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# Solutions to Problem Set 4

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## 4.1 Equilibrium Fluctuations

**(a)** From lecture we had

$$\begin{aligned}\Omega(E,V,N) &= \frac{1}{N!}\frac{3N}{2E}\left(\frac{4\pi EV^{2/3}e}{3h^2N}\right)^{3N/2} dE\\ &\propto E^{3N/2-1}V^N dE\end{aligned}$$

At equilibrium we have that the number of states of the total system is maximum thus we have

$$\frac{d\ln\Omega_{total}}{dE} = \frac{d\ln\Omega}{dE} + \frac{d\ln\Omega_r}{dE} = \frac{3N/2-1}{E} - \beta_r = 0$$

This gives

$$\frac{3N/2-1}{\bar{E}} = \beta_r = \frac{1}{kT}$$

For large $N$ we have

$$\Rightarrow \bar{E} = \frac{3}{2}NkT$$

Taylor exanding $\ln\Omega \approx (3N/2)\ln E + N\ln V$ and $\ln\Omega_r$ about $E = \bar{E}$,

$$\begin{aligned}\ln\Omega_{tot}(E) &\approx \ln\Omega(\bar{E}) + \bar{\beta}(E-\bar{E}) + \frac{1}{2}\left(\overline{\frac{\partial\beta}{\partial E}}\right)(E-\bar{E})^2 + O((E-\bar{E})^3) + \ln\Omega_r(\bar{E})\\ \Rightarrow P(E) &\propto \Omega(E) \propto \Omega(\bar{E})e^{(\bar{\beta}-\bar{\beta})(E-\bar{E})}e^{\frac{1}{2}\left(\frac{3N}{2\bar{E}^2}\right)(E-\bar{E})^2}\end{aligned}$$

Where there is only a first order term for $\ln\Omega_r = \beta(E_{tot} - E)$, as the temperature of the reservoir (and therefore $\beta$) is a constant.

Thus we have (normalizing)

$$P(E) = \frac{1}{\sqrt{2\pi}\sigma_E}e^{(E-\bar{E})^2/2\sigma_E^2}$$

where

$$\boxed{\sigma_E^2 = \bar{E}^2\frac{2}{3N} = \frac{3}{2}Nk^2T^2}$$

is the variance of $E$. With standard deviation

$$\sigma_E = \sqrt{\frac{3N}{2}}kT$$

**(c)** Similarly we have

$$\begin{aligned} P(E,V) &\propto \Omega_{tot}(E,V) = \exp[\ln\Omega_{tot}] \\ &\approx \exp\Big[\ln\Omega(\bar{E},\bar{V}) + \ln\Omega_r(\bar{E},\bar{V})(\bar{p}\bar{\beta} - \bar{p}\bar{\beta})(V-\bar{V}) \\ &\qquad + \frac{1}{2}\left(\overline{\frac{\partial\beta}{\partial E}}\right)(E-\bar{E})^2 + \frac{1}{2}\left(\overline{\frac{\partial p\beta}{\partial V}}\right)(E-\bar{E})^2\Big] \\ P(E,V) &\propto e^{\frac{1}{2}\left(\overline{\frac{\partial\beta}{\partial E}}\right)(E-\bar{E})^2 + \frac{1}{2}\left(\overline{\frac{\partial p\beta}{\partial V}}\right)(E-\bar{E})^2} \end{aligned}$$

At equilibrium we must have

$$\frac{\partial\ln\Omega_{tot}}{\partial V} = \frac{\partial\ln\Omega}{\partial V} + \frac{\partial\ln\Omega_r}{\partial V} = \frac{N}{\bar{V}} - p_r\beta_r = 0$$

Giving us $p\beta = \frac{N}{V}$ which gives an equilibrium volume of

$$\bar{V} = \frac{NkT}{p}$$

Noting that $\frac{\partial\beta}{\partial V} = 0 = \frac{\partial p\beta}{\partial E}$ we must have $E$ and $V$ statistically independent. Thus

$$P(E,V) = P(E) \times P(V)$$

with

$$P(E) = P(E) = \frac{1}{\sqrt{2\pi}\sigma_E} e^{(E-\bar{E})^2/2\sigma_E^2}$$

the same as before, with the same variance, and

$$P(V) = P(E) = \frac{1}{\sqrt{2\pi}\sigma_V} e^{(V-\bar{V})^2/2\sigma_V^2}$$

with the variance

$$\boxed{\sigma_V^2 = \frac{\bar{V}^2}{N} = N\left(\frac{kT}{p}\right)^2}$$

with standard deviation (and fluctuations) of the size $\sigma_V = \sqrt{N}kT/p$.

$\square$

## 4.2 Calorimetry

**Reif §4.2:** A 750-g copper calorimeter can containing 200 g of water is in equilibrium at a temperature of $20°C$. An experimenter now places 30 g of ice at $0°C$ in the calorimeter and encloses the latter with a heat-insulating shield.

**(a)** When all the ice has melted and equilibrium has been reached, what will be the temperature of the water? (The specific heat of copper is 0.418 joules $\text{g}^{-1}$ $\text{deg}^{-1}$. Ice has a specific gravity of 0.917 and its heat of fusion is 333 joules $\text{g}^{-1}$; ie it requires 333 joules of heat ot convert 1 g of ice to water at $0°C$.)

**(b)** Compute the total entropy change resulting from the process of part (a).

**(c)** After all the ice has melted and equilibrium has been reached, how much work, in joules, must be supplied to the system (e.g., by means of a stirring rod) to restore all the water to $20°C$?

**(a)** Since the calorimeter is enclosed in a heat insulating shield we have

$$0 = \Delta Q = m_{cu}c_{cu}(T_f - 20°C) + m_w c_w (T_f - 20°C) + m_i c_w (T_f - 0°C) + m_i L_f$$

solving for $T_f$ we find

$$T_f = \frac{m_{cu}c_{cu}20°C + m_w c_w 20°C - m_i L_f}{m_{cu}c_{cu} + (m_w + m_i)c_w}$$

where $c_w = 4.186 J/g°C$. This gives

$$\boxed{T_f = 10.205°C = 283.355K}$$

**(b)** The entropy for the ice melting is

$$\Delta S_{melt} = \frac{\Delta Q}{T_{melt}} = \frac{m_i L_f}{273.15K} = 36.57 J/K.$$

The net entropy change for heating a substance from temperature $T$ to temperature $T_f$ (with no phase changes) is

$$\Delta S = \int_T^{T_f} \frac{mcdT}{T} = mc \ln T_f/T \tag{1}$$

Thus we have

$$\boxed{\Delta S_{total} = \Delta S_{melt} + m_i c_w \ln T_f/273.15K + (m_w c_w + m_{cu} + c_{cu}) \ln T_f/293.15K = 2.0727 J/K}$$

**(c)** The extra work required to restore the water to $20°C$ is

$$W = \Delta Q = (m_{cu}c_{cu} + (m_i + m_w)c_w)(20°C - 10.205°C) = 12501.6J = 12.5kJ.$$

□

## 4.3 Pulling on a Polymer

**(a)** For $N \gg 1$ , we make a Gaussian approximation for the number of miccrostates. This problem is analogous to the random walk, and to Reif §2.4 which we covered in section. We have

$$\Omega = \frac{N!}{n_1!n_2!}dn_1$$

except we wish to write $\Omega$ in terms of $E$, $N$, and $al$ only. Hence we have

$$\Omega(E) = \frac{N!}{\left(\frac{N}{2}-\frac{E}{2al}\right)!\left(\frac{N}{2}+\frac{E}{2al}\right)!}\frac{dE}{2al}$$

Applying sterling's approximation

$$\ln n! \approx n\ln n - n + \frac{1}{2}\ln(2\pi n)$$

we see

$$\begin{aligned}
\ln\Omega(E) &\approx N\ln N - n_1\ln n_1 - n_2\ln n_2 + \frac{1}{2}[\ln(2\pi N) - \ln(2\pi n_1) - \ln(2\pi n_2)] + \ln\left(\frac{dE}{2al}\right) \\
&\approx -n_1\ln\frac{n_1}{N} - n_2\ln\frac{n_2}{N} + \frac{1}{2}\ln\frac{N}{2\pi n_1 n_2} + \ln\frac{dE}{2al} \\
&\approx -\left(\frac{N}{2}-\frac{E}{2al}\right)\ln\left(\frac{1}{2}-\frac{E}{2Nal}\right) - \left(\frac{N}{2}+\frac{E}{2al}\right)\ln\left(\frac{1}{2}+\frac{E}{2Nal}\right) \\
&\qquad +\frac{1}{2}\ln\left(\frac{N}{2\pi}\right) - \frac{1}{2}\left[2\ln N + \ln\left(\frac{1}{2}-\frac{E}{2Nal}\right)\ln\left(\frac{1}{2}+\frac{E}{2Nal}\right)\right] + \ln\frac{dE}{2al}
\end{aligned}$$

expanding in terms of $E/Nal$, and only keeping factors up to size $E/N$ we eventually get

$$\ln\Omega(E) \approx N\ln 2 - \frac{1}{2}\frac{1}{N}\left(\frac{E}{al}\right)^2 - \ln\left[\frac{1}{2}\sqrt{2N\pi}\right] + \ln\frac{dE}{2al}$$

which gives

$$\boxed{\Omega(E) \approx \frac{2^N}{al\sqrt{2\pi N}}e^{-\frac{E^2}{2Nl^2a^2}}}$$

**(b)** We have

$$\begin{aligned}
S &= k_b\ln\Omega = k_b\ln\left[\frac{2^N dE}{al\sqrt{2\pi N}}\right] - \frac{k}{2N}\left(\frac{E^2}{al}\right)^2 \\
&\approx k\ln\frac{2^N}{al\sqrt{2\pi N}} - \frac{k}{2N}\left(\frac{E}{al}\right)^2
\end{aligned}$$

**(c)** To find the equilibrium value $\bar{E}$ we see that at thermal equilibrium

$$\frac{\partial \ln \Omega}{\partial E} = \beta = \frac{1}{kT}$$

where $T$ is the temperature of the solution. this yields

$$\bar{E} = -\frac{Nl^2a^2}{kT}$$

with fluctuations characterized by the variance

$$\sigma^2 = Nl^2a^2$$

Note that this expression for the variance is only valid in the limit of $\beta, \bar{E} \to 0$, because of our Gaussian expansion. A more careful analysis without using the Gaussian expansion yields

$$\sigma^2 = Na^2l^2 \cosh^2(al\beta).$$

**(d)** We have the force

$$F_x = \frac{-\partial E}{dL_x} = \frac{-\partial E}{\partial x_N} = +a$$

In terms of the average length and energies we have

$$\bar{x}_N = \frac{-\bar{E}}{a} = \beta Nl^2a^2$$

Which gives

$$\boxed{F_x = a = \frac{\bar{x}_N}{\beta Nl^2}}$$

□

## 4.4 Ideal Work

**Reif §5.2:** The molar specific heat at constant volume of a monatomic ideal gas is known to be $\frac{3}{2}R$. Suppose that one mole of such a gas is subjected to a cyclic quasistatic process which appears as a circle on the diagram of pressure $p$ versus volume $V$ shown in the figure. Find the following quantities:

**(a)** The net work (in joules) done by the gas in one cycle.

**(b)** The internal energy difference (in joules) of the gas between state $C$ and state $A$.

**(c)** The heat absorbed (in joules) by the gas in going from $A$ to $C$ via the path $ABC$ of the cycle.

**(a)** The work done by the gas is the area under the lines in the p-V diagram

$$\boxed{\Delta W = \int_{ABCD} dW = \int_{ABCD} p dV = \pi(10^3 \text{cm}^3)(10^6 \text{dynes}\cdot\text{cm}^{-2})}$$

in joules,

$$\boxed{\Delta W = \pi \times 10^9 \text{erg} = \pi \times 10^2 J}$$

**(b)** The internal energy difference per mole is given by the difference in energy $E = \frac{3}{2}RnT$

$$\boxed{\Delta E_{CA} = E_C - E_A = 9 \times 10^9 - 3 \times 10^9 = 6 \times 10^9 \text{erg}}$$

in joules $\boxed{\Delta E_{CA} = 6 \times 10^2 J}$.

**(c)** The heat absorbed in going from $A$ to $C$ can be calculated from $dQ = dE + pdV$. $dE$ integrated from $A$ to $C$ is already calculated in (b), and $\int_{ABC} pdV$ is

$$\int_{ABC} pdV = \left(\frac{\pi}{2} + 4\right) \times 10^9 \text{erg}$$

Add this with the result of (b) we get

$$\boxed{\Delta Q_{ABC} = \Delta E_{CA} + \Delta W_{ABC} = \left(\frac{\pi}{2} + 10\right) \times 10^2 J}.$$

□

## 4.5 Elastic Rod

**Reif §5.14:** In a temperature range near absolute temperature $T$, the tension force $F$ of a stretched plastic rod is realted to its length $L$ by the expresssion

$$F = aT^2(L - L_0) \tag{2}$$

where $a$ and $L_0$ are positive constants, $L_0$ being the unstretched length of the rod. When $L = L_0$, the heat capacity $C_L$ of the rod (measured at constant length) is given by the relation $C_L = bT$, where $b$ is a constant.

**(a)** Write down the fundamental thermodynamic relation for this system, expressing $dS$ in terms of $dE$ and $dL$.

**(b)** The entropy $S(T, L)$ of the rod is a function of $T$ and $L$. Compute $(\partial S/\partial L)_T$.

**(c)** Knowing $S(T_0, L_0)$, find $S(T, L)$ at *any* other temperature $T$ and length $L$. (It is most convenient to calculate first the change of entropy with temperature at the length $L_0$ where the heat capacity is known.)

**(d)** If one starts at $T = T_i$ and $L = L_i$ and stretches the thermally insulated rod quasi-statically until it attains the length $L_f$ what is the final temperature $T_f$? Is $T_f$ larger or smaller than $T_i$?

**(e)** Calculate the heat capacity $C_L(L, T)$ of the rod when its length is $L$ instead of $L_0$.

**(f)** Calculate $S(T, L)$ by writing $S(T, L) - S(T_0, L_0) = [S(T, L) - S(T_0, L)] + [S(T_0, L) - S(T_0, L_0)]$ and using the result of part (e) to compute the first term in square brackets. Show that the final answer agrees with that found in (c).

**(a)** Using $F$ as an analog for $p$ and $L$ as an analog for $V$ we see

$$\boxed{dE = TdS + FdL}$$

where we've taken the positive sign in the last term since $F$ is the force on the rod, not the force by the rod.

**(b)** Taking the energy to be $E(S(T), L) \Rightarrow E(T, L)$ we have

$$dE = \left.\frac{\partial E}{\partial T}\right|_L dT + \left.\frac{\partial E}{\partial L}\right|_T dL$$

The entropy then must be

$$dS = \frac{dE}{T} - \frac{F}{T}dL = \frac{1}{T}\left.\frac{\partial E}{\partial T}\right|_L dT + \frac{1}{T}\left(\left.\frac{\partial E}{\partial L}\right|_T - F\right) dL$$

which gives the partial derivatives

$$\left.\frac{\partial S}{\partial T}\right|_L = \frac{1}{T}\left.\frac{\partial E}{\partial T}\right|_L \qquad \left.\frac{\partial S}{\partial L}\right|_T = \frac{1}{T}\left(\left.\frac{\partial E}{\partial L}\right|_T - F\right)$$

Remembering that $F = -\nabla E$ we have $\left.\frac{\partial E}{\partial L}\right|_T = -F$ which gives us

$$\boxed{\left.\frac{\partial S}{\partial L}\right|_T = \frac{-2F}{T} = -2aT(L - L_0)}$$

**(c)** We also know $\left.\frac{\partial E}{\partial T}\right|_L = C_L$ and $C_{L_o} = bT$ hence

$$dS = -2aT(L - L_0)dL + \frac{1}{T}C_L dT$$

Starting at $S(T_0, L_0)$ and first increasing in temperature at fixed $L = L_0$ and then increasing in $L$ with fixed $T$ we have

$$\begin{aligned} S(T, L) &= S(T_0, L_0) + \int_{T_0,L_0}^{T,L_0} dS + \int_{T,L_0}^{T,L} dS \\ &= S(T_0, L_0) + \int_{T_0}^{T} b dT - \int_{L_0}^{L} 2aT(L - L_0)dL \end{aligned}$$

Giving us

$$\boxed{S(T, L) = S(T_0, L_0) + b(T - T_0) - aT(L - L_0)^2} \tag{3}$$

**(d)** By quasi-statically stretching a thermally insulated rod we see that the process must be adiabatic, thus $\Delta S = 0$ and we must have

$$S(T_0, L_0) + b(T_i - T_0) - aT_i(L_i - L_0)^2 = S(T_0, L_0) + b(T_f - T_0) - aT_f(L_f - L_0)^2$$

Canceling terms we see

$$[b - a(L_i - L_0)^2]T_i = [b - a(L_f - L_0)^2]T_f$$

$$\Rightarrow \boxed{T_f = \frac{b - a(L_i - L_0)^2}{b - a(L_f - L_0)^2}T_i}$$

Thus if we have $L_f > L_i > L_0$, then we must have $T_f > T_i$.

**(e)** We have from part (c)

$$\frac{dS}{dT} = b - a(L - L_0)^2 - 2aT(L - L_0)\frac{dL}{dT}$$

We also have from above

$$dS = \frac{C_L}{T} dT - 2aT(L - L_0) dL \Rightarrow C_L = T \frac{dS}{dT} + 2aT^2 (L - L_0) \frac{dL}{dT}$$

which gives

$$\boxed{C_L = bT - aT(L - L_0)^2} \tag{4}$$

**(f)**

$$\begin{aligned} S(T, L) &= S(T_0, L_0) + \int_{T_0, L_0}^{T_0, L} dS + \int_{T_0, L}^{T, L} dS \\ &= S(T_0, L_0) - \int_{L_0}^{L} 2aT(L - L_0) dL + \int_{T_0}^{T} (b - a(L - L_0)^2) dT \end{aligned}$$

$$\boxed{S(T, L) = S(T_0, L_0) + b(T - T_0)0 - aT(L - L_0)^2} \tag{5}$$

the same as above.

$\square$

## 4.6 Van der Waals Gas

**(a)** At constant $E$ we have

$$0 = dE = TdS - pdV$$

The change in entropy $S(T,V)$ can be expressed as

$$dS = \left.\frac{\partial S}{\partial T}\right|_V dT + \left.\frac{\partial S}{\partial V}\right|_T dV = \frac{C_V}{T} dT + \left.\frac{\partial p}{\partial T}\right|_V dV$$

This gives

$$\begin{aligned} \Rightarrow 0 &= C_V dT + \left( T \left.\frac{\partial p}{\partial T}\right|_V - p \right) dV \\ \Rightarrow dT &= -\frac{T \left.\frac{\partial p}{\partial T}\right|_V - p}{C_V} dV \end{aligned}$$

$$\Rightarrow \boxed{\left.\frac{\partial T}{\partial V}\right|_E = -\frac{T \left.\frac{\partial p}{\partial T}\right|_V - p}{C_V}}$$

**(b)** Again fixing Energy we have

$$0 = dE = TdS - pdV \qquad \Rightarrow \qquad dS = \frac{P}{T} dV$$

$$\boxed{\left.\frac{\partial S}{\partial V}\right|_E = \frac{P}{T}}$$

**(c)** From part (a) we know

$$dT = -\frac{T \left.\frac{\partial p}{\partial T}\right|_V - p}{C_V} dV$$

From the Van der Waals equation of state we have

$$p = \frac{NkT}{V - Nb} - a\frac{N^2}{V^2} \qquad \Rightarrow \qquad \left.\frac{\partial p}{\partial T}\right|_V = \frac{Nk}{V - Nb}$$

giving us

$$dT = -\frac{1}{C_V} \left( \frac{aN^2}{V^2} dV \right)$$

$$\boxed{\Delta T = \frac{aN^2}{C_V} \left( \frac{1}{V_2} - \frac{1}{V_1} \right)} \tag{6}$$