

Physics 112 - Intro to Statistical and Thermal Physics - Spring 2023

Problem Set 02

Due Thursday, February 9 at 11:59 PM (PST)

Last Update: February 2, 2023

- **Reading for the material on this week's problem set:**

- Schroeder, Sections 1.4, 1.5, 1.6, 3.1, 3.2, 4.1

- **Reading for next week:**

- Schroeder, Sections 1.4, 1.5, 1.6, 3.4, 4.1, 4.2, 4.3, 4.4

Problem 2.1 - Partial Derivatives

A lot of physically significant quantities in thermodynamics and statistical mechanics will be defined in terms of partial derivatives. There are two important partial derivative relations that will be crucial for us - the *cyclic chain rule* (also called the *Euler chain rule*) and the *Maxwell relations*.

Consider a relation between three thermodynamic quantities. This could, for example, be an equation of state like the ideal gas law where the three quantities are T , P , and V (with the number of particles N assumed some fixed constant so we have one fewer variable to deal with). We can generically write such a relation as

$$\mathcal{R}(T, P, V) = 0.$$

For the ideal gas, we would have $\mathcal{R} = PV - Nk_B T$.

(a) Extra Part (*Not for Credit*) Use the chain rule to express $d\mathcal{R}$ in terms of partial derivatives and differentials of our quantities.

Answer (highlight to reveal): $[d\mathcal{R} = \frac{\partial \mathcal{R}}{\partial P} dP + \frac{\partial \mathcal{R}}{\partial V} dV + \frac{\partial \mathcal{R}}{\partial T} dT]$

Since our gas must obey our equation of state, any process must maintain $\mathcal{R}(T, P, V) = 0$ which means we will always have $d\mathcal{R} = 0$.

(b) Use this fact and your answer from (a) to determine $(\frac{\partial T}{\partial V})_P$ and $(\frac{\partial V}{\partial T})_P$ in terms of partial derivatives of \mathcal{R} (see the spoiler-answer below for an example).

Hint (highlight to reveal): [Remember that we are keeping the pressure P constant!]

(c) Extra Part (*Not for Credit*) Repeat for the quantities $(\frac{\partial V}{\partial P})_T$ and $(\frac{\partial P}{\partial T})_V$.

Spoilers! For part (c) you should have found

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{(\partial \mathcal{R}/\partial P)_{T,V}}{(\partial \mathcal{R}/\partial V)_{T,P}}, \quad \left(\frac{\partial P}{\partial T}\right)_V = -\frac{(\partial \mathcal{R}/\partial T)_{P,V}}{(\partial \mathcal{R}/\partial P)_{T,V}}.$$

(d) Using your previous answers, show the *cyclic chain rule*,

$$\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V = -1.$$

(e) **Extra Part** (*Not for Credit*) Show this alternate forms of the cyclic chain rule,

$$\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P; \quad \left(\frac{\partial V}{\partial P}\right)_T = -\frac{(\frac{\partial V}{\partial T})_P}{(\frac{\partial P}{\partial T})_V}.$$

Commentary: Note that this is *almost* what we would naively expect just manipulating “numerators and denominators” in a partial derivative... except for the minus sign. Hopefully this derivation gives some insight to that minus sign.

We will soon define a number of “free energies”, each of which will take different state variables as the natural independent variables. For example, the internal energy U naturally takes entropy S , volume V , and number of particles N as its independent variables, $U(S, V, N)$. The Helmholtz free energy in contrast takes temperature T , volume V , and number of particles N as its independent variables $F(T, V, N)$. The infinitesimal change in the function due to infinitesimal changes in the independent variables can be found via the chain rule. For example,

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN.$$

Comparing to the first law, $dU = T dS - P dV + \mu dN$, we see

$$T \equiv \left(\frac{\partial U}{\partial S}\right)_{V,N}, \quad P \equiv -\left(\frac{\partial U}{\partial V}\right)_{S,N}, \quad \mu \equiv \left(\frac{\partial U}{\partial N}\right)_{S,V}. \quad (1)$$

Neat! Temperature is the increase of energy due to increasing entropy isochorically, pressure is the decrease of energy due to increasing volume in a reversible adiabatic (isentropic) process, and chemical potential is the increase of energy due to adding particles adiabatically and isochorically. Now, for a function of two independent variables, the partial derivatives will commute,

$$Z(x, y) \implies \frac{\partial^2 Z}{\partial x \partial y} = \frac{\partial^2 Z}{\partial y \partial x} \implies \frac{\partial}{\partial x} \left(\frac{\partial Z}{\partial y}\right) = \frac{\partial}{\partial y} \left(\frac{\partial Z}{\partial x}\right) \quad (2)$$

This is at the heart of the **Maxwell relations**, which will relate two different partial derivatives.

(f) Use Eqs. 1 and 2 to show the Maxwell relation between temperature and pressure,

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

(g) Find a Maxwell relation between pressure and chemical potential.

Problem 2.2 - Heat Capacities and Calorimetry

We defined the *heat capacity* and at constant volume C_V as

$$C_V = \left(\frac{\delta Q}{dT} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V.$$

The *specific heat* at constant volume is the heat capacity-per-unit-mass, $c_V = C_V/m$. Infinitesimal heats from quasistatic processes can be determined using inexact differentials. For an *isochoric* (i.e. constant-volume) process, for example,

$$\delta Q = C_V dT. \quad (\text{Isochoric process})$$

The infinitesimal entropy change for an isochoric process is therefore

$$dS = \frac{\delta Q}{T} = \frac{C_V dT}{T}. \quad (\text{Isochoric process})$$

(a) What is the entropy change for a system with *temperature-independent* heat capacity C_V being isochorically heated from T_1 to T_2 ?

We can approximate the specific heat (at either constant volume or constant pressure) of liquid water as constant at roughly¹ 4200 J/kg·K. Consider an effectively thermally isolated system (e.g. a thick Styrofoam cup) so that no net heat can flow into or out of the system. Consider two samples of water, one of mass m_1 at temperature T_1 and the other with mass m_2 at temperature T_2 . The samples are mixed in our isolated system and the combined system is allowed to come into thermal equilibrium.

(b) Determine the final equilibrium temperature T_{eq} of the water.

(c) Is the process described above a reversible or irreversible process? If it is reversible, describe how we can reverse it! If it is irreversible, describe a reversible process that can bring the *system* (our two samples of water) from the initial state (system \mathcal{S}_1 of mass m_1 at temperature T_1 and system \mathcal{S}_2 of mass m_2 at temperature T_2) to the final state (both systems at the temperature T_{eq} we found earlier).

[Note: Remember, for a reversible process, both the systems and the environment have to be returned to their original state. When we invent our reversible process, we can introduce new bits of the environment that weren't present in our original setup. We just care about keeping our system the same.]

(d) What is the total change in entropy of the system in this mixing process?

Hint (highlight to reveal): [Remember, since S is a state variable we can use our result from part (a) and our process from part (c).]

(e) Show or argue that $\Delta S \geq 0$ for the result you found in the specific case $m_1 = m_2$.

[Note: You should find that $\Delta S = 0$ only in the case $T_1 = T_2$ which confirms the process is irreversible if our system doesn't start in equilibrium!]

[Supplementary Part (Not for Credit): Show that $\Delta S > 0$ in the case $m_1 \gg m_2$. You can do this by letting $m_2 \equiv \epsilon m_1$ and expanding to first order in epsilon.]

¹This value will vary slightly based on temperature and whether we are considering an isochoric or isobaric process. However, we will ignore that for this part.

In the **Debye model** of a solid (which we will study later in the semester), the heat capacity at constant volume for low temperatures² is given by

$$C_V = \alpha N k_B T^3,$$

where α is some constant. Consider two identical Debye solids (so their N s are equal), one with temperature T_1 and the other with higher temperature $T_2 > T_1$. We keep the two solids isolated from everything but each other and bring them into thermal contact, allowing them to equilibrate.

(f) Determine the final equilibrium temperature T_{eq} .

(g) **Extra Part** (*Not for Credit*) Find the total change in entropy of the two-solid system.

We can non-dimensionalize this system by letting $T_2 = \tau T_1$ and $S = \sigma(\alpha N k_B T_1^3)$. In terms of the non-dimensionalized temperature τ and entropy σ , our answer from the previous part should turn into

$$\Delta\sigma = \frac{1}{3} \left(2 \left(\frac{1 + \tau^4}{2} \right)^{3/4} - 1 - \tau^3 \right).$$

(h) **Extra Part** (*Not for Credit*) Plot $\Delta\sigma$ -vs- τ and show that we always have $\Delta\sigma \geq 0$ with $\Delta\sigma = 0$ if and only if $\tau = 1$.

[Note: We can interpret this as saying our process is irreversible except in the case where the two solids start out at the same temperature and are thus already in equilibrium.]

Problem 2.3 - Thermodynamic Processes and Cycles

In this problem we will consider a system containing N particles of an ideal gas and assume that the ideal gas has f degrees of freedom-per-particle. We start with our system in an equilibrium state at pressure P_1 and volume V_1 , which determines the temperature T_1 . Consider the following four reversible/quasistatic processes:

- An **isochoric** or isovolumetric (constant volume) heating at volume V from temperature T_1 to temperature $T_2 > T_1$.
- An **isobaric** (constant pressure) expansion at pressure P from volume V_1 to volume $V_2 > V_1$.
- An **isothermal** (constant temperature) expansion at temperature T from volume V_1 to volume $V_2 > V_1$.
- An **isentropic** (reversible and adiabatic, which implies “constant entropy”) expansion from volume V_1 and temperature T_1 to temperature $T_2 < T_1$.

Recall that in an isentropic change, PV^γ is constant, where $\gamma \equiv C_P/C_V$.

(a) For each of the four processes detailed, plot the transformation on a PV diagram and determine the change in internal energy ΔU , the heat Q , and the work W . Make sure to keep proper track of signs.

[Note: Recall that $Q > 0$ implies heat is flowing into the system and $W > 0$ implies work is being done on the system.]

²“Low” temperature here means low compared to the characteristic temperature scale for the Debye solid, the so-called **Debye temperature**.

The (idealized) **Stirling cycle**³ is a heat engine that takes the following reversible/quasistatic four-step path:

1. An isothermal expansion at a high temperature T_H from an initial volume V_1 to final volume $V_2 > V_1$.
2. An isochoric cooling at volume V_2 from high temperature T_H to low temperature T_L .
3. An isothermal compression at low temperature T_L from volume V_2 back to volume V_1 .
4. An isochoric heating at volume V_1 back to the original state.

(b) Determine the *net* work W done in this cycle and the heat flow Q_{in} *into* the system (that is, the sum of all positive heats only). What is the thermodynamic efficiency $\eta = |W|/|Q_{in}|$ for this cycle? Are we satisfying the Carnot statement of the second law (that $\eta \leq \eta_{Carnot} = 1 - \frac{T_L}{T_H}$)?

Hint (highlight to reveal): [Your denominator should consist of a sum of two positive terms. To show the inequality, try “ignoring” one of the terms. Recall that, if $a, b > 0$ then $1/a + b < 1/a$.]

For a van der Waals gas, recall that the equation of state is

$$\left(P + \frac{aN^2}{V^2}\right)(V - bN) = Nk_B T \implies P = \frac{Nk_B T}{V - bN} - a \frac{N^2}{V^2}.$$

The internal energy for a monoatomic van der Waals gas is given by

$$U(T, N, V) = \frac{3}{2}Nk_B T - a \frac{N^2}{V}.$$

Let’s assume that we are operating in pressure, volume, and temperature ranges large enough so that no phase transitions occur.

(c) **Extra Part (Not for Credit)** Repeat part (a) for the isochoric transformation and the isothermal transformation.

(d) By using the first law of thermodynamics, find $\frac{dT}{dV}$ for an isentropic transformation of the van der Waals gas.

Hint (highlight to reveal): [Start by using the equation for the internal energy of the van der Waals gas to express dU in terms of the differentials dT and dV . Then use the first law to get another expression for dU . Remember that we are strictly dealing with an isentropic process...]

Suppose we have a van der Waals gas and isentropically expand it from initial temperature T_1 and volume V_1 to volume V_2 .

(e) What is the temperature T_2 ? Compare your result to what you would have gotten had this been a monoatomic *ideal* gas.

[Note: Last week we solved for isentropic behavior of an ideal gas using kinetic theory. This part is much simpler since we now have the first law and concepts of heat and work at our disposal!]

³See Schroeder, Problem 4.21 and/or the Wikipedia page https://en.wikipedia.org/wiki/Stirling_cycle for more information about how physical Sterling engines are constructed and how they deviate from this idealized model.

Problem 2.4 - The Carnot Efficiency and Carnot Engine

A **Carnot engine** is a reversible engine where the system exchanges heat with the environment only through two reservoirs - a high temperature heat bath at temperature T_H and a low temperature heat bath at temperature T_L . In terms of our transformations from the previous problem, this means that we can build a Carnot cycle out of four steps:

1. An isothermal expansion at temperature T_H . This is the only source of heat input into the system.
2. An isentropic cooling to temperature T_L . There is no heat flow in this process.
3. An isothermal compression at temperature T_L . This is the only source of heat output from the system.
4. An isentropic heating⁴ back to temperature T_H to close the cycle. There is no heat flow in this process.

The **Carnot statement** of the second law of thermodynamics is as follows:

The efficiency of a quasi-static or reversible Carnot cycle depends only on the temperatures of the two heat reservoirs, and is the same, whatever the working substance. A Carnot engine operated in this way is the most efficient possible heat engine using those two temperatures.

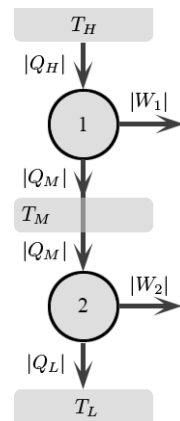
That is, the efficiency of the Carnot engine must be given by a function $\eta_C(T_H, T_L)$ and not is not dependant on any other feature of the engine - it doesn't matter if we are using an ideal polyatomic gas or a van der Waals gas, etc. It also doesn't depend on the starting volume or the scale of expansion/compression being carried out.

(a) Extra Part (Not for Credit) Find the efficiency of a Carnot engine operating between reservoirs T_H and T_L and where the isothermal expansion at T_H goes from volume V_1 to volume V_2 . As an intermediate step you will need to find the volumes V_3 and V_4 , the starting and ending volumes of the isothermal compression at T_L .

[Note: This is similar to what we did for the Sterling engine and is a lot of algebra, which is why this is a not-for-credit part.]

Even without explicitly knowing the explicitly formula for the Carnot efficiency, we can get a lot of information from the Carnot statement. Let's save ourselves some writing and define $\eta_{ij} \equiv \eta_C(T_i, T_j)$.

Consider a series of three reservoirs, of temperatures $T_H > T_M > T_L$ and let's operate two Carnot engines, one between T_H and T_M and one between T_M and T_L . The first engine takes in heat $|Q_H|$ from T_H , deposits heat $|Q_M|$ to T_M , and in the process does work $|W_1|$. When the second engine takes in the same heat $|Q_M|$ from T_M , it deposits heat $|Q_L|$ to T_L , and in the process does work $|W_2|$. Let the efficiencies of the two engines individually be η_{HM} and η_{ML} . Define η_{combo} to be the efficiency of the combined-engine setup. A schematic showing energy flows is to the right.



(b) What is the efficiency η_{combo} of this combined-engine setup in terms of η_{HM} and η_{ML} ?

[Note: The relevant output here is the total work done by both engines and the relevant input is only the heat flow into the first engine, since the heat flow into the second engine is directly from the heat flow out of the first engine and is occurring at the same temperature.]

⁴We are using "heating" in the colloquial sense of "raising the temperature" here. Since this is an isentropic transformation, there is no heat flow in this step!

Another way of conceptualizing our two-engine setup is that we have a single system operating under an eight-step process (we start at step 4 of the earlier Carnot cycle description to better visualize):

1. An isentropic heating from T_M to T_H .
2. An isothermal expansion at temperature T_H .
3. An isentropic cooling to temperature T_M .
4. An isothermal compression at temperature T_M to close the first cycle.
5. *Reversing* the isothermal compression at temperature T_M making this the first step in the second Carnot cycle - an isothermal expansion at temperature T_M .
6. An isentropic cooling to temperature T_L .
7. An isothermal compression at temperature T_L .
8. An isentropic heating to temperature T_M to close the second cycle.

(c) **Extra Part** (*Not for Credit*) Show or argue that by letting steps 4 and 5 “cancel each other out”, and thus combining steps 3 and 6 and combining steps 8 and 1, we are left with a *single* Carnot cycle acting between T_L and T_H !

By the previous part and the Carnot statement of the second law, the efficiency of our combined-system must be

$$\eta_{\text{combo}} = \eta_{HL}, \quad (3)$$

where we found η_{combo} in part (b).

(d) Show that if we define a supplemental variable ζ_{ij} so that $\eta_{ij} \equiv 1 - e^{\zeta_{ij}}$ then Eq. 3 becomes equivalent to $\zeta_{HM} + \zeta_{ML} = \zeta_{HL}$.

Ah! That last equation is *easy* to satisfy! If we have *any* dimensionless, monotonically increasing function of temperature, $f(T)$, then we can just set $\zeta_{ij} \equiv f(T_j) - f(T_i)$.

(e) Show that if we choose $f(T) = \ln(T/T_0)$ (where T_0 is some arbitrary fixed reference temperature) then we recover the known Carnot efficiency formula,⁵

$$\eta_C(T_H, T_L) = 1 - \frac{T_L}{T_H}.$$

Some closing discussion of this result from (e): It turns out that there had been a long-standing puzzle in thermometry prior to Carnot - and that many of you identified in the tap-backs - temperatures as defined by different thermometers didn't always or necessarily agree! That is, setting two common reference temperatures between two thermometers with different working substances or principles (e.g. a mercury thermometer vs. a bimetallic thermometer) and evenly subdividing the interval doesn't always yield equal intermediate temperatures. The different thermometers essentially correspond to different choices of the function $f(T)$! The Carnot result allows us to set a **universal standard** to calibrate thermometers - we just define the “absolute” temperature via $T_{\text{abs}} \equiv T_0 e^{f(T)}$, where T_0 is some temperature scale factor and $f(T)$ is the monotonically increasing function of temperature as read on a given device. That is, we ultimately *use* the Carnot efficiency formula to define the absolute temperature scale.

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⁵Neat. Soooo neat!