

Problem Set 6
Solutions
3.20 MIT
Dr. Anton Van Der Ven
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Problem 1

- We are in the canonical ensemble
- The lowest energy state E_o has degeneracy $\Omega(E_o)$ with all other $E_j > E_o$.

$$Q = \sum_j e^{-\beta E_j} \quad \text{and} \quad P_j = \frac{e^{-\beta E_j}}{Q}$$

- We are asked to find the entropy. Remember the formula for the entropy derived in the homework

$$S = -k \sum_j P_j \ln P_j$$

We can write the partition function in a slightly different way

$$Q = e^{-\beta E_o} \underbrace{\sum_j e^{-\beta(E_j - E_o)}}_{\tilde{Q}} = e^{-\beta E_o} \tilde{Q}$$

So S is

$$S = -k \sum_j \left(\frac{e^{-\beta(E_j - E_o)}}{\tilde{Q}} \right) \ln \left(\frac{e^{-\beta(E_j - E_o)}}{\tilde{Q}} \right)$$

We can also write

$$\tilde{Q} = \Omega(E_o) + \sum_j e^{-\beta(E_j - E_o)}$$

since $e^{-\beta(E_o - E_o)} = 1$ and there are $\Omega(E_o)$ such terms in \tilde{Q} . Also.

$$\lim_{T \rightarrow 0} \tilde{Q} = \Omega(E_o)$$

and

$$\lim_{T \rightarrow 0} e^{-\beta(E_j - E_o)} = \begin{cases} \rightarrow 0 & \text{if } E_j > E_o \\ \rightarrow 1 & \text{if } E_j = E_o \end{cases}$$

$$\implies \lim_{T \rightarrow 0} S = \lim_{T \rightarrow 0} -k \sum_j \left(\frac{e^{-\beta(E_j - E_o)}}{\tilde{Q}} \right) \ln \left(\frac{e^{-\beta(E_j - E_o)}}{\tilde{Q}} \right)$$

$$\lim_{T \rightarrow 0} S = -k \sum_{\substack{j \text{ with} \\ E_j = E_o}} \frac{1}{\Omega(E_o)} \ln \frac{1}{\Omega(E_o)} = k \ln \Omega(E_o)$$

i.e. the log of the degeneracy of the lowest energy state $\Omega(E_o)$ is typically at most of the order of N .

$$S(0) \leq k \ln N \ll N$$

$\frac{S(T)}{N} \rightarrow 0$ (entropy per particle in the system) in the thermodynamic limit as $T \rightarrow 0$ consistent with the third law of thermodynamics.

Problem 2

(See Figure 2-2 on page 45 of McQuarrie)

(a) Since it is an isolated system, i.e. E is constant we work in the microcanonical ensemble (also N, V fixed).

(b) Second law for an isolated system is

$\Delta S \geq 0$ for a spontaneous process, when ΔS is the difference in entropy between the final and initial state

(c) In the microcanonical ensemble

$$S = k \ln \Omega$$

with Ω being the degeneracy of the energy level E (which is fixed). For an ideal gas $\Omega \sim V^N$. The initial state is volume V and the final state (after the expansion) is volume $2V$

$$S = k \ln \frac{\Omega_{final}}{\Omega_{initial}} = k \ln \left(\frac{2V}{V} \right)^N = Nk \ln 2 > 0$$

which is the result we got with classical thermodynamics.

• The statistical mechanics interpretation of the second law:

→ a system spontaneously evolves to a thermodynamic state with the highest possible number of available microstates (i.e. degeneracy).

Problem 3

We are reminded of this relationship

$$S = -k \sum_j [\bar{n}_j \ln(\bar{n}_j) + (1 - \bar{n}_j) \ln(1 - \bar{n}_j)]$$

where

$$\bar{n}_j = \frac{1}{e^{-\beta(\varepsilon_j - \mu)} + 1} = f(\varepsilon)$$

(a) We can rewrite this by summing over the energy levels if we introduce the density of states.

$$S = -k \sum_{\varepsilon} g(\varepsilon) \{ f(\varepsilon) \ln f(\varepsilon) + (1 - f(\varepsilon)) \ln(1 - f(\varepsilon)) \}$$

(b) Which state contribute the most?

$$n_j = f(\varepsilon) = \frac{1}{e^{-\beta(\varepsilon_j - \mu)} + 1}$$

only states with ε within kT of μ are different from 0 or 1.

$$\begin{aligned} \text{if } f = 0 &\rightarrow f \ln f = 0 && \& \quad (1 - f) \ln(1 - f) = 0 \\ \text{if } f = 1 &\rightarrow f \ln f = 0 && \& \quad (1 - f) \ln(1 - f) = 0 \end{aligned}$$

So only energies ε within kT of μ contribute to the electronic entropy.

(c)

(i) For a metal there are many states around μ (since $g(\mu)$ is large) thus the electronic entropy will be high.

(ii) μ is somewhere within the band gap for an insulator. If the band gap is much larger than kT , then there is no electronic entropy.

Problem 4

(a)

$$q = \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} V$$

Using the Boltzmann approximation,

$$Q(N, V, T) = \frac{q^N}{N!} = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3N}{2}} V^N$$

(b) In the canonical ensemble the characteristic potential, F , is related to the partition function Q by

$$F = -kT \ln Q$$

$$F = -kT \left\{ \frac{3N}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) + N \ln V - N \ln N + N \right\}$$

We know from thermodynamics

$$dF = -SdT - pdV + \mu dN$$

• From this relation we can get expressions for S , p , μ and E . Starting with S

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V, N} = k \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{\frac{3N}{2}} \frac{V^N}{N!} \right] + kT \left(\frac{3N}{2T} \right)$$

$$S = Nk \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \frac{V}{N} \right] + k \frac{5}{2} N = Nk \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \frac{V}{N} e^{\frac{5}{2}} \right]$$

• Now for p

$$p = - \left(\frac{\partial F}{\partial V} \right)_{T, N} = \frac{kTN}{V}$$

• For μ

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{V, T} = -kT \left\{ \frac{3}{2} \ln \left[\frac{2\pi mkT}{h^2} \right] + \ln V - \ln N - 1 + 1 \right\}$$

$$\mu = -kT \left\{ \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \right] + \ln \frac{kTN}{p} - \ln N \right\}$$

$$\mu = \underbrace{-kT \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} kT \right]}_{\mu^{\circ}(T) + kT \ln p} + kT \ln p$$

• For E

$$E = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V, N} = kT^2 \left(\frac{3N}{2} \frac{1}{T} \right) = \frac{3}{2} NkT$$

- The average energy of an ideal gas of N particles is $\frac{3}{2} NkT$
- The average energy per particles is $\frac{3}{2} kT$
- Note: The average energy is proportional to the temperature.
- The heat capacity is therefore constant

$$C_v = \left(\frac{\partial E}{\partial T} \right) = \frac{3}{2} Nk$$

Problem 5

(a) Diamond, which is stiffer than lead, has a higher vibrational frequency, ν_E , and therefore a higher Einstein temperature.

$$\Theta_E^{diamond} > \Theta_E^{lead}$$

where $\Theta_E = \frac{h\nu_E}{k}$. This means that the heat capacity of Pb will be higher than that of diamond. (See handout from class)

(b)

$$dS = \frac{C_v}{T} dT \rightarrow S(T) = \int_0^T \frac{C_v}{T} dT$$

Since the vibrational heat capacity of Pb is higher than that of diamond, the vibrational entropy of Pb will be higher than that of diamond. In general stiffer materials have lower vibrational entropies than softer materials.