Chem 576 HW3

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Problem 5.9

Consider a mass m attached to one end of a massless spring, with the other end fixed, and take $x = 0$ to mark the unextended length of the spring. Apply a constant force F to the mass which stretches the spring. The hamiltonian for this one-dimensional system is $H = p^2/2m + \kappa x^2/2 - Fx$

(a)

For the Hamiltonian

$$H = \frac{p^2}{2m} + \frac{\kappa x^2}{2} - Fx$$

The partition function $(p.f.)_F$

$$(p.f.)_F = \frac{1}{h}\int_{-\infty}^{\infty} e^{-p^2/2mk_BT}dp \underbrace{\int_{-\infty}^{\infty} e^{-\kappa x^2/2k_BT}dx \int_{-\infty}^{\infty} e^{Fx/k_BT}dx}_{1}$$

$$\begin{aligned}
1 &= \int_{-\infty}^{\infty} e^{(-\kappa x^2+2Fx)/2k_BT}dx \\
&= \int_{-\infty}^{\infty} e^{-[\kappa x^2-2Fx+F^2/\kappa-F^2/\kappa]/2k_BT}dx \\
&= \int_{-\infty}^{\infty} e^{-\kappa[x^2-2Fx/\kappa+(F/\kappa)^2]/2k_BT}\ e^{F^2/2\kappa k_BT}dx \\
&= e^{F^2/2\kappa k_BT}\int_{-\infty}^{\infty} e^{-\kappa(x-F/\kappa)^2/2k_BT}dx
\end{aligned}$$

$$(p.f.)_F = \frac{1}{h}e^{F^2/2\kappa k_BT}\int_{-\infty}^{\infty} e^{-p^2/2mk_BT}dp\int_{-\infty}^{\infty} e^{-\kappa(x-F/\kappa)^2/2k_BT}dx$$

For a free oscillator with $F = 0$,

$$H = \frac{p^2}{2m} + \frac{\kappa x^2}{2}$$

$$(p.f.)_{osc} = \frac{1}{h}\int_{-\infty}^{\infty} e^{-p^2/2mk_BT}dp\int_{-\infty}^{\infty} e^{-\kappa x^2/2k_BT}dx$$

If we set $x_F = x - F/\kappa$, then $dx_F = dx$, and plug in to the partition function,

$$(p.f.)_F = e^{F^2/2\kappa k_BT}\cdot\underbrace{\frac{1}{h}\int_{-\infty}^{\infty} e^{-p^2/2mk_BT}dp\int_{-\infty}^{\infty} e^{-\kappa x_F^2/2k_BT}dx_F}_{(p.f.)_{osc}}$$

Therefore,

$$(p.f.)_F = e^{F^2/2\kappa k_B T}(p.f.)_{osc}$$

(b)

$$\begin{aligned}
A(N,T,V)_F &= -Nk_BT\ln(p.f.)_F \\
&= -Nk_BT\ln\left(e^{F^2/2\kappa k_B T}(p.f.)_{osc}\right) \\
&= -Nk_BT\left(\ln(p.f.)_{osc} + \frac{F^2}{2\kappa k_B T}\right) \\
&= -Nk_BT\ln(p.f.)_{osc} - \frac{NF^2}{2\kappa} \\
&= A(N,T,V)_{osc} - \frac{NF^2}{2\kappa}
\end{aligned}$$

(c)

The internal energy E can be calculated from A by

$$E = -T^2\frac{\partial}{\partial T}\left(\frac{A}{T}\right)_V$$

Denote E_F as the internal energy under constant force F and E_{osc} as the internal energy for free oscillator, in which $F = 0$.

$$\begin{aligned}
E_F &= -T^2\frac{\partial}{\partial T}\left(\frac{A_F}{T}\right)_V \\
&= -T^2\frac{\partial}{\partial T}\left(\frac{A_{osc} - \frac{NF^2}{2\kappa}}{T}\right)_V \\
&= -T^2\left[\frac{\partial}{\partial T}\left(\frac{A_{osc}}{T}\right)_V - \frac{\partial}{\partial T}\left(\frac{NF^2}{2\kappa T}\right)\right] \\
&= E_{osc} - T^2\cdot\frac{NF^2}{2\kappa T^2} \\
&= E_{osc} - \frac{NF^2}{2\kappa}
\end{aligned}$$

Therefore,

$$\Delta E = E_F - E_{osc} = -\frac{NF^2}{2\kappa}$$

The derivation by balancing forces in shown in section **(d)**.
For entropy,

$$S = -\left(\frac{\partial A}{\partial T}\right)_V$$

and

$$S_F = -\frac{\partial}{\partial T}\left(A_{osc} - \frac{NF^2}{2\kappa}\right)_V = -\left(\frac{\partial A_{osc}}{\partial T}\right)_V = S_{osc}$$

Therefore,

$$\Delta S = 0$$

(d)

For a constant force F, it can be balanced by the spring where

$$F = \kappa x$$

and energy,

$$E_F = F\Delta x = \int \kappa x \; dx = \frac{1}{2}\kappa x^2 = \frac{F^2}{2\kappa}$$

When F is changed by dF,

$$dW = dE_F = d\left(\frac{F^2}{2\kappa}\right) = \frac{1}{2\kappa}dF^2 = \frac{FdF}{\kappa}$$

Therefore, for N such systems, the work done from 0 to F is

$$\Delta W = N\int_0^F dW = N\int_0^F \frac{FdF}{\kappa} = \frac{NF^2}{2\kappa}$$

(e)

Since $\Delta E = -W$, there is no heat flow in the system.
$Q = T\Delta S = 0$, and $T \neq 0$, thus $\Delta S = 0$.

Problem 5.10

(a) Start from the partition function ($p.f.$) in Prob. 5.9(a). Show the mean displacement per system is $\langle x\rangle = k_BT(\partial/\partial F)\ln(p.f.) = F/\kappa$;
(b) Similarly, show $\langle\varepsilon\rangle = k_BT^2(\partial/\partial T)\ln(p.f.) = \langle\varepsilon\rangle_{osc} - F^2/2\kappa$;
(c) Write the Helmholtz free energy per system as $a(T,V,N,F) = -k_BT\ln(p.f.)$ and work per system as dw. Show

$$\left(\frac{a}{F}\right)_{T,V,N} dF = -\left(\frac{F}{\kappa}\right) dF = -\langle x\rangle dF = -dW$$

(a)

$$\begin{aligned}\langle x\rangle &= k_BT\frac{\partial}{\partial F}\ln{(p.f.)_F} \\ &= k_BT\frac{\partial}{\partial F}\ln\left[e^{F^2/2\kappa k_BT}(p.f.)_{osc}\right]\end{aligned}$$

Since $(p.f.)_{osc}$ is free of variable F,

$$\begin{aligned}\langle x\rangle &= k_BT\frac{\partial}{\partial F}\ln\left[e^{F^2/2\kappa k_BT}\right] \\ &= \frac{F}{\kappa}\end{aligned}$$

(b)

$$\begin{aligned}\langle\varepsilon\rangle &= k_B T^2 \frac{\partial}{\partial T}\ln(p.f.)_F \\ &= k_B T^2 \frac{\partial}{\partial T}\ln\left[e^{F^2/2\kappa k_B T}(p.f.)_{osc}\right] \\ &= -\frac{F^2}{2\kappa} + k_B T^2 \frac{\partial}{\partial T}\ln\left[(p.f.)_{osc}\right] \\ &= \langle\varepsilon\rangle_{osc} - \frac{F^2}{2\kappa}\end{aligned}$$

(c)

For Helmholtz energy per system, a,

$$\begin{aligned}a(T,V,N,F) = \frac{A(T,V,N,F)}{N} &= -k_B T\ln(p.f.)_F \\ &= a(N,T,V)_{osc} - \frac{F^2}{2\kappa}\end{aligned}$$

From problem 5.9,

$$dw = \frac{FdF}{\kappa}$$

Therefore,

$$\begin{aligned}\left(\frac{\partial a(T,V,N,F)}{\partial F}\right)_{A,T,V} dF &= \left[\left(\frac{\partial a(T,V,N)_{osc}}{\partial F}\right)_{A,T,V} - \frac{d}{dF}\frac{F^2}{2\kappa}\right] dF \\ &= -\frac{F}{\kappa}dF \\ &= -\langle x\rangle dF \\ &= -dW\end{aligned}$$

and for N such systems,

$$\left(\frac{\partial A(T,V,N,F)}{\partial F}\right)_{A,T,V} dF = -N\langle x\rangle dF$$

Define induced dipole moment $\mathcal{D}$ as

$$\mathcal{D} = N\langle x\rangle$$

The analog of the thermodynamic relation is

$$dA = -SdT - PdV + \mu dN - \mathcal{D}dF$$

Problem 5.11