M98Q3 - Anharmonic Oscillator (Solution by Jim Wu)

Using the anharmonic potential $V(x) = cx^2 + gx^3 + fx^4$, for a one-dimensional classical harmonic oscillator, find the approximate heat capacity at low temperatures including terms of order T.

Solution:

For a one-dimensional anharmonic oscillator, the classical partition function for single particle is

$$\zeta = \frac{1}{2\pi\hbar}\int dp\, e^{-\frac{\beta p^2}{2m}}\int dx\, e^{-\beta(cx^2+gx^3+fx^4)} = \sqrt{\frac{mkT}{2\pi\hbar^2}}\int dx\, e^{-\beta cx^2}e^{-\beta(gx^3+fx^4)}$$

Assuming that the harmonic potential is the dominant term, lets expand the second exponential term containing anharmonic terms:

$$\begin{aligned} e^{-\beta(gx^3+fx^4)} &\approx 1-\beta(gx^3+fx^4)+\frac{1}{2}\beta^2(gx^3+fx^4)^2 \\ &\approx 1-\beta gx^3-\beta fx^4+\frac{1}{2}\beta^2g^2x^6 \end{aligned}$$

Note that I expanded up to second order of the exponential term and then kept the terms that will give me a nonzero integral for g and f. Note that the integral of the x^3 term will certainly give a zero because we have an even function (a gaussian) times and odd function (a cubic term) integrated over all space.

So, we get

$$\begin{aligned} \zeta &\approx \sqrt{\frac{mkT}{2\pi\hbar^2}}\int dx\, e^{-\beta cx^2}\left(1-\beta gx^3-\beta fx^4+\frac{1}{2}\beta^2g^2x^6\right) \\ &= \sqrt{\frac{mkT}{2\pi\hbar^2}}\left[\sqrt{\frac{\pi}{\beta c}}-0-\beta f\left(\frac{d}{d(\beta c)}\right)^2\sqrt{\frac{\pi}{\beta c}}-\frac{1}{2}\beta^2g^2\left(\frac{d}{d(\beta c)}\right)^3\sqrt{\frac{\pi}{\beta c}}\right] \\ &= \sqrt{\frac{mkT}{2\pi\hbar^2}}\left[\sqrt{\frac{\pi}{\beta c}}-\frac{3}{4}\beta f\sqrt{\frac{\pi}{(\beta c)^5}}+\frac{15}{16}\beta^2g^2\sqrt{\frac{\pi}{(\beta c)^7}}\right] \\ &= \frac{1}{\beta}\sqrt{\frac{m}{2\hbar^2c}}\left(1-\frac{3}{4}\frac{f}{\beta c^2}+\frac{15}{16}\frac{g^2}{\beta c^3}\right) \end{aligned}$$

The average energy of the particle is

$$\begin{aligned} E = -\frac{\partial\ln\zeta}{\partial\beta} &= -\frac{\partial}{\partial\beta}\left[\ln\sqrt{\frac{m}{2\hbar^2c}}-\ln\beta+\ln\left(1-\frac{3}{4}\frac{f}{\beta c^2}+\frac{15}{16}\frac{g^2}{\beta c^3}\right)\right] \\ &\approx -\frac{\partial}{\partial\beta}\left[\ln\sqrt{\frac{m}{2\hbar^2c}}-\ln\beta-\frac{3}{4}\frac{f}{\beta c^2}+\frac{15}{16}\frac{g^2}{\beta c^3}\right] \\ &= \frac{1}{\beta}-\frac{3}{4}\frac{f}{\beta^2c^2}+\frac{15}{16}\frac{g^2}{\beta^2c^3} \\ &= kT+(kT)^2\left(\frac{15g^2}{16c^3}-\frac{3f}{4c^2}\right) \end{aligned}$$

where I have exploited $\ln(1+x) \sim x$ for small x. Hence, the heat capacity per particle to first order in T is

$$C = \frac{\partial E}{\partial T} = k + k^2 T \left(\frac{15g^2}{8c^3} - \frac{3f}{2c^2} \right)$$

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