

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

Problem Set 03

Due Thursday, February 16 at 11:59 PM (PST)

Last Update: February 9, 2023

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

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

- **Reading for next week:**

- Schroeder, Sections 1.7, 2.1, 2.2

Problem 3.1 - Equivalent Statements of the Second Law

Let's warm up with some problems on heat engines and the second law! In this problem we will explore the equivalence of some statements of the second law of thermodynamics. The main statements are:

- **Carnot Statement:** *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.*
- **Clausius Statement (Engine version):** *Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time.* In other words, heat cannot flow from cold temperatures to hot temperatures without external work being performed on the system.
- **Kelvin-Planck Statement:** *It is impossible to devise a cyclically operating device, the sole effect of which is to absorb energy in the form of heat from a single thermal reservoir and to deliver an equivalent amount of work.* In other words, we can't convert heat directly into work - there must be some waste heat. A third way of stating this is that the efficiency of a cyclic heat engine must be strictly less than 1.
- **Planck Statement:** *Every process occurring in nature proceeds in the sense in which the sum of the entropies of all bodies taking part in the process is increased. In the limit, i.e. for reversible processes, the sum of the entropies remains unchanged.* In other words, the entropy of an isolated system can never decrease. The "isolated system" of course may be the full universe with actual system of interest considered as a subsystem.¹

Recall that to show two statements A and B are equivalent, we must show that A implies B and B implies A or, equivalently, "not B " implies "not A " and "not A " implies "not B ".

¹We can decrease the entropy of a system by letting it interact with the environment, at the cost of at equal or greater entropy increase of the environment.

- Let's call an engine that violates the Carnot statement a ***super-Carnot*** engine. That is, a super-Carnot engine operates between two heat baths with an efficiency greater than the Carnot efficiency.
- Let's call an engine that violates the Clausius statement an ***anti-Clausius engine***. That is, an anti-Clausius engine's net effect is only to pull heat from a cold bath and deposit it into a hot bath.
- Let's call an engine that violates the Kelvin statement an ***anti-Kelvin engine***². That is, an anti-Kelvin engine is that takes heat from the high-temperature bath and directly converts it to work.

(a) Show that using the work output of a super-Carnot engine to drive a Carnot engine in reverse results in an anti-Clausius engine. Conversely, show that combining an anti-Clausius engine with a Carnot engine in parallel yields a super-Carnot engine.

[Note: This proves the equivalence of the Carnot and Clausius statements.]

(b) Using similar constructions to (a), show that if we have an anti-Kelvin engine then we can use it to construct an anti-Clausius device. Conversely, show that if we have an anti-Clausius engine then we can use it to construct an anti-Kelvin device.

[Note: This proves the equivalence of the Clausius and Kelvin-Planck statements.]

(c) Show or argue either of the following:

- An anti-Clausius engine violates the Planck statement.
- An anti-Kelvin engine violates the Planck statement.

Problem 3.2 - Entropy, Engines, and the Third Law

Consider an ideal gas of N particles with f degrees of freedom initially in an equilibrium state α at temperature T_0 and with volume V_0 . Let equilibrium state β be at temperature T and volume V .

(a) Find the change in entropy ΔS in the gas in going from state α to state β .

Hint (highlight to reveal): [Since we are dealing with an ideal gas and a set number of degrees of freedom we may take C_V and C_P to be temperature-independent for this problem.]

Suppose we had two bodies, each with the same heat capacity C_P which will be assumed to be independent of temperature in the temperature ranges being considered. One starts at temperature T_H and the other at lower temperature T_C . We will use these two bodies as the hot and cold reservoirs for a Carnot engine. We will operate this engine under the condition that the two bodies are held at constant pressure.³ The twist now is that running the engine and pulling heat from the hot bath will lower the temperature of the hot bath and depositing heat into the cold bath will raise the temperature of the cold bath. Eventually by running the engine the two temperatures of the baths will become identical, T_f .

²Anti-Kelvin devices are also known as ***perpetual motion machines of the second kind***.

³The pressure of the working substance of the engine can change as necessary, though!

(b) Since we are running a Carnot engine, what can we say about the total change of entropy of the “environment” during this process? In terms of the total heat extracted from the hot body and the total heat deposited into the cold body, what is the total entropy change of the environment this process? Use these answers to determine the final temperature T_f of the two bodies.

(c) **Extra Part** (*Not for Credit*) If our engine were a real engine (and thus less efficient than the Carnot engine), would the final temperature reached be larger or smaller than what you found in (b)? How does the final temperature you found in (b) compare to what we would get if we directly placed the bodies in thermal contact and let them equilibrate (as we did in the prior problem set)?

(d) What is the total amount of work we can get out of this engine (and thus the maximum amount of work we can extract using a heat engine)?

The **third law of thermodynamics** states:

■ The entropy of a system approaches a constant value when the temperature of the system approaches absolute zero.

(e) Argue that the third law implies that the heat capacities at constant temperature and at constant pressure must approach 0 in the limit as temperature goes to absolute zero.

We can define the **thermal expansion coefficient** β as the fractional increase in volume per unit change in temperature (with the pressure held fixed),

$$\beta \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P,N}.$$

In the second problem set we explored the Maxwell relations which allowed us to relate various partial derivatives.

(f) Using a Maxwell relation to manipulate the derivative, show that β must also be zero at $T = 0$.

Hint (highlight to reveal): [If we look at the derivative we have, $(\frac{\partial V}{\partial T})_{P,N}$, we want to use the thermodynamic potential whose natural variables are T , P , and N . Note that V can now be related to a derivative of this potential with respect to one of the natural variables.]

Problem 3.3 - Thermodynamic Stability

Consider an isolated system made of two subsystems S_1 and S_2 . Let these subsystems individually be at equilibrium with internal energies U_1 and U_2 , entropies S_1 and S_2 , and volumes V_1 and V_2 . These may depend on the other natural extensive variables like N as well but we will just consider these three variables in this problem. The two subsystems are *not* assumed to be in equilibrium with each other... yet. Because energy and entropy are extensive quantities, we must have $U_{tot} = U_1 + U_2$ and $S_{tot} = S_1 + S_2$. Because the system is isolated we must have U_{tot} remain constant. We can write $S_{tot}(U_1, V_1, U_2, V_2) = S_1(U_1, V_1) + S_2(U_{tot} - U_1, V_{tot} - V_1)$. By adjusting the balance of energy between the two subsystems we can change the entropy of the total system.

(a) Show that the condition for entropy to be at an extremum as we vary U_1 keeping V_1 fixed implies $\frac{1}{T_1} = \frac{1}{T_2}$, equivalent to our condition for thermal equilibrium. What do we get if we extremize entropy by varying V_1 keeping U_1 fixed at its thermal equilibrium value?

The previous result shows that in thermal equilibrium the entropy reaches an extremum. Now we will argue that it must be a *maximum* by looking at the second derivative.

(b) Show that $\left(\frac{\partial^2 S}{\partial U^2}\right)_V < 0$ implies $\left(\frac{\partial T}{\partial U}\right)_V > 0$. That is, if entropy is convex then increasing/decreasing the energy at constant volume increases/decreases the temperature.

Hint (highlight to reveal): [Start with $\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$ and take the derivative with respect to U on both sides.]

Thermodynamic stability requires the graph of entropy-vs-energy to be concave-down (convex), $\left(\frac{\partial^2 S}{\partial U^2}\right)_V < 0$. To see this, again consider our two systems. Suppose they start in equilibrium with each other.

(c) Argue that if $\left(\frac{\partial^2 S}{\partial U^2}\right)_V > 0$ then the equilibrium is *unstable*.

Hint (highlight to reveal): [Recall that differences in temperature drive heat flow from hot to cold. What happens to the temperatures of the two systems if a little bit of energy gets nudged from one system to the other? Why does this lead to a cascade/runaway effect away from equilibrium?]

Similar arguments can be made for convexity of entropy with respect to any other natural extensive variable of the system. The extremum condition combined with convexity show that the entropy is indeed at a *maximum* in equilibrium. The above result may be written as the **principle of maximum entropy**,

For an isolated system (a system with fixed energy, volume, and other extensive variable), the entropy is maximized at equilibrium.

Problem 3.4 - Thermodynamic Potentials

In class we looked at four thermodynamic potentials that depended on different sets of natural variables - the internal energy $U(S, V, N_i)$, the enthalpy $H(S, P, N_i)$, the Helmholtz Free Energy $F(T, V, N_i)$, and the Gibbs Free Energy $G(T, P, N_i)$. These were all related by various Legendre transformations. In short,

$$H = U + PV, \quad F = U - TS, \quad G = U - TS + PV.$$

Note that we have to be careful with our variables in these expressions. For example, the Helmholtz free energy is given by a Legendre transformation from the internal energy $U(S, V, N_i)$ on the conjugate pair (S, T) ,

$$F(T, V, N_i) = U(S(T, V, N_i), V, N_i) - S(T, V, N_i)T. \quad (1)$$

The expressions of the differentials of these with respect to the differentials of the natural variables are called the **thermodynamic identities**. The thermodynamic identity for F is

$$dF = -S dT - P dV + \sum_i \mu_i dN_i.$$

(a) Use Eq. 1 to find $\left(\frac{\partial F}{\partial T}\right)_{V, N_i}$ and show that your answer agrees with what is suggested by the thermodynamic identity for F .

[Supplementary Part (Not for Credit): Then do the same thing for $\left(\frac{\partial F}{\partial V}\right)_{T, N_i}$ and $\left(\frac{\partial F}{\partial N_i}\right)_{T, V, N_{j \neq i}}$ to recover the full thermodynamic identity.]

Hint (highlight to reveal): [Remember, we have temperature dependence in the entropy now! You will have to use the chain rule for the first term in F and the product rule for the second term.]

(b) Show the **Gibbs-Helmholtz equation** (a relationship between the Gibbs free energy and the enthalpy),

$$\left(\frac{\partial(G/T)}{\partial T}\right)_{P, N_i} = -\frac{H}{T^2}.$$

We haven't really touched the number of particles/chemical potential pair of conjugate variables yet. Let's look at that now. Consider a system with just a single species of particle so we only have one chemical potential μ and number of particles variable N to deal with. The **grand potential** (also called the **Landau free energy**), $\Psi(T, V, \mu)$, is the free energy using the natural variables T , V , and μ . That is, we do Legendre transformations from the internal energy $U(S, V, N_i)$ on both conjugate pairs (S, T) and (N, μ) .

(c) Express $\Psi(T, V, \mu)$ in terms of the internal energy to come up with a similar expression as in Eq. 1.

(d) Find the thermodynamic identity for Ψ and express the conjugates to the natural variables as partial derivatives of Ψ . Be sure to indicate what quantities are held constant.

(e) **Extra Part (Not for Credit)** Use the fact that Ψ and V are extensive while T and μ are intensive to show that $\Psi = -PV$. Argue that this agrees with your result from (a).

Hint (highlight to reveal): [We did something similar in lecture to show $U = TS - PV + \mu N$.]

(f) [Short] Find a Maxwell relation between N and S .



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