

Answers E

Problem 5.23(a-b)

a)

$$d\Phi = -SdT - PdV - Nd\mu$$

$$\left(\frac{\partial\Phi}{\partial T}\right)_{V,\mu} = -S, \quad \left(\frac{\partial\Phi}{\partial V}\right)_{T,\mu} = -P, \quad \left(\frac{\partial\Phi}{\partial\mu}\right)_{V,T} = -N.$$

b) The system can exchange energy and particles but not volume with a reservoir. Therefore T , μ , and V are constant, i.e. $dT = d\mu = dV = 0$. The total entropy $S_{\text{total}} = S + S_R$ tends to increase. Using the thermodynamic identity and that the system is in equilibrium with the reservoir, the change in the entropy of the reservoir can be expressed as

$$dS_R = \frac{1}{T}dU_R + \frac{P}{T}dV_R - \frac{\mu}{T}dN_R = -\frac{1}{T}dU - \frac{P}{T}dV + \frac{\mu}{T}dN = -\frac{1}{T}dU + \frac{\mu}{T}dN$$

Since $dT = d\mu = 0$, we have

$$d\Phi = dU - TdS - \mu dN.$$

The change in the total entropy is then

$$dS_{\text{total}} = dS + dS_R = dS - \frac{1}{T}dU + \frac{\mu}{T}dN = -\frac{1}{T}(dU - TdS - \mu dN) = -\frac{1}{T}d\Phi.$$

dS_{total} is positive for $d\Phi$ negative, and hence Φ tends to decrease under the considered conditions.

Problem 6.37

The average value of v^2 is

$$\overline{v^2} = \int_0^\infty v^2 D(v) dv = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty v^4 e^{-\frac{mv^2}{2kT}} dv = \frac{8kT}{m\sqrt{\pi}} \int_0^\infty x^4 e^{-x^2} dx,$$

where

$$\int_0^\infty x^4 e^{-x^2} dx = \frac{3}{8}\sqrt{\pi}.$$

Therefore

$$\overline{v^2} = \frac{3kT}{m}.$$

This answer agrees with equation (6.41) in Schroeder.

Problem E1

$$E(\vec{p}) = -\vec{p} \cdot \vec{E}, \quad \vec{p} = (\pm 1, \pm 1, \pm 1) \frac{p}{\sqrt{3}}, \quad \vec{E} = (1, 1, 1) \frac{E}{\sqrt{3}}$$

a)

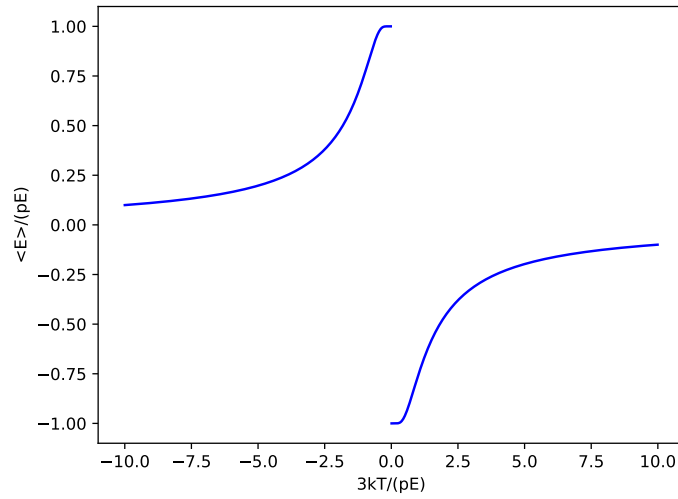
Energy	Degeneracy
$-pE$	1
$-pE/3$	3
$+pE/3$	3
$+pE$	1

b)

$$\begin{aligned}
Z &= e^{pE/(kT)} + 3e^{pE/(3kT)} + 3e^{-pE/(3kT)} + e^{-pE/(kT)} \\
&= e^{3x} + 3e^x + 3e^{-x} + e^{-3x} = (e^x + e^{-x})^3 = 8 \cosh^3(x), \quad x \equiv \frac{pE}{3kT}.
\end{aligned}$$

c)

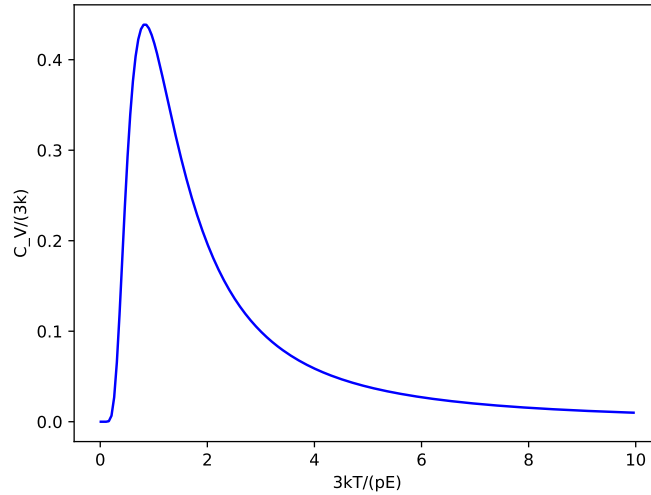
$$\bar{E} = -\frac{\partial \ln(Z)}{\partial \beta} = -\frac{pE}{3} \frac{\partial \ln(Z)}{\partial x} = -pE \tanh\left(\frac{pE}{3kT}\right)$$



$$\bar{E} = -pE \frac{1 - e^{-\frac{2pE}{3kT}}}{1 + e^{-\frac{2pE}{3kT}}} \quad \text{so} \quad \lim_{T \rightarrow 0^+} \bar{E} = -pE \frac{1 - 0}{1 + 0} = -pE \quad \text{and} \quad \lim_{T \rightarrow \infty} \bar{E} = -pE \frac{1 - 1}{1 + 1} = 0$$

d)

$$C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_{E,N} = \frac{p^2 E^2}{3kT^2} \frac{1}{\cosh^2(pE/(3kT))}$$



$$\lim_{T \rightarrow 0^+} C_V = 0, \quad \lim_{T \rightarrow \infty} C_V = 0$$

The heat capacity must go to zero when T goes to zero according to the third law of thermodynamics. When the temperature is high, all eight states are almost equally probable. A small increase in energy will only increase the entropy a little and will increase the temperature a lot. Therefore the change of energy per change of temperature is small.

e)

$$S = \frac{\bar{E}}{T} + k \ln(Z) = -\frac{pE}{T} \tanh\left(\frac{pE}{3kT}\right) + k \ln\left(8 \cosh^3\left(\frac{pE}{3kT}\right)\right),$$

We can also write the entropy as

$$\begin{aligned} \frac{S}{k} &= -3x \frac{e^x - e^{-x}}{e^x + e^{-x}} + 3 \ln(e^x + e^{-x}) = -3x \frac{1 - e^{-2x}}{1 + e^{-2x}} + 3x + 3 \ln(1 + e^{-2x}) \\ &= \frac{6xe^{-2x}}{1 + e^{-2x}} + 3 \ln(1 + e^{-2x}). \end{aligned}$$

From this we see that

$$\lim_{T \rightarrow 0^+} S = \lim_{x \rightarrow \infty} S = \frac{0}{1 + 0} + 3k \ln(1 + 0) = 0$$

and

$$\lim_{T \rightarrow \infty} S = \lim_{x \rightarrow 0^+} S = \frac{0}{1 + 1} + 3k \ln(1 + 1) = k \ln(8).$$

In the limit $T \rightarrow 0$, the system is in the ground state, and since the ground state is not degenerate, $S = k \ln(1) = 0$. The result $S \rightarrow k \ln(8)$ for $T \rightarrow \infty$ is because the defect is in any of the 8 states with equal probability at infinite temperature, since this maximizes the entropy.

Problem E2

a) The partition function is

$$Z = \frac{1}{N_A!} Z_A^{N_A} \frac{1}{N_B!} Z_B^{N_B} \frac{1}{N_{AB}!} Z_{AB}^{N_{AB}}$$

We can compute the free energy $F = U - TS$ from $F = -kT \ln(Z)$. Using Stirling's approximation $\ln(N_i!) \approx N_i \ln(N_i) - N_i$ for $N_i \gg 1$, we get

$$F = -kT(-N_A \ln(N_A) + N_A - N_B \ln(N_B) + N_B - N_{AB} \ln(N_{AB}) + N_{AB}) \\ - kTN_A \ln(Z_A) - kTN_B \ln(Z_B) - kTN_{AB} \ln(Z_{AB})$$

b) Inserting $N_A = N_A^0 - N_{AB}$ and $N_B = N_B^0 - N_{AB}$ in the expression for F gives

$$F = -kT(-(N_A^0 - N_{AB}) \ln(N_A^0 - N_{AB}) + N_A^0 - N_{AB} \\ - (N_B^0 - N_{AB}) \ln(N_B^0 - N_{AB}) + N_B^0 - N_{AB} - N_{AB} \ln(N_{AB}) + N_{AB}) \\ - kT(N_A^0 - N_{AB}) \ln(Z_A) - kT(N_B^0 - N_{AB}) \ln(Z_B) - kTN_{AB} \ln(Z_{AB})$$

F is minimal when

$$\left(\frac{\partial F}{\partial N_{AB}} \right)_{V,T} = 0$$

This gives

$$0 = \left(\frac{\partial F}{\partial N_{AB}} \right)_{V,T} = kT(-\ln(N_A^0 - N_{AB}) - \ln(N_B^0 - N_{AB}) + \ln(N_{AB}) + \ln(Z_A) + \ln(Z_B) - \ln(Z_{AB})) \\ = kT(-\ln(N_A) - \ln(N_B) + \ln(N_{AB}) + \ln(Z_A) + \ln(Z_B) - \ln(Z_{AB}))$$

Rewriting this gives

$$\ln \left(\frac{N_{AB}}{N_A N_B} \right) = \ln \left(\frac{Z_{AB}}{Z_A Z_B} \right).$$

Taking the exponential and multiplying by V then gives

$$\frac{n_{AB}}{n_A n_B} = V \frac{Z_{AB}}{Z_A Z_B}.$$

From Schroeder equations (6.83) and (6.84) we have

$$Z_A = V \left(\frac{h}{\sqrt{2\pi m_A kT}} \right)^{-3} Z_{A,int}, \\ Z_B = V \left(\frac{h}{\sqrt{2\pi m_B kT}} \right)^{-3} Z_{B,int}, \\ Z_{AB} = V \left(\frac{h}{\sqrt{2\pi m_{AB} kT}} \right)^{-3} Z_{AB,int},$$

where the partition functions for the internal parts cannot depend on the volume. Therefore

$$\frac{n_{AB}}{n_A n_B} = \left(\frac{h}{\sqrt{2\pi kT}} \right)^3 \left(\frac{m_{AB}}{m_A m_B} \right)^{3/2} \frac{Z_{AB,int}}{Z_{A,int} Z_{B,int}} \equiv K(T).$$

c) After putting all internal partition functions equal to unity, the above expression reduces to

$$\frac{n_{AB}}{n_A n_B} = \left(\frac{h}{\sqrt{2\pi kT}} \right)^3 \left(\frac{m_{AB}}{m_A m_B} \right)^{3/2} \equiv K(T). \quad (1)$$

If T increases, we have that n_{AB} decreases, while n_A and n_B increases. This means that at higher T more AB molecules break apart to form separated A and B atoms. To minimize F , we should maximize Z . Both Z_A , Z_B , and Z_{AB} increase with increasing temperature. Therefore high temperature favors having two separated atoms rather than one molecule.

If $m_{AB}/(m_A m_B)$ increases, we have that n_{AB} increases, while n_A and n_B decreases. This means that at higher $m_{AB}/(m_A m_B)$ more A and B atoms join to form AB molecules. Increasing $m_{AB}/(m_A m_B)$ can be done by decreasing the masses. Both Z_A , Z_B , and Z_{AB} decrease with decreasing masses, so low masses favor having one molecule rather than two separated atoms.

Problem E3

a) The partition function Z for all N atoms in the gas is

$$Z = \frac{1}{N!} Z_1^N$$

where Z_1 is the partition function for one atom.

$$Z_1 = Z_{tr} Z_{int},$$

where Z_{tr} is the translational part and Z_{int} is the internal part. From equation (6.82) in Schroeder, we have

$$Z_{tr} = V \left(\frac{h}{\sqrt{2\pi m k T}} \right)^{-3}.$$

The internal part is given by

$$Z_{int} = e^{-\epsilon_1/(kT)} + e^{-\epsilon_2/(kT)}.$$

b) We have

$$U = -\frac{\partial}{\partial \beta} \ln(Z) = -N \frac{\partial}{\partial \beta} \ln(Z_{tr}) - N \frac{\partial}{\partial \beta} \ln(Z_{int}) \equiv U_{tr} + U_{int},$$

where

$$U_{tr} = -N \frac{\partial}{\partial \beta} \ln(Z_{tr}) = \frac{3}{2} N k T$$

and

$$U_{int} = -N \frac{\partial}{\partial \beta} \ln(Z_{int}) = \frac{N \epsilon_1 + N \epsilon_2 e^{-(\epsilon_2 - \epsilon_1)/(kT)}}{1 + e^{-(\epsilon_2 - \epsilon_1)/(kT)}}$$

Hence

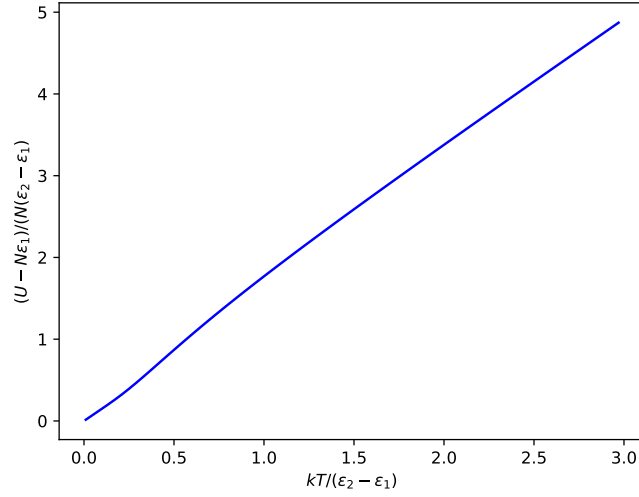
$$U = \frac{3}{2} N k T + \frac{N \epsilon_1 + N \epsilon_2 e^{-(\epsilon_2 - \epsilon_1)/(kT)}}{1 + e^{-(\epsilon_2 - \epsilon_1)/(kT)}}.$$

The limits are

$$\begin{aligned} U &\approx \frac{3}{2} N k T + N \epsilon_1 \quad \text{when } T \ll (\epsilon_2 - \epsilon_1)/k, \\ U &\approx \frac{3}{2} N k T + N \frac{\epsilon_2 + \epsilon_1}{2} \quad \text{when } T \gg (\epsilon_2 - \epsilon_1)/k. \end{aligned}$$

To plot U , we rewrite it to

$$\frac{U - N \epsilon_1}{N(\epsilon_2 - \epsilon_1)} = \frac{3}{2} \frac{kT}{\epsilon_2 - \epsilon_1} + \frac{e^{-(\epsilon_2 - \epsilon_1)/(kT)}}{1 + e^{-(\epsilon_2 - \epsilon_1)/(kT)}}$$



We can also divide the heat capacity into a translational and an internal part

$$C_V = C_{V,tr} + C_{V,int}$$

where

$$C_{V,tr} = \left(\frac{\partial U_{tr}}{\partial T} \right)_{V,N} = \frac{3}{2} Nk$$

and

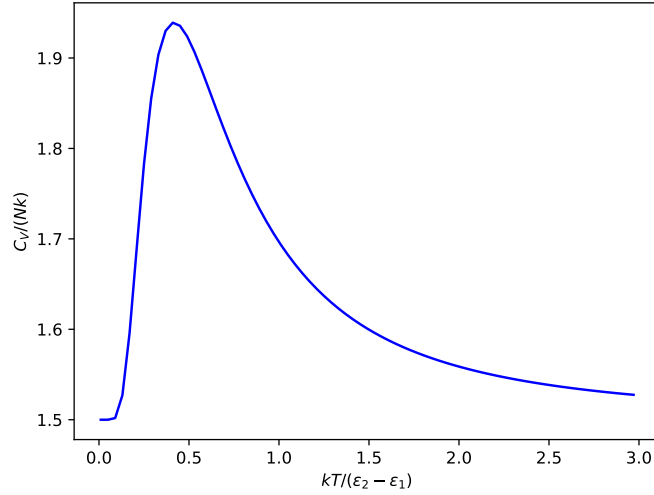
$$\begin{aligned} C_{V,int} &= \left(\frac{\partial U_{int}}{\partial T} \right)_{V,N} \\ &= N \frac{\epsilon_2 \frac{\epsilon_2 - \epsilon_1}{kT^2} e^{-(\epsilon_2 - \epsilon_1)/(kT)} (1 + e^{-(\epsilon_2 - \epsilon_1)/(kT)}) - \frac{\epsilon_2 - \epsilon_1}{kT^2} e^{-(\epsilon_2 - \epsilon_1)/(kT)} (\epsilon_1 + \epsilon_2 e^{-(\epsilon_2 - \epsilon_1)/(kT)})}{(1 + e^{-(\epsilon_2 - \epsilon_1)/(kT)})^2} \\ &= \frac{N(\epsilon_2 - \epsilon_1)^2}{kT^2} \frac{e^{-(\epsilon_2 - \epsilon_1)/(kT)}}{(1 + e^{-(\epsilon_2 - \epsilon_1)/(kT)})^2} = \frac{Nk}{2} \left(\frac{\epsilon_2 - \epsilon_1}{kT} \right)^2 \frac{1}{1 + \cosh \left(\frac{\epsilon_2 - \epsilon_1}{kT} \right)} \end{aligned}$$

Hence

$$C_V = \frac{3}{2} Nk + \frac{Nk}{2} \left(\frac{\epsilon_2 - \epsilon_1}{kT} \right)^2 \frac{1}{1 + \cosh \left(\frac{\epsilon_2 - \epsilon_1}{kT} \right)}.$$

The limits are

$$\begin{aligned} C_V &\approx \frac{3}{2} Nk \quad \text{when} \quad T \ll (\epsilon_2 - \epsilon_1)/k, \\ C_V &\approx \frac{3}{2} Nk \quad \text{when} \quad T \gg (\epsilon_2 - \epsilon_1)/k. \end{aligned}$$



c) The entropy can be computed from

$$S = \frac{U}{T} + k \ln(Z) = \frac{U_{tr}}{T} + k \ln\left(\frac{1}{N!} Z_{tr}^N\right) + \frac{U_{int}}{T} + k \ln(Z_{int}^N) \equiv S_{tr} + S_{int}.$$

Here

$$S_{tr} = \frac{U_{tr}}{T} + k \ln\left(\frac{1}{N!} Z_{tr}^N\right) = \frac{5}{2} Nk + Nk \ln\left(\frac{V}{N} \left(\frac{2\pi m k T}{h^2}\right)^{3/2}\right)$$

(this is the Sackur-Tetrode equation) and

$$S_{int} = \frac{U_{int}}{T} + k \ln(Z_{int}^N) = N \frac{\frac{\epsilon_1}{T} + \frac{\epsilon_2}{T} e^{-(\epsilon_2 - \epsilon_1)/(kT)}}{1 + e^{-(\epsilon_2 - \epsilon_1)/(kT)}} + Nk \ln\left(e^{-\epsilon_1/(kT)} + e^{-\epsilon_2/(kT)}\right).$$

To obtain the limits, we rewrite the internal entropy as

$$\begin{aligned} \frac{S_{int}}{Nk} &= \frac{\frac{\epsilon_1}{kT} + \frac{\epsilon_2}{kT} e^{-(\epsilon_2 - \epsilon_1)/(kT)}}{1 + e^{-(\epsilon_2 - \epsilon_1)/(kT)}} - \frac{\epsilon_1}{kT} + \ln\left(1 + e^{-(\epsilon_2 - \epsilon_1)/(kT)}\right) \\ &= \frac{\frac{\epsilon_2 - \epsilon_1}{kT} e^{-(\epsilon_2 - \epsilon_1)/(kT)}}{1 + e^{-(\epsilon_2 - \epsilon_1)/(kT)}} + \ln\left(1 + e^{-(\epsilon_2 - \epsilon_1)/(kT)}\right). \end{aligned}$$

The limits are

$$S_{int} \approx \frac{0}{1+0} + Nk \ln(1+0) = 0 \quad \text{when} \quad T \ll (\epsilon_2 - \epsilon_1)/k$$

and

$$S_{int} \approx \frac{0}{1+1} + Nk \ln(1+1) = Nk \ln(2) \quad \text{when} \quad T \gg (\epsilon_2 - \epsilon_1)/k.$$

Problem Hand-in E

a)

$$Z = (e^{-\beta\epsilon_1} + 1 + e^{\beta\epsilon_1}) (e^{-\beta\epsilon_2} + e^{\beta\epsilon_2}), \quad \beta = \frac{1}{kT}$$

b)

$$E(T) = \epsilon_1 \frac{e^{-\beta\epsilon_1} - e^{\beta\epsilon_1}}{e^{-\beta\epsilon_1} + 1 + e^{\beta\epsilon_1}} + \epsilon_2 \frac{e^{-\beta\epsilon_2} - e^{\beta\epsilon_2}}{e^{-\beta\epsilon_2} + e^{\beta\epsilon_2}}$$

$$E(0) = -\epsilon_1 - \epsilon_2 \quad \lim_{T \rightarrow \infty} E(T) = 0$$

c)

$$P = \frac{e^{\beta(\epsilon_1 + \epsilon_2 + U)} + e^{\beta(-\epsilon_1 - \epsilon_2 + U)}}{e^{\beta(\epsilon_1 + \epsilon_2 + U)} + e^{\beta\epsilon_2} + e^{\beta(\epsilon_2 - \epsilon_1)} + e^{\beta(\epsilon_1 - \epsilon_2)} + e^{-\beta\epsilon_2} + e^{\beta(-\epsilon_1 - \epsilon_2 + U)}}$$

$$\lim_{U \rightarrow \infty} P = 1$$