Ideal Gas

Final

Stat Physics

(Dated: 03-20-2008)

Abstract

Euler-Maclaurin formula

$$\sum_{k=1}^{n-1} f(k) \approx \int_0^n f(k)\,dk - \frac{1}{2}\left[f(n) + f(0)\right] + \frac{1}{12}\left[f'(n) - f'(0)\right] - \frac{1}{720}\left[f'''(n) - f'''(0)\right] + \ldots$$

$$\sum_{k=0}^{n-1} f(k) \approx \int_0^n f(k)\,dk - \frac{1}{2}\left[f(n) - f(0)\right] + \frac{1}{12}\left[f'(n) - f'(0)\right] - \frac{1}{720}\left[f'''(n) - f'''(0)\right] + \ldots$$

In cases below, $n = \infty$ and $f^{(j)}(\infty) = 0$, $j = 0, 1, 2, \ldots$

1. Consider ideal gas of diatomic molecules composed of unlike atoms and whose moment of inertia is I.

   (a) In the limit $T >> \hbar^2/2I$, evaluate the first quantum correction to the rotational specific heat per molecule (see Footnote on p. 140).

   Hint: Use Euler-Maclaurin formula.

   (b) Using eq. (47.3), numerically evaluate and plot rotational specific heat (see Fig. 4 on p.141).

Solution

Introduce dimensionless parameter

$$\alpha = \frac{\hbar^2}{2IT} << 1$$

Partition function can be converted to integral form using change of variable

$$x = \sqrt{\alpha}\left(K + \frac{1}{2}\right)$$

.Namely, using Euler-Maclaurin formula to the 3rd order correction to the integral,

$$\begin{aligned}
Z_{rot} &= 2\exp\left(\frac{\alpha}{4}\right)\sum_0^\infty \left(K+\frac{1}{2}\right)\exp\left[-\alpha\left(K+\frac{1}{2}\right)^2\right] \\
&\approx 2\alpha^{-1/2}\exp\left(\frac{\alpha}{4}\right)\left[\alpha^{-1/2}\int_{\sqrt{\alpha}/2}^{\infty} dx x\exp\left(-x^2\right) + \alpha^{1/2}\left(\frac{1}{4}-\frac{1}{12}+\frac{\alpha}{24}-\frac{\alpha}{120}\right)\exp\left(-\frac{\alpha}{4}\right)\right] \\
&= 2\exp\left(\frac{\alpha}{4}\right)\left[\frac{\alpha^{-1}}{2}\int_{\alpha/4}^{\infty} dy\exp\left(-y\right) + \left(\frac{1}{6}+\frac{\alpha}{30}\right)\exp\left(-\frac{\alpha}{4}\right)\right] \\
&= \alpha^{-1} + \frac{1}{3} + \frac{\alpha}{15}
\end{aligned}$$

whereof, with notation $\theta = T^{-1}$

$$\log Z_{rot} \approx -\log\alpha + \frac{\alpha}{3} + \frac{\alpha^2}{90} = -\log\left(\frac{\hbar^2\theta}{2I}\right) + \frac{\hbar^2\theta}{6I} + \frac{\theta^2}{90}\left(\frac{\hbar^2}{2I}\right)^2$$

and

$$c_{v,rot} = \frac{1}{T^2}\frac{\partial^2 \log Z_{rot}}{\partial\theta^2} \approx 1 + \frac{1}{45}\left(\frac{\hbar^2}{2IT}\right)^2 \tag{1}$$

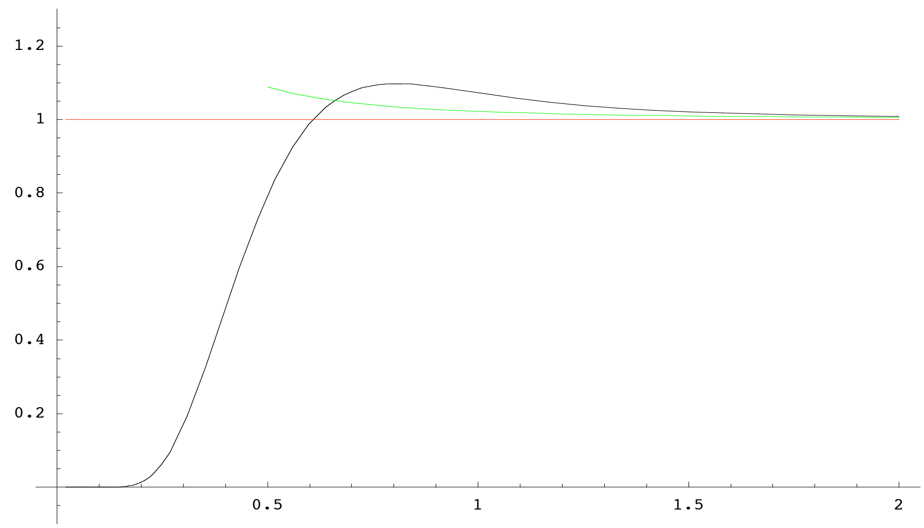

FIG. 1: Rotational specific heat per molecule of an ideal gas of diatomic molecules in 3D vis-a-vis high-temperature approximation 1 (green) and asymptotic behavior (red).

2. Consider now the case when the gas described in the preceding problem is in two dimensions.

   (a) Write down the rotational partition function as a sum and numerically evaluate and plot rotational specific heat.

   For the rotational specific heat:

   (b) In the limit $T << \hbar^2/2I$, find the leading term.

   (c) In the limit $T >> \hbar^2/2I$, evaluate the classical result and the first quantum correction.

Solution

The energy states of the rotator are

$$E_m = \frac{\hbar^2 m^2}{2I}$$

and are doubly degenerate, except $m = 0$.Therefore,

$$Z_{rot} = 1 + 2\sum_{m=1}^{\infty} \exp\left[-\alpha m^2\right]$$

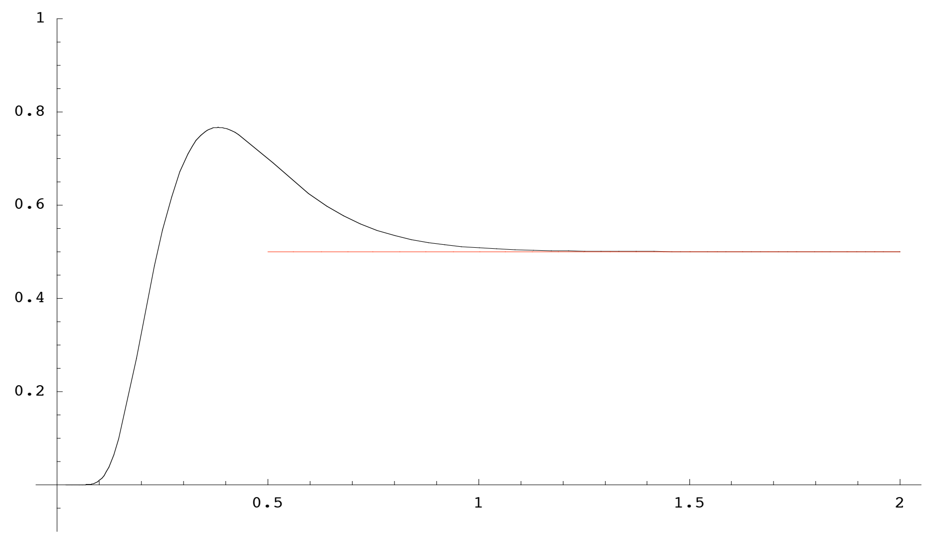

FIG. 2: Rotational specific heat per molecule of an ideal gas of diatomic molecules in 2D vis-a-vis high-temperature approximation (2), which obviously coincides with asymptotic behavior (red).

For $T << \hbar^2/2I$ ($\alpha >> 1$),

$$Z_{rot} \cong 1 + 2\exp(-\alpha)$$

$$\log Z_{rot} \cong 2\exp(-\alpha) = 2\exp\left(-\frac{\hbar^2\theta}{2I}\right)$$

$$c_{v,rot} = \frac{1}{T^2}\frac{\partial^2 \log Z_{rot}}{\partial\theta^2} = 2\left(\frac{\hbar^2}{2IT}\right)^2 \exp\left(-\frac{\hbar^2}{2IT}\right) = 2\alpha^2\exp(-\alpha)$$

For $T >> \hbar^2/2I$ ($\alpha << 1$), partition function can be converted to integral form using Euler-Maclaurin formula

$$Z_{rot} \approx 1 + 2\alpha^{-1/2}\int_0^\infty dx \exp\left(-x^2\right) - 2\frac{1}{2} = \sqrt{\frac{\pi}{a}}$$

with no further corrections since $f^{(2j+1)}(0) = 0$, $j = 0, 1, 2, \ldots$

$$\log Z_{rot} \approx -\frac{1}{2}\log\frac{\alpha}{\pi} = -\frac{1}{2}\log\left(\frac{\hbar^2\theta}{2\pi I}\right)$$

$$c_{v,rot} = \frac{1}{T^2}\frac{\partial^2 \log Z_{rot}}{\partial\theta^2} \approx \frac{1}{2} \tag{2}$$

3. Evaluate specific heat per particle in an infinite one-dimensional square well of size L in the limits of high and low temperatures.

Solution

Partition function (compare to the preceding problem)

$$Z = \sum_{n=1}^{\infty} \exp\left[-\alpha n^2\right]$$

where

$$\alpha = \frac{\hbar^2 \pi^2}{2mL^2 T}$$

For $\alpha >> 1$ (low temperature),

$$Z \cong \exp\left(-\alpha\right)\left(1 + \exp\left(-3\alpha\right)\right)$$

$$\log Z \cong -\alpha + \exp\left(-3\alpha\right) = -\frac{\hbar^2\pi^2\theta}{2mL^2} + \exp\left(-\frac{3\hbar^2\pi^2\theta}{2mL^2}\right)$$

$$c = \frac{1}{T^2}\frac{\partial^2 \log Z}{\partial \theta^2} = 9\alpha^2 \exp\left(-3\alpha\right)$$

For $\alpha << 1$ (high temperature),

$$Z_{1d} \approx \alpha^{-1/2}\int_0^\infty dx \exp\left(-x^2\right) - \frac{1}{2} = \frac{1}{2}\left(\sqrt{\frac{\pi}{a}} - 1\right) = \frac{1}{2}\sqrt{\frac{\pi}{a}}\left(1 - \sqrt{\frac{\alpha}{\pi}}\right)$$

$$c = \frac{1}{2} + \left(\frac{\hbar^2}{8\pi I T}\right)^{1/2} = \frac{1}{2} + \frac{1}{4}\sqrt{\frac{\alpha}{\pi}} \qquad (3)$$

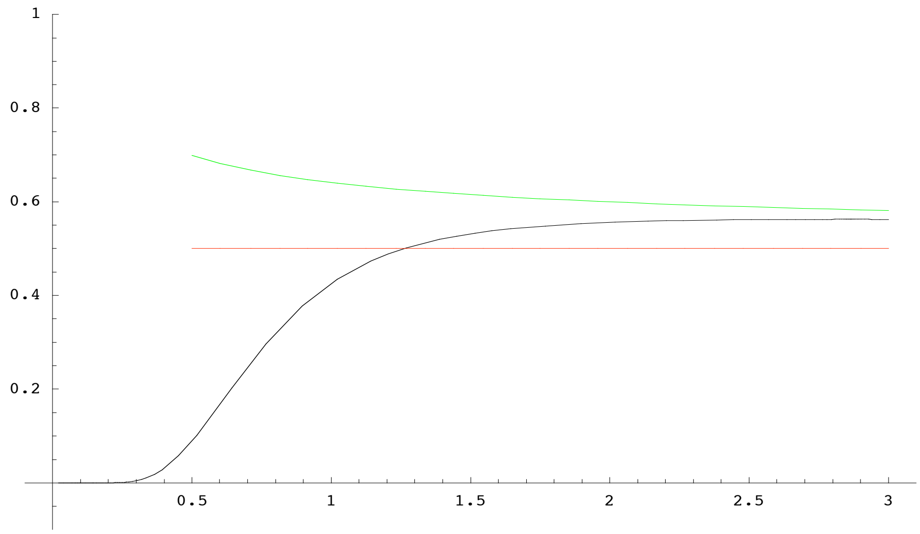

FIG. 3: Specific heat per particle in an infinite, 1d square well vis-a-vis high-temperature approximation 3 (green) and asymptotic behavior (red).

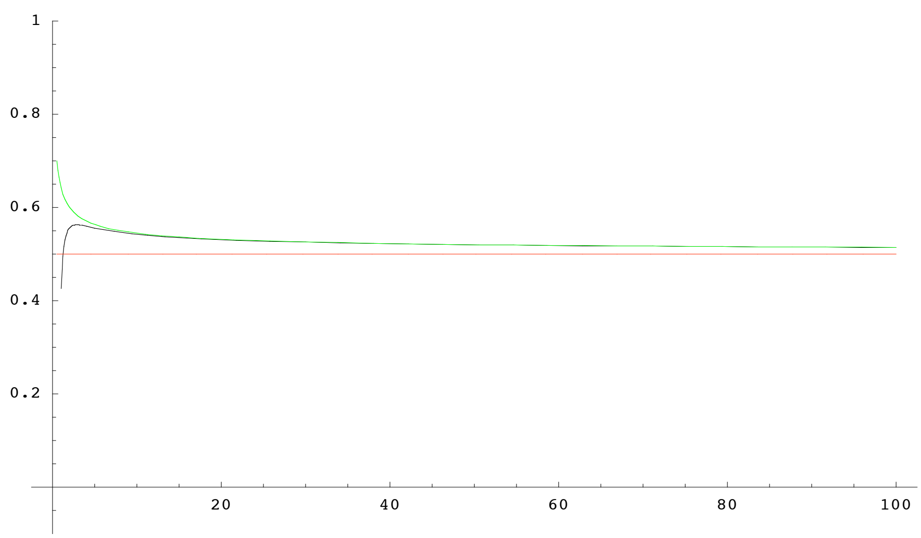

FIG. 4: Same as above; notice slow approach to asymptotic behavior.