Homework 5 Solutions due 9 am on Feb 26 (Tu), 2019.
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You may discuss with your friends AFTER you have made due efforts of your own to solve
the problems. I trust you. I wish you to fully understand the solutions when you submit
your homeworks (and get the full credit).

No solution without your justification will get any credit.

1 [Disparate time scales; easy question but important].
We organisms live, taking advantage of miracles (extremely rare events). Our biological time
(increment) scale is 1 msec and the molecular time scale is 1 fs. Suppose you can throw 40
coins (assume all are fair) at once every 1 ps. How many times can you experience ‘all up
simultaneously’ in 1 s on the average? If you do the throwing once every second, how many
years do you expect to take for all the 40 coins to exhibit heads simultaneously? [This is
an easy question; only I wish you to remember the vast time scale difference between micro
and macro scales.]

Soln.
This ‘problem’ requires very rough estimates; the lessons are important that we could learn
even from a very crude analysis.

If every trial takes 1 ps, our Microsystems can try $10^{12}$ times in one second. The prob-
ability to have all H for 40 fair coins at once is one over $2^{40} \approx 10^{12}$ [You should remember
$2^{10} \approx 10^3$]. Thus, on the average this ‘miracle’ can happen once every ~second. Thus, for
us it is only banal, but for an enzyme the event that it can promote a certain reaction could
be a miracle.

If every trial takes a second, $10^{12}$ s is about 32 ka, so with 30 thousand years we are pretty
sure this happens.

2 [Elementary problem].
One mole of an ideal gas expands adiabatically against the external constant pressure
$P_0 = 1.7$ atm. The gas is initially at temperature $T_1 = 273$ K and the pressure is $3P_0 = 5.1$
atm. After expansion the gas reaches a final equilibrium state. You may assume that the
gas is an ideal monatomic gas. What is the final temperature $T_2$?

Soln.
The work done by the gas is $P_0(V_2 - V_1)$, where $V_1$ is the initial volume and $V_2$ is the
final volume. The final pressure must be $P_0$, so $3P_0V_1 = RT_1$ and $P_0V_2 = RT_2$. Since the system
is adiabatic,

$$\Delta E = -P_0(V_2 - V_1).$$  \hspace{1cm} (DH5.1)

The internal energy of an ideal gas is directly related to its temperature, so

$$\Delta E = C_V(T_2 - T_1).$$  \hspace{1cm} (DH5.2)
These formulas imply
\[ RT_1/3 - RT_2 = C_V(T_2 - T_1). \] (DH5.3)

Therefore, noting that \( C_V = (3/2)R \),
\[ T_2 = \frac{R + 3C_V}{3(R + C_V)} T_1 = \frac{1 + 9/2}{3(5/2)} \times 273 = \frac{11}{15} \times 273 = 200.2 \] (DH5.4)

That is, 200 K.

**Remark.** Some of you might have thought about using ‘Poisson’s relation’ such as \( PV^\gamma = \) const. However, this is for quasistatic processes. Our process is not quasistatic, because the pressures inside and outside are not the same (initially, in particular, the inside pressure is much larger than the external pressure, so the expansion is rapid and some dissipation must happen. Thus, the final temperature we arrive at must be significantly higher than the reversible case (about 170 K?).

### 3 [Reviewing the existence of entropy]

Let us take an ideal gas system consisting of \( n \) moles of point particles (monatomic gas) and demonstrate the existence of entropy \( S \) for this system. The convenient thermodynamic space for this system is spanned by the internal energy \( E \) and the volume \( V \). Notice that for this system the reversible infinitesimal work has the expression: \( dW = -PdV \), where \( P \) is the pressure.

1. The internal energy \( E \) of this system depends only on the temperature \( T \). How can you justify this statement? [Hint: a trivial question, so do not think too much. Go back to the kinetic theory. You could answer (1) and (2) at once.]
2. Let \( C_V \) be the constant volume specific heat of this ideal gas (don’t forget that it is \( n \) moles) defined by \( dE/dT = C_V \). Compute it. You must know the answer, so you must be able to derive it from what we have learned up to this point in this course. [Hint: \( E \) is the total energy of the gas. What is it as a function of \( T \)?]
3. In the figure below (Fig. DH5.1; cf. Fig. 9.6) choose a point \( P \) at \((E_0,V_0)\). The work coordinate (i.e., \( V \) in our case) of the vertical line \( L \) is \( V \).

![Diagram](image)

Figure DH5.1: The red curve is the adiabatic and reversible process starting from \( P \). \( Q \) is unique on \( L \) according to Planck’s law.

You can reach \( Q \) reversibly and adiabatically from \( P \). Explain why there is no point other
than Q on L that can be reached from P adiabatically and reversibly.

(4) Find the $E$ coordinate of Q in terms of $V, V_0$ and $E_0$.

(5) The surface (the red curve in Fig. DH5.1) consisting of points (= equilibrium states) that may be reached from P reversibly and adiabatically should be described by a relation $f(E, V) = \text{constant}$, where $f$ is an appropriate function. Find or choose such a function $f$. (You should have virtually obtained this in (4)).

(6) Show that different such curves do not cross (that is, $f(E, V) = c_1$ and $f(E, V) = c_2 \neq c_1$ do not have any common point), and also that each curve defines a function of $V$ (i.e., there is no overhang; cf. Fig. 9.7). Therefore there is at most one point on L that can be reached from P reversibly and adiabatically. Notice that ‘reversibility’ is crucial.

Soln.

(1) The average particle energy (monatomic ideal gas!) is $(3/2)k_BT$. Since there is no interaction among particles, the energy of the system consists of kinetic energy alone. Thus, the law of large numbers tells us that the total energy is very closed to $(3/2)k_BT$ times the number of particles $nN_A$. Thus, $E = 3nRT/2$.

(2) We have almost answered the question in (1): $C_V = 3nR/2$. Notice that such a result cannot be obtained by thermodynamics.

(3) If we could reach from P reversibly and adiabatically to a point B above Q (cf. Fig. 9.6), then we can go to Q from B reversibly and adiabatically, violating Planck’s law.

(4) Since the process is quasistatic and adiabatic, we can change the system energy only by modifying the volume $V$. As noted at the beginning $d'W = -PdV$ is the only way to change $E$. Therefore,

$$dE = -PdV = -\frac{nRT}{V}dV, \quad \text{(DH5.5)}$$

but our coordinates are $E$ and $V$, so we must write $T$ as a function of $E$ (and $V$, generally speaking). (1) and (2) tell us that $T = E/C_V$. Therefore,

$$dE = -\frac{nRE}{C_VV}dV, \quad \text{(DH5.6)}$$

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1We know $dS$ is proportional to $d'Q$ without any change of work coordinates, so $S$ must be extensive. That is, even if you double the system size $E \rightarrow 2E$, $V \rightarrow 2V$, $C_V \rightarrow 2C_V$, $n \rightarrow 2n$, the formula for $dS$ should be intact with doubling the increments $dS$, $dE$ and $dV$. If you take this condition into account, there is almost no freedom of choice for $f$, but this will not be required here, so invent your ‘$S$’ freely.
or
\[ C_V d \log E + nRd \log V = 0. \]  
(DH5.7)

Integrating this, we get
\[ C_V \log E + nR \log V = \text{const.} \]  
(DH5.8)

This constant is determined by the 'initial condition' P:
\[ C_V \log E_0 + nR \log V_0 = \text{const.} \]  
(DH5.9)

Therefore,
\[ C_V \log \frac{E}{E_0} + nR \log \frac{V}{V_0} = 0. \]  
(DH5.10)

Solving this, we get
\[ E = E_0 \left( \frac{V}{V_0} \right)^{-nR/C_V} = E_0 \left( \frac{V}{V_0} \right)^{-2/3}. \]  
(DH5.11)

(5) For example, we may choose
\[ f(E, V) = C_V \log E + nR \log V. \]  
(DH5.12)

\[ f(E, V) = \text{const.} \] implies \( E^{3/2} V = \text{constant} \). This is a monotone decreasing curve of \( V \), so there cannot be any overhang. \( E^{3/2} V = c_1 \) and \( E^{3/2} V = c_2 \neq c_1 \) cannot have any common point, since these simultaneous equations cannot have any solution (or if there were, obviously \( c_1 = c_2 \)). Thus, \( f \) foliates (or stratifies) the thermodynamic space of the ideal gas.

(6) \( S = f(E, V) \) or my entropy is
\[ S = C_V \log E + nR \log V. \]  
(DH5.13)

Now, thermal contact means we cannot change \( V \).\(^3\) \( E \) may be changed only through transfer of heat \( dE = d'Q \), so
\[ dS = C_V d \log E = \frac{C_V}{E} dE = \frac{1}{T} dE = \frac{1}{T} d'Q. \]  
(DH5.14)

Here, you may perhaps say that I chose too convenient a function (knowing the standard result). For example, I could invent my entropy \( S \) as
\[ S = f(E, V) = \log E + \frac{2}{3} \log V. \]  
(DH5.15)

Now, quasiequilibrium thermal contact implies \( dE = d'Q \), and \( dV = 0 \) (no work), so
\[ dS = \frac{1}{E} dE = \frac{1}{E} d'Q \]  
(DH5.16)

\(^3\)Very precisely speaking, thermal contact is a ‘vertical move’ in the thermodynamic space, and is different from ‘no work.’ For example, if there are two work coordinates, \( X \) and \( Y \), you could change both while keeping \( dW = xdX + ydY = 0 \). This is NOT thermal contact.
In our case $E \propto T$, so, although in this case the temperature scale is not the standard K scale, $E$ is still a respectable absolute temperature.

However, as noted in footnote 1, in reality, we must respect the extensivity of $S$. Look at (DH5.15):

$$dS = \frac{1}{E} dE + \frac{2}{3V} dV$$  \hspace{1cm} (DH5.17)

This unfortunately does not satisfy the ‘doubling invariance’ mentioned in the footnote: $dS$ is intact under system doubling in this case. Therefore, ‘my’ choice is actually ‘unthermodynamic.’

In contrast the choice (DH5.13) gives

$$dS = \frac{C_V}{E} dE + \frac{nR}{V} dV.$$  \hspace{1cm} (DH5.18)

Therefore, all the coefficients of differentials are intensive (invariant), and doubling all the differential is consistent. That is, this formula is intact under doubling the system size.

4 [Rudimentary linear algebra]

$$B = \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}.$$  \hspace{1cm} (DH5.19)

(i) Give all the eigenvalues of $B$.
(ii) What is its determinant?
(iii) Give normalized eigenvectors corresponding to the eigenvalues in (i). You must make these three vectors to make an ON basis of $\mathbb{R}^3$.
(iv) Find an orthogonal matrix $U$ defining an orthogonal transformation that diagonalizes $B$.
(v) Confirm that the resolution of unity in terms of the eigenvectors.
(vi) Confirm the spectral decomposition formula for $B$.

[Hint: you can almost copy what is in Discussion, but please understand the storyline. If you think you are very familiar with linear algebra, you may simply write the notable differences only from the above example(s).]

Soln.

(i) - (ii) we can read off the results from Discussion 5 6(2): $B = A + [-1, -1, -1]$ ($\lambda_B = \lambda_A - 1$).
(i) 2, $-1$, $-1$ are the eigenvalues.
(ii) 2 [Of course you can use an elementary method to get this as $2 - 0$, but don’t do that after knowing the eigenvalues.]
(iii) For this you might think you have to solve honestly (note that the following equation is exactly the same as that we already encountered.)

$$(B - 2I) \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -2 & 1 & 1 \\ 1 & -2 & 1 \\ 1 & 1 & -2 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = 0.$$  \hspace{1cm} (DH5.20)
but we already know a solution

$$|2\rangle = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}.$$  \hfill (DH5.21)

The eigenvectors belonging to $-1$ are the basis vector of the (hyper) plane perpendicular to $|2\rangle$, so, for example, we can choose (there are two eigenvectors belonging to $-1$, so we must distinguish them with suffixes)

$$|-1_1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}, \quad |-1_2\rangle = \frac{1}{\sqrt{6}} \begin{pmatrix} -2 \\ 1 \\ 1 \end{pmatrix}.$$  \hfill (DH5.22)

At least one of them, you can get honestly solving

$$(B + I) \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = 0,$$  \hfill (DH5.23)

Since the rank of the matrix is 1, there are two linearly independent solutions. One may be $x = 0$ and $y + z = 0$, which is indeed $|-1_1\rangle$ after normalization. $|-1_2\rangle$ must be perpendicular to $|-1_1\rangle$, so $(a, 1, 1)^T$ is easily guessed for it. This must also be perpendicular to $|2\rangle$, so we can fix $a$. The result is $|-1_2\rangle$.

(iv) Summarizing the results so far, we have

$$B \begin{pmatrix} 1/\sqrt{3} & 0 & -2/\sqrt{6} \\ 1/\sqrt{3} & 1/\sqrt{2} & 1/\sqrt{6} \\ 1/\sqrt{3} & -1/\sqrt{2} & 1/\sqrt{6} \end{pmatrix} = \begin{pmatrix} 1/\sqrt{3} & 0 & -2/\sqrt{6} \\ 1/\sqrt{3} & 1/\sqrt{2} & 1/\sqrt{6} \\ 1/\sqrt{3} & -1/\sqrt{2} & 1/\sqrt{6} \end{pmatrix} \begin{pmatrix} 2 \\ 0 \\ 0 \end{pmatrix}.$$  \hfill (DH5.24)

The matrix is an orthogonal (unitary) matrix, so its transposition is its inverse. It is exactly the same we encountered already. Therefore, (DH5.24) gives

$$\begin{pmatrix} 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \\ 0 & 1/\sqrt{3} & -1/\sqrt{2} \\ -2/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} \end{pmatrix} A \begin{pmatrix} 1/\sqrt{3} & 0 & -2/\sqrt{6} \\ 1/\sqrt{3} & 1/\sqrt{2} & 1/\sqrt{6} \\ 1/\sqrt{3} & -1/\sqrt{2} & 1/\sqrt{6} \end{pmatrix} = \begin{pmatrix} 2 \\ 0 \\ 0 \end{pmatrix}.$$  \hfill (DH5.25)

That is, the needed unitary matrix is (just as before)

$$U = \begin{pmatrix} 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} \\ -2/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} \end{pmatrix}.$$  \hfill (DH5.26)

(v) The following should hold:

$$1 = |2\rangle \langle 2| + |-1_1\rangle \langle -1_1| + |-1_2\rangle \langle -1_2|.$$  \hfill (DH5.27)
but this is exactly the same as the exercise we already did. Let’s skip it.

(vi) We expect the spectral decomposition as well:

\[
B = \begin{pmatrix}
0 & 1 & 1 \\
1 & 0 & 1 \\
1 & 1 & 0 \\
\end{pmatrix} = |2\rangle\langle 2| - |−1_1\rangle\langle −1_1| - |−1_2\rangle\langle −1_2|
\]

(DH5.28)

should hold. Using our component representations of the kets, we can proceed as

\[
\frac{2}{3} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} (1,1,1) - \frac{1}{2} \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix} (0,1,-1) - \frac{1}{6} \begin{pmatrix} -2 \\ 1 \\ 1 \end{pmatrix} (-2,1,1)
\]

(DH5.29)

\[
= \frac{2}{3} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} - \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & -1 \\ 0 & -1 & 1 \end{pmatrix} - \frac{1}{6} \begin{pmatrix} 4 & -2 & -2 \\ -2 & 1 & 1 \\ -2 & 1 & 1 \end{pmatrix}
\]

\[
= \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}
\]

(DH5.30)