\,\omega \qquad \text{where} \qquad \beta\,\hbar = (N+1)\,\epsilon$$

we have

$$\tilde{\omega}_e = \frac{2}{\epsilon}\sinh^{-1}\left(\frac{1}{2}\epsilon\,\omega\right) \qquad \frac{\partial\,\epsilon}{\partial\,\beta} = \frac{\hbar}{N+1} = \frac{\epsilon}{\beta} \tag{2.598a}$$

$$\cosh\left(\frac{\epsilon\,\tilde{\omega}_e}{2}\right) = \sqrt{1+\left(\frac{\epsilon\,\omega}{2}\right)^2}$$

$$\rightarrow \qquad \frac{\partial\,\tilde{\omega}_e}{\partial\,\beta} = \left[-\frac{2}{\epsilon^2}\sinh^{-1}\left(\frac{1}{2}\epsilon\,\omega\right) + \frac{2}{\epsilon}\frac{\omega}{\sqrt{\epsilon^2\,\omega^2+4}}\right]\frac{\epsilon}{\beta}$$

$$= -\frac{\tilde{\omega}_e}{\beta} + \frac{\omega}{\beta\cosh\left(\frac{\epsilon\,\tilde{\omega}_e}{2}\right)}$$

$$\frac{\partial(\beta\,\tilde{\omega}_e)}{\partial\,\beta} = \tilde{\omega}_e + \beta\,\frac{\partial\,\tilde{\omega}_e}{\partial\,\beta} = \frac{\omega}{\cosh\left(\frac{\epsilon\,\tilde{\omega}_e}{2}\right)} \tag{2.598b}$$

$$\frac{\partial(\epsilon\,\tilde{\omega}_e)}{\partial\,\beta} = \frac{\partial\,\epsilon}{\partial\,\beta}\,\tilde{\omega}_e + \epsilon\,\frac{\partial\,\tilde{\omega}_e}{\partial\,\beta} = \frac{\epsilon\,\omega}{\beta\cosh\left(\frac{\epsilon\,\tilde{\omega}_e}{2}\right)} = \frac{2}{\beta}\tanh\left(\frac{\epsilon\,\tilde{\omega}_e}{2}\right) \tag{2.598}$$

The internal energy E is related to the free energy F by

$$F = E - T\,S = E + T\,\frac{\partial\,F}{\partial\,T} = E - \beta\,\frac{\partial\,F}{\partial\,\beta} \qquad (\,S = \text{entropy}\,)$$

$$= \frac{1}{\beta}\ln\left[2\sinh\left(\frac{\beta\,\hbar\,\tilde{\omega}_e}{2}\right)\right] \qquad \text{[(2.482) used.]}$$

$$\rightarrow \qquad E = \frac{\partial}{\partial\,\beta}(\beta\,F)$$

$$= \frac{\partial}{\partial\,\beta}\ln\left[2\sinh\left(\frac{\beta\,\hbar\,\tilde{\omega}_e}{2}\right)\right]$$

$$= \frac{1}{\sinh\left(\frac{\beta\,\hbar\,\tilde{\omega}_e}{2}\right)}\,\frac{\hbar}{2}\,\frac{\partial(\beta\,\tilde{\omega}_e)}{\partial\,\beta}\cosh\left(\frac{\beta\,\hbar\,\tilde{\omega}_e}{2}\right)$$

$$= \frac{\hbar\,\omega}{2}\,\frac{\coth\left(\frac{\beta\,\hbar\,\tilde{\omega}_e}{2}\right)}{\cosh\left(\frac{\epsilon\,\tilde{\omega}_e}{2}\right)} \tag{2.599}$$

The specific heat C at constant volume is given by

$$C = T\,\frac{\partial\,S}{\partial\,T} = \frac{\partial\,E}{\partial\,T} = -k_B\,\beta^2\,\frac{\partial\,E}{\partial\,\beta} = -k_B\,\beta^2\,\frac{\partial^2\,(\beta\,F)}{\partial\,\beta^2} \tag{2.600}$$

$$= -k_B\,\beta^2\,\frac{\hbar\,\omega}{2}\left\{-\frac{\operatorname{csch}\left(\frac{\beta\,\hbar\,\tilde{\omega}_e}{2}\right)}{\cosh\left(\frac{\epsilon\,\tilde{\omega}_e}{2}\right)}\,\frac{\hbar}{2}\,\frac{\partial(\beta\,\tilde{\omega}_e)}{\partial\beta} - \frac{\coth\left(\frac{\beta\,\hbar\,\tilde{\omega}_e}{2}\right)}{\cosh^2\left(\frac{\epsilon\,\tilde{\omega}_e}{2}\right)}\sinh\left(\frac{\epsilon\,\tilde{\omega}_e}{2}\right)\frac{1}{2}\,\frac{\partial(\epsilon\,\tilde{\omega}_e)}{\partial\beta}\right\}$$

$$= k_B\,\beta^2\,\frac{\hbar\,\omega}{2}\left\{\frac{\operatorname{csch}^2\left(\frac{\beta\,\hbar\,\tilde{\omega}_e}{2}\right)}{\cosh\left(\frac{\epsilon\,\tilde{\omega}_e}{2}\right)}\,\frac{\hbar\,\omega}{2\cosh\left(\frac{\epsilon\,\tilde{\omega}_e}{2}\right)}+\frac{\coth\left(\frac{\beta\,\hbar\,\tilde{\omega}_e}{2}\right)}{\cosh^2\left(\frac{\epsilon\,\tilde{\omega}_e}{2}\right)}\,\frac{\epsilon\,\omega}{2}\,\frac{1}{\beta}\tanh\left(\frac{\epsilon\,\tilde{\omega}_e}{2}\right)\right\}$$

$$= k_B\,\frac{(\beta\,\hbar\,\omega)^2}{4\cosh^2\left(\frac{\epsilon\,\tilde{\omega}_e}{2}\right)}\left\{\operatorname{csch}^2\left(\frac{\beta\,\hbar\,\tilde{\omega}_e}{2}\right)+\frac{\epsilon}{\hbar\,\beta}\coth\left(\frac{\beta\,\hbar\,\tilde{\omega}_e}{2}\right)\tanh\left(\frac{\epsilon\,\tilde{\omega}_e}{2}\right)\right\} \qquad (2.600a)$$

Using

$$\tilde{\omega}_e = \frac{2\,(N+1)}{\hbar\,\beta}\sinh^{-1}\left(\frac{\hbar\,\beta\,\omega}{2\,(N+1)}\right) \qquad\qquad \epsilon = \frac{\beta\,\hbar}{N+1}$$

we can express E & C as a function of N:

$$E = \frac{\hbar\,\omega}{2}\,\frac{\coth\left[(N+1)\sinh^{-1}\left(\frac{\hbar\,\beta\,\omega}{2\,(N+1)}\right)\right]}{\cosh\left[\sinh^{-1}\left(\frac{\hbar\,\beta\,\omega}{2\,(N+1)}\right)\right]} \qquad (2.600b)$$

$$C = k_B\,\frac{(\beta\,\hbar\,\omega)^2}{4\cosh^2\left[\sinh^{-1}\left(\frac{\hbar\,\beta\,\omega}{2\,(N+1)}\right)\right]}\left\{\operatorname{csch}^2\left[(N+1)\sinh^{-1}\left(\frac{\hbar\,\beta\,\omega}{2\,(N+1)}\right)\right]\right. \qquad (2.600c)$$

$$\left.+\frac{1}{N+1}\coth\left[(N+1)\sinh^{-1}\left(\frac{\hbar\,\beta\,\omega}{2\,(N+1)}\right)\right]\tanh\left[\sinh^{-1}\left(\frac{\hbar\,\beta\,\omega}{2\,(N+1)}\right)\right]\right\}$$

At high T, or $\beta \to 0$,

$$\epsilon \to 0 \qquad\qquad \tilde{\omega}_e \to \omega$$

so that (2.599) & (2.600a) become

$$E \to \frac{\hbar\,\omega}{2}\,\frac{\left(\frac{\beta\,\hbar\,\omega}{2}\right)^{-1}}{1} = \frac{1}{\beta} = k_B\,T \qquad (2.602)$$

$$C \to k_B\,\frac{(\beta\,\hbar\,\omega)^2}{4}\left\{\left(\frac{\beta\,\hbar\,\omega}{2}\right)^{-2}+\frac{\epsilon}{\hbar\,\beta}\left(\frac{\beta\,\hbar\,\omega}{2}\right)^{-1}\left(\frac{\epsilon\,\omega}{2}\right)\right\} = k_B \qquad (2.603)$$

$$F \to \frac{1}{\beta}\ln\left[2\left(\frac{\beta\,\hbar\,\omega}{2}\right)\right] = \frac{1}{\beta}\ln(\beta\,\hbar\,\omega) \qquad (2.601)$$

These limits obey the equipartition law which states that each quadratic term in the Hamiltonian contributes $\frac{1}{2}\,k_B\,T$ to E. When phrased in terms of C, it is called the Dulong-Petit law.

We now wish to plot E & C as a function of T with N as a parameter using (2.600b-c).
As always, the 1st thing to do is to normalize all variables and make them dimensionless.

Since the only energy scale is $\hbar\,\omega$, we set

$$\hat{E} = \frac{E}{\hbar\,\omega} \qquad\qquad \hat{C} = \frac{C}{k_B}$$

$$\hat{\beta} = \beta\,\hbar\,\omega \qquad \to \qquad \hat{T} = \frac{1}{\hat{\beta}} = \frac{k_B\,T}{\hbar\,\omega}$$

(2.600b-c) thus become

$$\hat{E} = \frac{1}{2}\,\frac{\coth\left[(N+1)\sinh^{-1}\left(\frac{1}{2\,(N+1)\,\hat{T}}\right)\right]}{\cosh\left[\sinh^{-1}\left(\frac{1}{2\,(N+1)\,\hat{T}}\right)\right]} \qquad (A)$$

$$\hat{C} = \frac{1}{4\,\hat{T}^2 \cosh^2\left[\sinh^{-1}\left(\frac{1}{2(N+1)\hat{T}}\right)\right]} \left\{ \operatorname{csch}^2\left[(N+1)\sinh^{-1}\left(\frac{1}{2(N+1)\hat{T}}\right)\right] + \frac{1}{N+1}\coth\left[(N+1)\sinh^{-1}\left(\frac{1}{2(N+1)\hat{T}}\right)\right]\tanh\left[\sinh^{-1}\left(\frac{1}{2(N+1)\hat{T}}\right)\right]\right\} \quad \text{(B)}$$

Mathematica code for the plots can be found in the file “2.16._Code.nb”.

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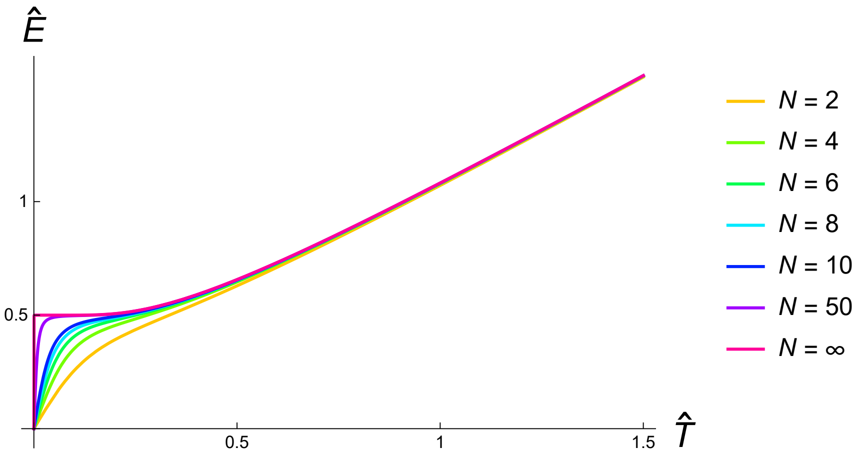

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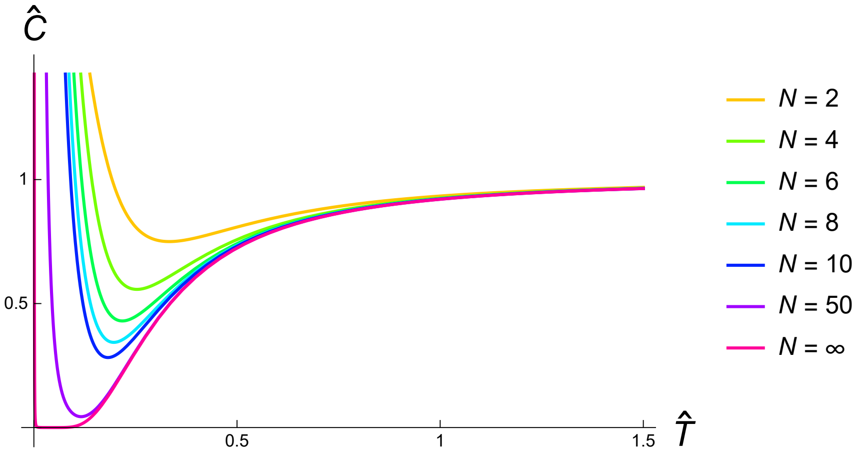

For low T, or $\beta \to \infty$,

$$\epsilon \to \infty \qquad \tilde{\omega}_e = \frac{2}{\epsilon}\ln\left(\frac{1}{2}\epsilon\,\omega + \sqrt{1+\frac{1}{4}\epsilon^2\,\omega^2}\right) \to \frac{2}{\epsilon}\ln(\epsilon\,\omega) \quad \text{(2.604a)}$$

$$\cosh\left(\frac{\epsilon\,\tilde{\omega}_e}{2}\right) \to \frac{1}{2}\exp\left(\frac{\epsilon\,\tilde{\omega}_e}{2}\right) \to \frac{1}{2}\epsilon\,\omega \quad \text{(2.604)}$$

Hence,

$$E \xrightarrow[T\to 0]{} \frac{\hbar\,\omega}{2}\,\frac{\coth\left[\frac{\beta\hbar}{\epsilon}\ln(\epsilon\,\omega)\right]}{\frac{1}{2}\epsilon\,\omega} = \frac{\hbar}{\epsilon}\coth\left[(N+1)\ln(\epsilon\,\omega)\right]$$

$$= \frac{N+1}{\beta}\coth\left[(N+1)\ln(\epsilon\,\omega)\right] \to \frac{N+1}{\beta} \to 0 \quad \text{(2.605)}$$

$$\therefore \qquad C = \frac{\partial E}{\partial T} \xrightarrow[T\to 0]{} k_B\,(N+1) \quad \text{(2.606)}$$

which are both strongly N-dependent.

(2.598a) can be expanded as a power series:

$$\tilde{\omega}_e = \frac{2}{\epsilon}\left[\frac{1}{2}\epsilon\,\omega - \frac{1}{6}\left(\frac{1}{2}\epsilon\,\omega\right)^3 + \ldots\right]$$

$$= \omega - \frac{1}{24}\epsilon^2\,\omega^3 + \ldots \tag{2.607}$$

$$= \omega - \frac{1}{24}\left(\frac{\beta\hbar}{N+1}\right)^2 \omega^3 + \ldots \tag{2.608}$$

Thus, for high T or $\beta \to 0$, $\tilde{\omega}_e$ converges to ω as $(N+1)^{-2} \approx N^{-2}$ for large N. This means all thermodynamic quantities also converge as N^{-2}, in accordance with the Trotter formula (2.26).