SM-2 January 2018

1D anharmonic oscillator.

Potential energy: $u(x) = cx^2 - gx^3 + fx^4$. $f$ & $g > 0$ & small.

a. Find classical partition function.

$$H = \frac{p^2}{2m} + u = \frac{p^2}{2m} + cx^2 - gx^3 + fx^4 = \frac{p^2}{2m} + cq^2 - gq^3 + fq^4$$

$$Z = \frac{1}{h}\iint e^{-\beta H}\,dp\,dq = \frac{1}{h}\underbrace{\int_{-\infty}^{\infty} e^{-\beta p^2/2m}\,dp}_{\sqrt{\frac{2m\pi}{\beta}}}\int e^{-\beta c q^2} e^{\beta g q^3} e^{-\beta f q^4}\,dq$$

$$= \sqrt{\frac{2\pi m}{\beta h^2}}\int_{-\infty}^{\infty} e^{-\beta c q^2} e^{\beta g q^3} e^{-\beta f q^4}\,dq$$

expand $2^{nd}$ & $3^{rd}$ terms

$e^{\beta g q^3} = 1 + \beta g q^3$

$e^{-\beta f q^4} = 1 - \beta f q^4$

$e^{-\beta c q^2}(1+\beta g q^3)(1-\beta f q^4)$

$e^{-\beta c q^2}(1 + \beta g q^3 - \beta f q^4 - \beta^2 f g q^7)$

$$= \sqrt{\frac{2\pi m}{\beta h^2}}\left[\underbrace{\int_{-\infty}^{\infty} e^{-\beta c q^2}dq}_{\sqrt{\frac{\pi}{\beta c}}} + \beta g\underbrace{\int_{-\infty}^{\infty} q^3 e^{-\beta c q^2}dq}_{0} - \beta f\underbrace{\int_{-\infty}^{\infty} q^4 e^{-\beta c q^2}dq}_{\frac{3}{4}\sqrt{\frac{\pi}{\beta^5 c^5}}} - fg\beta^2\underbrace{\int_{-\infty}^{\infty} q^7 e^{-\beta c q^2}dq}_{0}\right]$$

$$= \sqrt{\frac{2m\pi}{\beta h^2}}\left[\sqrt{\frac{\pi}{\beta c}} - \frac{3}{4}\sqrt{\frac{f^2\pi}{\beta^3 c^5}}\right] = \frac{\pi}{\beta h}\sqrt{\frac{2m}{c}} - \frac{3\pi f_1}{4\beta^2 h}c^{-5/2}\sqrt{m}$$

$$= T\left[\frac{k_B\pi}{h}\sqrt{\frac{2m}{c}} - \frac{3k_B^2\pi f\sqrt{m}}{4h}c^{-5/2}T\right] = T\frac{k_B\pi}{h}\sqrt{\frac{2m}{c}}\left[1 - \frac{3k_B f}{\sqrt{2}\,4c^2}T\right] = TB\left[1 - AT\right]$$

b. Find specific heat to leading orders.

$$C_v = \frac{\partial U}{\partial T} \qquad -U = \frac{\partial}{\partial\beta}\ln Z = k_B T^2\frac{\partial}{\partial T}\ln Z$$

$$\ln Z = \ln(TB + ABT^2) \rightarrow \frac{\partial}{\partial T}\ln(TB + ABT^2) = \frac{1}{TB + ABT^2}\cdot(B + 2ABT)$$

$$U = k_B T^2\left(\frac{1+2AT}{T+AT^2}\right) = \frac{k_B T^2(1+2AT)}{T(1+AT)} = k_B T(1+2AT)(1+AT)^{-1} \approx k_B T(1+2AT)(1-AT)$$

$$= k_B T\left[1 + AT + O(T^2)\right]$$

$$\frac{\partial U}{\partial T} = k_B + 2AT + O(T^2)$$

Find leading term $\langle x \rangle$

$$\langle x \rangle = \frac{1}{Z}\frac{1}{h}\sqrt{\frac{2m\pi}{\beta}}\left[\cancelto{0}{\int_{-\infty}^{\infty} q e^{-\beta c q^2}\,dq} + \int_{-\infty}^{\infty} q^4 \beta g e^{-\beta c q^2}\,dq + \cancelto{0}{\int_{-\infty}^{\infty} q^5 \beta f e^{-\beta c q^2}\,dq} + O(\beta^2)\right]$$

$$= \frac{\beta g \int_{-\infty}^{\infty} q^4 e^{-\beta c q^2}\,dq}{\sqrt{\frac{\pi}{\beta c}} - \beta f \frac{3}{4}\left(\frac{\pi}{\beta^5 c^5}\right)^{\frac{1}{2}}} = \frac{\beta g \frac{3}{4}\left(\frac{\pi}{\beta^5 c^5}\right)^{\frac{1}{2}}}{\sqrt{\frac{\pi}{\beta c}} \underbrace{- \beta f \frac{3}{4}\left(\frac{\pi}{\beta^5 c^5}\right)^{\frac{1}{2}}}_{\text{ignore for leading term.}}} \approx \frac{3}{4}\beta g\left(\frac{\beta c}{\beta^5 c^5}\right)^{\frac{1}{2}} = \frac{3}{4}\beta g \frac{1}{\beta^2 c^2} = \frac{3}{4} k_B T \frac{g}{c^2}$$