Midterm Phys 504 Solutions

M1 [Very basic thermodynamics]
(1) There is a substance whose true thermodynamic space is spanned by $E$, $V$ and $M$ (magnetization), but the experimenter totally ignored the magnetic property of the substance and only $E$ and $V$ were recognized as its thermodynamic variables.
(i) The first law may be violated. Describe a possible scenario for (i.e., propose an experiment\(^1\) to demonstrate) the violation.
(ii) The first law might not be violated, but the second law may be violated. Describe a possible scenario for the violation.

Soln.
(i) The true Gibbs relation (i.e., infinitesimal and quasistatic change of internal energy) reads for this system

$$dE = TdS - PdV + BdM.$$ 

If we fail to recognize $M$ or its change, $dE - TdS + PdV \neq 0$. This obviously means $\oint dE \neq 0$ is possible even if $S$ and $V$ are fixed. This implies the violation of conservation of energy. A practical way is to prepare a thermally isolated rigid box and introduce some magnetic fluid (oxygen gas/liquid, which is paramagnetic,\(^2\) may be convenient). Then, apply sinusoidal $B$ and measure the system temperature (= fluid temperature, not the inaccessible spin temperature) that steadily increases.

(ii) To consider the second law violation, let us try to violate Planck’s law, or let us decrease the system entropy under an ‘adiabatic condition’. Especially, let us try to reduce the system (fluid) temperature under the constant volume adiabatic condition. This can be done by adiabatic demagnetization for oxygen gas or liquid. The system entropy should not change if all the variables are taken into account, since presumably the system is isolated. However, if you measure the temperature of the fluid, certainly it goes down. Then, you conclude that the entropy of the system (ignoring magnetic ordering) has been reduced. In this case you must conclude the first law is also violated.

You could mimic the Carnot cycle using a high temperature heat bath at $T_H$ and adiabatic cooling. (1) While absorbing heat appropriately and increasing the magnetic field, do work to the external world (heat exchange with the bath at $T_H$). (2) Then, adiabatically cool the system to $T_L$ by expansion. (3) Compress the system while demagnetizing to keep the system temperature at $T_L$. (4) Adiabatically compress the system to $T_H$. Thus, we could make an engine with a single heat bath. However, this is really contrived; you cannot invent such an engine without knowing the magnetic properties of your work substance.

Comments: Theoretically, it is easy to make an ‘illegal situation’ by ignoring a work coordinate, but you must propose a way to detect ‘violation’ without using the ignored work coordinate and its conjugate variable.

\(^1\) in which you are free to do any magnetic operation
\(^2\) [https://www.youtube.com/watch?v=Lt4P6ctf06Q](https://www.youtube.com/watch?v=Lt4P6ctf06Q), esp after 2:10.
(2) We know enthalpy $H$ can jump at a phase transition under constant $P$ condition with infinitesimal $T$ change.\footnote{That is, $H$ may not be a continuous function of $T$ under constant $P$.} Can $H$ jump when the pressure is infinitesimally changed at a phase transition under adiabatic condition?\footnote{Needless to say, for example, you could induce boiling of water at 373 K by slightly reducing the pressure. Assume that our thermodynamic space is spanned by $E$ and $V$.}

**Soln.**

Notice that $H$ is obtained from $E$ by the following Legendre transformation:

$$-H = \sup_V [-PV - E].$$

Therefore, $-H$ must be a convex function of $P$ under constant $S$. Since a convex function must be continuous, no jump is possible for $H$ as a function of $P$.

**Comments:** There may be other ways to show the assertion, but this must be the cleanest.

**Warning:** $E$ is a convex function of $S$, so $H$ is a convex function of $S$. Therefore, $-H$ is NOT a convex function of $P$ and $S$.

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**M2 [Simple thermodynamics]**

(1) There is a pure material consisting of molecules of molecular weight 232. The thermodynamic equation of state was experimentally determined for 510 grams of this substance as

$$e = 25v^{0.52}T^{0.45},$$

where $e$ is the internal energy in J, $v$ in m$^3$, and $T$ in K. For $n$ moles of the same material let $E$ be its internal energy (in J), and $V$ its volume in m$^3$. Find $E$ as a function of $V$, $n$ and $T$.

**Soln.**

Note that this experiment uses $510/232 = 2.20$ moles of the material. Therefore, the extensivity of $E$ and $V$ implies

$$e = 2.20E/n, \quad v = 2.20V/n.$$

Introducing these relations into the original experimental result, we get

$$E = 25 \times 2.20^{-0.48}n^{0.48}V^{0.52}T^{0.45} = 17.12n^{0.48}V^{0.52}T^{0.45}.$$  

(2) The fundamental equation of state of a gas reads

$$PV = \alpha E,$$

where $E$ is the internal energy. Determine the functional form of $E$. Assume that $E/V$ does not depend on $V$ (a function of $T$ only).

**Soln.**

Let us start with the Gibbs relation [a much better solution follows after this ‘standard way’.]

$$dE = TdS - PdV,$$
From this we see
\[
\left( \frac{\partial V(E/V)}{\partial V} \right)_T = \frac{E}{V} = T \left( \frac{\partial S}{\partial V} \right)_T - P = T \frac{\partial (S,T)}{\partial (V,P)} \frac{\partial (V,P)}{\partial (V,T)} - P = T \left( \frac{\partial P}{\partial T} \right)_V - P = T \frac{1}{V} \left( \frac{\partial E}{\partial T} \right)_V - \frac{\alpha E}{V}
\]
or
\[
(1 + \alpha) E = \alpha T \left( \frac{\partial E}{\partial T} \right)_V.
\]
This means
\[
(1 + 1/\alpha) \frac{1}{T} = \left( \frac{\partial \log E}{\partial T} \right)_V,
\]
so
\[
E = f(V) T^{1+1/\alpha}.
\]
Since \(E/V\) is a function of \(T\) only, we may conclude that
\[
E = c V T^{1+1/\alpha},
\]
where \(c\) is a positive constant.

A wiser approach is in 30.8. Start with \(E = TS - PV\), which reads
\[
TS = (1 + \alpha) E \ (+ \text{const}).
\]
Here, strictly speaking, we have not specified the origin of energy (although \(S= 0\) at \(T = 0\) may be assumed), so there can be an additive constant. However, since we differentiate this, it is a benign factor.

Under constant \(V\), let us differentiate this with \(E\):
\[
\left( \frac{\partial T}{\partial E} \right)_V S + 1 = (1 + \alpha)
\]
Therefore
\[
S = \alpha \left( \frac{\partial E}{\partial T} \right)_V = (1 + \alpha) \frac{E}{T},
\]
which is the same differential equation we got above.

**M3** [Negative temperature is hot] Hint: **Q24.2**

Let us consider a two-state-spin system containing 1 mole of spins (cf. 24.16). Assume that under the magnetic field \(B\), the energy gap between the up and down spin states is 300 K. Suppose the initial temperature of the magnet is \(-500\) K.\(^5\) What is the temperature of this system measured\(^6\) with an ideal gas thermometer containing \(10^{-4}\) moles of monatomic gas

\(^5\) We have already discussed (see Q14.1 (2)) the impossibility of \(T < 0\), if the spatial degrees of freedom are involved. Here, we assume that the spins and lattice vibrations (phonons) are for a sufficiently long time decoupled.

\(^6\) In this case, upon contact with the thermometer, the system temperature changes drastically, so the process cannot be a temperature measuring process. Here, we simply wish to know what happens after the drastic change.
particles? (Assume the initial temperature of the thermometer is around room temperature 300 K, so its initial internal energy may be ignored.)

\[ M = \mu N_A \tanh \frac{150}{T}. \]

Energy conservation or the first law tells us that

\[ 150 N_A k_B \tanh \frac{150}{500} = -150 N_A k_B \tanh \frac{150}{T} + \frac{3}{2} \times 10^{-4} N_A k_B T. \quad (*) \]

or, since we may expect \( T \gg 1 \)

\[ 150 \tanh \frac{150}{500} = 43.7 = \frac{3}{2} \times 10^{-4} T. \]

Thus, \( T = 2.9 \times 10^5 \) K.

This is very hot but the mean speed of a gas molecule of molecular weight 100 may be less than 10 km/s,\(^7\) so we do not need a relativistic correction.

**Comment:** Some people might throwing the equation (*) into Mathematica or whatever, never do such a thing blindly.

**M4 [Ring fluctuation]**

There is a mesoscopic ring of radius \( a \). Due to fluctuation, its shape changes as

\[ r = a + \rho(\theta), \quad (M3) \]

in the plane, where \((r, \theta)\) is the usual polar coordinates around the center of the ring. The deformation free energy may be expressed as

\[ F = \frac{K}{2} \int_0^{2\pi} d\theta \left( \frac{1}{R} - \frac{1}{a} \right)^2, \quad (M4) \]

where \( K \) is a parameter related to the elasticity of the ring and \( R \) is the curvature radius of the deformed ring (a function of \( \theta \)). We know\(^8\) for a small deformation

\[ \frac{1}{R} = \frac{1}{a} - \frac{\rho + \rho''}{a^2}. \quad (M5) \]

We assume the lowest energy nontrivial deformation is

\[ \rho(\theta) = A(\cos 2\theta + \sin 2\theta). \quad (M6) \]

The distribution of the amplitude \( A \) may be observed. Determine \( K \) in terms of the variation of \( A \) and the temperature \( T \) of the ring.

**Soln.**

\(^7\)\( v \propto \sqrt{T} \). At around room temperature the speed of sound is of order 10\(^2\) m/s, so for \( T \sim 10^5 \) K, the speed of the molecules should be of order 10\(^3\) m/s.

The key point is that the probability of fluctuation is proportional to $e^{-\beta W}$, where $W$ is the (isothermal) reversible work required to create the fluctuations. That is exactly $F$ in the problem. The rest is a mere calculation. Introducing $\rho$ into the formula for $F$ we get

$$F = \frac{K}{2} \int_0^{2\pi} d\theta \left( \frac{1}{a^2} (A - 4A)(\cos \theta + \sin \theta) \right)^2 = \frac{9KA^2}{2a^4} \times 2\pi.$$ 

Therefore the probability density for $A$ is proportional to

$$\exp \left( -\beta \frac{9\pi KA^2}{a^4} \right).$$

This implies

$$\langle A^2 \rangle = k_B T a^4 / 18\pi K,$$

or

$$K = k_B T a^4 / 18\pi \langle A^2 \rangle.$$

**M5** [Quantum ideal gas]

(0) Adiabatic free expansion of ideal fermion gas increases its temperature. Although discussed in 29.10, summarize the qualitative supporting argument.

**Soln.** Note that adiabatic free expansion keeps the internal energy constant. Basically, the level spacings shrink, so particles with high energies must ‘climb up’ the energy ladder to keep the total energy constant. Inevitably, a lot of particles end up with excited states. Thus, the system temperature must increase.

Now, let us be quantitative a bit. Suppose $\mu(0) = 1.5$ eV.

(1) Show the following approximate relation for low temperatures $T$, looking at 29.5 ($\alpha$ is given in a footnote; this is a trivial question in order to set the stage):

$$E(T) = E(0) + \frac{3\pi^2}{20} \frac{(Nk_B T)^2}{E(0)}.$$  \hspace{1cm} (M7)

**Soln.**

(29.9) gives

$$E(T) = E(0) + \frac{\pi^2 k_B^2 N T^2}{4\mu(0)}.$$

We also know $\mu(0) = 5E(0)/3N$. Combining these, we get (M7).

(2) If the volume of an ideal fermion gas at $T = 0$ K is 10% expanded by free expansion, what is the final temperature?

**Soln.**
Note that $\mu(0) \propto n^{2/3}$. Under the condition of the problem the total energy is conserved. The density is reduced about 10%. Therefore, $E(0)$ is reduced to $E(0)/(1.1)^{2/3} = 0.938E(0)$. Therefore, we get $E(0)$ original = $E(T)$ after expansion:

$$E(0) = 0.938E(0) + \frac{3\pi^2}{20} \left( \frac{Nk_BT}{E_0} \right)^2.$$ 

That is,$$
1 - 0.938 = 0.062 = \frac{3\pi^2}{0.938 \times 20} \left( \frac{Nk_BT}{E_0} \right)^2.
$$

Therefore, $$\frac{Nk_BT}{E_0} = \sqrt{\frac{0.062 \times 0.938 \times 20}{3\pi^2}} = 0.1982,$$
or $$k_BT = 0.2 \frac{E_0}{N} = 0.2 \times 3 \frac{\mu(0)}{5} = 0.12 \times 1.5 \text{ eV} = 0.18 \text{ eV} = 2088 \text{ K}.$$ Notice that $1 \text{ eV} = 1.16 \times 10^4 \text{ K}$.

**Comment** Is this too large? Well, this should be compared with $\mu(0) = 1.5 \text{ eV}$. The answer should be about 10% of this energy. Thus, the answer is reasonable. How accurate? About $\pm$ 10%, because the next order correction is $O[(T/\mu)^4]$.

**M6** [Chemical potential for low temperature free fermions in 1 and 2-spaces]

Assume that $C_V = \alpha T$; here $\alpha (>0)$ depends on the spatial dimensionality, but it is a constant. Expand $\mu(T)$ to order $T^2$ for 2 and 1-spaces.

**Soln.**

We can immediately see $$E(T) = E(0) + \frac{1}{2} \alpha T^2$$ and $S = \alpha T$ in any space. We wish to mimic our calculation in PST. We need $PV$. Since $D(\epsilon) \propto \epsilon^{3/2-1}$ we get $$PV = \frac{2}{\partial} E.$$ Therefore, to $O[T^2]$ $$N\mu(T) = E - ST + PV = \frac{\partial + 2}{\partial} E - ST = N\mu(0) + \frac{\partial + 2}{2\partial} \alpha T^2 - \alpha T^2 = N\mu(0) + \frac{2 - \partial}{2\partial} \alpha T^2.$$

**M7** ['Entropic' driving force]

There is a membrane through which a polypeptide chain (red string in the figure below) is transported. To expedite this transport, let us use a macromolecule M (say, HSP70) to pull

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the chain. Assume that the molecule M is a ball of radius $a$. There is no energetic interaction between the membrane and M, but they mutually exclude with volume exclusion. Compare the pulling force with and without M.

Let us solve this problem crudely\(^{10}\) through answering the following subproblems.

(1) Before M attaches to the end of the chain, what is the pulling force due to entropy increase? If the length $r$ is increased to $r + dr$, the entropy of the partial chain on the right of the membrane increases, so there is a driving force to pull the chain to the right. (There is of course a force opposing this due to the chain on the other side of the membrane, but that is not our concern.) This is equivalent to counting the number of random walks on a certain lattice. Assume that the bond (monomer) length is $\ell$ and at each joint the chain can choose $n$ ways (cf. $n \approx 2$ for polypeptides). What is the total number of conformations for the chain of length $r$? (This is a trivial question.)

**Soln.**

The number of joints is $r/\ell$, so the total number of conformations is $n^{r/\ell}$.

(2) Due to the membrane half the space is not accessible. Let us use a crude approximation that the number of conformations is proportional to the volume of the accessible space. Then, one half of the conformations obtained in (1) are the relevant conformations to the right of the membrane. Estimate the entropic force pulling the chain along the channel.

**Soln.**

The entropy for length $r$ reads, because $w(r) = n^{r/\ell} \times \text{geometrical factor}$ (which is $1/2$),

$$S(r) = k_B \log n^{r/\ell} + \text{const.} = k_B (r/\ell) \log n + \text{const.}$$

where ‘const’ is due to the spatial constraint, which does not depend on $r$ in this case. Therefore, the free energy is given by

$$A(r) = -k_B T (r/\ell) \log n + \cdots.$$

\(^{10}\text{Any paper you can reach from the HSP70 related paper such as Nature struct. biol., 23, 766 (2016) always use simulation.}\)
Consequently, the force is
\[ f_0(r) = -\frac{dA(r)}{dr} = k_B T \frac{1}{\ell} \log n. \]

Thus, this force certainly pulls the chain, but since we have the other portion of the chain on the opposite side of the membrane, there is no net driving force to pull the chain. That is, the chain undergoes a random walk through the channel.

3) Now, M binds to the end of the chain. Using the same approximation (especially as to the effect of spatial restriction) as above, estimate the entropic force (to show that the effect of M is large if \( r \) is not much larger than \( a \).

**Soln.**

Because of the bulky attachment M the space where the chain can go around freely is restricted, especially severely when \( r \) is small. Since we use the same approximation relying on the geometrical spatial restriction, we may crudely estimate the geometrical factor as the volume of the accessible cone for M as illustrated below:

The restriction is due to the solid angle of the cone which is \( 2\pi (1 - a/r) \), so the restriction ratio is this/4\( \pi \)
\[ \frac{1}{2} \left( 1 - \frac{a}{r} \right) \]

Thus, we approximate
\[ A(r) = -k_B T (r/\ell) \log n - k_B T \log(1 - a/r), \]

Therefore, the force is
\[ f(r) = k_B T \frac{1}{\ell} \log n + k_B T \frac{a/r^2}{1 - a/r} = f_0 + k_B T \frac{a}{r^2 - ar}. \]

The result \( f(r) - f_0 \), that is the net force pulling the chain to the right, is plotted as follows. Here the length unit is \( a \).
**Comment:** I am sure you would say this geometrical estimate is too crude, because the actual accessible space is smaller than this. For example, the particle M can never be in the less-than-$a$-distance zone from the wall. Thus, here, I require only your interpretation (not so outrageous one) and its consistent math implementation.

You may also object that the chain inside M cannot bend so, the total number of conformations should be $n^{(r-a)/\ell}$ instead of the simple $n^{r/\ell}$. That is correct, but this does not affect the result (as we have seen in (2), the total length of the chain does not matter).

(4) The papers on the topic always say the force we obtained is an entropic force. Do you have any comment/objection, etc.?

**Soln.**

**Comment:** This simply asks for your opinion, so any reasonable comments will do. The following is my thought.

It is indeed an entropic effect, IF you totally ignore the cost of attaching M to the chain end. If the chain end is far from the membrane, not much cost is needed to attach M. If this reaction (to make a new bond) reduces the free energy by a few $k_B T$, you can stably attach M to the chain. However, if the chain end is near the membrane, you must overcome the entropy decrease due to the excluded volume effect as well. That is, the new bond formation must include this extra cost. However, this extra cost is just what we need to produce the ‘entropic’ force. This entropic effect is not free; it is paid ‘beforehand’ by the chemical free energy to produce the M-chain bond. Thus, you could think this is a mechanism to convert chemical free energy into mechanical work.

In other words, if you think $M$ is already there, it is undoubtedly an entropic effect. However, if you also have to worry about how to put M on the chain end (since M must be attached after the chain end comes out of the channel), you must think about your total expenditure. It must be paid as chemical free energy. If you are a living cell, you must worry about the total free energy expenditure.