Homework 3 Solution

1. We have two ideal gases with the same volume \( V \), pressure \( P \), and temperature \( T \). These two gases consist of different chemical species. Assume the whole system is thermally isolated during the following processes.

(1) Two boxes containing the above gases are connected. That is, now the total volume of the mixture is \( 2V \). Find the entropy change due to this procedure of joining two boxes.

See the illustration at the end.
Before answering the question, let us consider the indistinguishable case. The entropy formula for the gas in box \( V \) is

\[
S_1 = N k_B \left( \log \frac{V}{N} + \frac{3}{2} \log \frac{E}{N} + c \right). \tag{1}
\]

If two boxes are joined, then

\[
S_{1+2} = 2N k_B \left( \log \frac{2V}{2N} + \frac{3}{2} \log \frac{2E}{2N} + c \right) = 2S_1 \tag{2}
\]

as expected.

Now, the distinguishable case.

\[
S_{1+2} = (2N) k_B \left( \log \frac{2V}{2N} + \frac{3}{2} \log \frac{2E}{2N} + c \right) = 2S_1 + 2N k_B \log 2 \tag{3}
\]

This can be considered as the superposition of each gas expanded to \( 2V \):

\[
S'_1 = N k_B \left( \log \frac{2V}{N} + \frac{3}{2} \log \frac{E}{N} + c \right) = S_1 + N k_B \log 2. \tag{4}
\]

Superposing these two, we have

\[
S_{1+2} = 2S_1 + 2N k_B \log 2. \tag{5}
\]

(2) Find the entropy change if two gases are mixed into a single volume of \( V \).

Indistinguishable case:

Obviously

\[
S_{1+2} = 2N k_B \left( \log \frac{V}{2N} + \frac{3}{2} \log \frac{2E}{2N} + c \right) = 2S_1 - 2N k_B \log 2. \tag{6}
\]

This is the entropy decrease due to compression = halving the volume.

The distinguishable case: This is a simple superposition, so

\[
S'_{1+2} = 2S_1 \tag{7}
\]
That is, this is the result of Problem (1) compressed to the half volume: the entropy decrease due to compression is $2Nk_B \log 2$, which exactly cancels the mixing entropy.

(3) How can you actually measure the entropy change in (1) experimentally?

Notice that there is no exchange of heat during the mixing process in either of the two cases, distinguishable or indistinguishable. Therefore, to measure the mixing entropy you must somehow connect the mixed final state to the initial separated state (in a quasistatic way) and study this de-mixing process: for example, how much work do you have to supply to do this (or gain by doing this). There is a possibility of obtaining the absolute entropy of a gas with the aid of the Sackur-Tetrode formula. However, there is no way to use the result for the present purpose.

The above conclusion implies that to measure the mixing entropy you must be able to separate the mixture. If you did not know it is indeed a mixture, there would be no way to separate the ‘mixture.’ That is, you must be able to distinguish the components to measure the mixing entropy. You cannot use this experiment to tell whether two gases are identical or not.

You might say someone gave you a semipermeable membrane to separate the two components. However, since you have the membrane you can distinguish the components already.

2. The internal motion of some ring puckering molecules (e.g., cyclobutanone) can be described by the following Hamiltonian:

$$H = \frac{p^2}{2m} + \frac{a}{4}x^4,$$

where $m$ is the effective mass of the oscillator and $a$ is a positive constant. Obtain the constant volume specific heat of this gas around the room temperature.

We use the equipartition of energy:

$$2 \left\langle \frac{p^2}{2m} \right\rangle = k_B T. \quad (8)$$

and

$$4 \left\langle ax^4 \right\rangle = k_B T. \quad (9)$$
Therefore,
\[
\langle H \rangle = \frac{3}{4} k_B T. \tag{10}
\]
We must pay attention to the translational and rotational degrees of freedom. This gives
\[3k_B T.\]
Therefore,
\[
C_V = \frac{15}{4} k_B \tag{11}
\]
per molecule.

3. Let \( \rho \) be the density operator of a single 1/2 quantum spin system whose Hamiltonian is given by
\[H = -\gamma \mathbf{\sigma} \cdot \mathbf{B},\]
where \( \mathbf{\sigma} \) is \((\sigma_x, \sigma_y, \sigma_z)\) in terms of the Pauli spin operators.

(1) Obtain the matrix representation of \( \rho \) that diagonalizes \( \sigma_z \).

We take the direction of \( \mathbf{B} \) to be the \( z \) axis.

\[
\rho = \frac{1}{C} \begin{pmatrix} e^{\beta \gamma B} & 0 \\ 0 & e^{-\beta \gamma B} \end{pmatrix},\tag{12}
\]
where \( C \) is the normalization constant: the trace of the matrix in the above formula, so
\[C = 2 \cosh \beta \gamma H.\]

If you wish to do the original problem we need the following calculation. Notice that
\[(\mathbf{n} \cdot \mathbf{\sigma})^2 = I, \]
where \( \mathbf{n} \) is a unit vector.

\[
e^{\gamma B \cdot \mathbf{\sigma}} = \sum_{n=0}^{\infty} \frac{1}{(2n)!} (\gamma B)^{2n} + \sum_{n=0}^{\infty} \frac{1}{(2n+1)!} (\gamma B)^{2n+1} \mathbf{B} \cdot \mathbf{\sigma} = \cosh \gamma B + \frac{\mathbf{B} \cdot \mathbf{\sigma}}{B} \sinh \gamma B. \tag{13}\]

(2) Find the average of \( \sigma_y \).

\[
\langle \sigma_y \rangle = \text{Tr}\sigma_y \rho = \text{Tr} \begin{pmatrix} 0 & i e^{\beta \gamma B} e^{-\beta \gamma B} \\ -i e^{-\beta \gamma B} & 0 \end{pmatrix} = 0. \tag{14}
\]
This should be obvious without any calculation.

(3) Obtain the matrix representation of \( \rho \) that diagonalizes \( \sigma_x \).

With the basis that diagonalizes \( \sigma_z \) we have
\[
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{15}
\]
Therefore
\[
\sigma_x \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ -1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ -1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix}. \tag{16}
\]
That is, the following orthogonal (actually, unitary as well) matrix:

\[
U = \begin{pmatrix}
\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\
-\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}}
\end{pmatrix}
\]  

(17)
diagonalizes \( \sigma_x \) as \( U^* \sigma_x U \). Therefore,

\[
U^* \begin{pmatrix}
0 & ie^{-\beta \gamma B} \\
-ie^{-\beta \gamma B} & 0
\end{pmatrix} U = \frac{1}{2} \begin{pmatrix}
1 & -\tanh \beta \gamma B \\
-\tanh \beta \gamma B & 1
\end{pmatrix}.
\]  

(18)

4. The potential energy of a permanent electric dipole \( \mathbf{p} \) is \( U = -\mathbf{p} \cdot \mathbf{E} \) in the electric field \( \mathbf{E} \). Obtain the electric susceptibility of the system.

We must obtain the expectation value of the polarization \( \mathbf{P} \) per unit volume of the gas. In this case we ignore the interaction among gas particles, the partition function becomes a product of one particle partition functions. Furthermore, the translational motion of the particles has nothing to do with the polarization we have only to compute the canonical partition function for a single dipole:

\[
z(\mathbf{E}) = \int d\mathbf{e} \, e^{\beta \mathbf{pe} \cdot \mathbf{E}} = \int d\mathbf{e} \, e^{\beta \mathbf{pE} \cos \theta},
\]  

(19)
where \( \mathbf{e} \) is the directional unit vector of the dipole moment with respect to the electric field direction, \( E = |\mathbf{E}| \), and the angle between \( \mathbf{E} \) and \( \mathbf{p} \) (or \( \mathbf{e} \)) is \( \theta \). The integration is on the unit sphere and can be computed as

\[
z(\mathbf{E}) = 2\pi \int d\theta \, \sin \theta \, e^{\beta \mathbf{pE} \cos \theta} = 2\pi \int_{-1}^{1} dx \, e^{\beta \mathbf{pEx}} = \frac{4\pi}{\beta \mathbf{pE}} \sinh \beta \mathbf{pE}.
\]  

(20)

From the structure of \( z \) we can immediately see

\[
\langle \mathbf{p} \rangle = k_B T \frac{\partial}{\partial \mathbf{E}} \log z(\mathbf{E}) = pL(\beta \mathbf{pE}) \frac{\mathbf{E}}{\mathbf{E}}
\]  

(21)
where \( L(x) \) is the Langevin function

\[
L(x) = \coth x - \frac{1}{x}.
\]  

(22)
\( \langle \mathbf{p} \rangle \) times the number of particle per volume \( n \) (= the number density) is the polarization \( \mathbf{P} = n \langle \mathbf{p} \rangle \).

The correspondence to thermodynamics is as follows. \(-k_B TN \log z(\mathbf{E})\) is, as \( \mathbf{E} \) is written explicitly, not the Helmholtz free energy \( A(\mathbf{P}) \), but its Legendre transformation \( \Phi(\mathbf{E}) = A(\mathbf{P}) - \mathbf{P} \cdot \mathbf{E} \). That is,

\[
dA = -SdT + \mathbf{E} \cdot d\mathbf{P}, \quad d\Phi = -SdT - \mathbf{P} \cdot d\mathbf{E}.
\]  

(23)
Therefore,

\[ P = -\frac{\partial}{\partial E} \Phi(E) = k_B TN \frac{\partial}{\partial E} \log z(E), \]  

(24)

which is equivalent to (including the correct sign) (21).

To obtain the susceptibility (dielectric constant), we must differentiate \( P \) with respect to \( E \). It is a diagonal matrix proportional to the unit 3 \( \times \) 3 matrix \( I \) as

\[ \epsilon = \beta p^2 NL'(\beta pN)I. \]  

(25)