

Thermodynamics II

Reading: chapters 11-14 and 16-17 in Blundell and Blundell cover classical thermodynamics. The first four chapters of Fermi also cover this material carefully, if you want more rigor.

1 The First Law

In this section we'll cover the first law of thermodynamics, taking the opportunity to introduce some multivariable calculus. The first law states that

$$dU = dQ + dW$$

where U is the internal energy, Q is the heat given to the system, and W is the work done on the system. The use of d rather than d indicates that Q and W are not state functions, while dU is indeed the differential of a state function.

In the case of a gas, the state of the system is specified by the pressure P , volume V , and temperature T , and the three are related by an equation of state. The infinitesimal work done is

$$dW = -PdV.$$

Since the state of a gas is described by two parameters (since one is taken care of by the equation of state), we need to use partial derivatives, generalizations of derivatives which specify which parameter is being held constant. This is not fundamentally different than what you did in introductory thermodynamics; all basic thermodynamic processes are already phrased in terms of keeping something constant. The notation for partial derivatives is a bit complicated, but everything we do will rely on only a single principle.

Idea 1: Multivariable Differential

If the variables x and y may be varied independently, we may write

$$df = \left. \frac{\partial f}{\partial x} \right|_y dx + \left. \frac{\partial f}{\partial y} \right|_x dy$$

for a function $f(x, y)$. This is also valid when the differential doesn't correspond to a function, in which case we must write $d\vec{f}$ on the left-hand side.

Note that Olympiad questions will not be written in this notation, because multivariable calculus is not on the USAPhO or IPhO syllabus. However, the formalism of partial derivatives is a useful way to clarify what you've already been doing, and figure out what's going on in complicated situations. However, if you find this formalism overwhelming, it isn't necessary to solve Olympiad problems and the other problems in this problem set.

Example 1: Heat Capacities

The heat capacities at constant volume and constant pressure are defined as

$$C_V = \left. \frac{\partial Q}{\partial T} \right|_V, \quad C_P = \left. \frac{\partial Q}{\partial T} \right|_P.$$

Find a general formula for $C_P - C_V$.

The internal energy is a function of T , V , and P . Suppose we eliminate P using the equation of state, so we have $U(T, V)$ where T and V may be varied independently. Then

$$dU = \left. \frac{\partial U}{\partial T} \right|_V dT + \left. \frac{\partial U}{\partial V} \right|_T dV.$$

That is, if we change the system infinitesimally, so that the temperature is changed by dT and the volume is changed by dV , the change in the internal energy dU is given by two terms: the change due to dT alone, and the change due to dV alone. Applying the first law gives

$$\bar{d}Q = \left. \frac{\partial U}{\partial T} \right|_V dT + \left(\left. \frac{\partial U}{\partial V} \right|_T + P \right) dV.$$

Just like dU , the differential of heat $\bar{d}Q$ can be written as

$$\bar{d}Q = C_V dT + \left. \frac{\partial Q}{\partial V} \right|_T dV \quad \text{or} \quad \bar{d}Q = C_P dT + \left. \frac{\partial Q}{\partial P} \right|_T dP.$$

In the former case, we can compare our expressions for $\bar{d}Q$ in terms of dT and dV to find

$$C_V = \left. \frac{\partial U}{\partial T} \right|_V.$$

As for C_P , we need to write our original expression for $\bar{d}Q$ in terms of dT and dP . To do this, consider V as a function $V(T, P)$, giving the differential

$$dV = \left. \frac{\partial V}{\partial T} \right|_P dT + \left. \frac{\partial V}{\partial P} \right|_T dP.$$

By plugging this into our first expression for $\bar{d}Q$ and simplifying, we get

$$C_P - C_V = \left(\left. \frac{\partial U}{\partial V} \right|_T + P \right) \left. \frac{\partial V}{\partial T} \right|_P.$$

Intuitively, the extra heat we have to put in at constant pressure, when we allow the volume to change, comes from two sources. First, we have to make up for the energy lost to PdV work. Second, we have to make up for the energy intrinsically needed to expand the gas, by doing work against the attractive intermolecular forces between the gas molecules. This term is zero for an ideal gas by definition, as you'll see in the following exercise.

Exercise 1. For an monatomic ideal gas, we have $U = (3/2)nRT$ and the equation of state $PV = nRT$. Evaluate C_V and C_P using the results above.

Exercise 2 (BB 11.4). It's dangerous to use partial derivatives without specifying what is held constant. In polar coordinates, we have $x = r \cos \theta$ and $y = r \sin \theta$. Then

$$\frac{\partial x}{\partial r} = \cos \theta = \frac{x}{r}.$$

On the other hand, we have $r^2 = x^2 + y^2$, so taking the partial derivative with respect to r gives

$$2r = 2x \frac{\partial x}{\partial r}, \quad \frac{\partial x}{\partial r} = \frac{r}{x}.$$

Hence we have two different expressions for $\partial x / \partial r$. How can these be consistent?

Problem 1. In this problem we modify the ideal gas to account for a short-ranged attractive intermolecular force. This attraction yields a negative contribution to the energy, so that

$$U = \frac{3}{2}nRT - \frac{an^2}{V}.$$

- (a) Explain why the change in energy is proportional to n^2 and inversely proportional to V .
- (b) Argue that because of this extra term, the pressure is an^2/V^2 less than it would be for an ideal gas. Hence the equation of state is

$$\left(P + \frac{an^2}{V^2}\right)V = nRT.$$

- (c) Show that the heat capacities are

$$C_V = \frac{3}{2}nR, \quad C_P - C_V = nR + \frac{2an^2}{TV} + O(n^3)$$

in the limit where the gas is dilute.

Idea 2: Partial Derivative Identities

The partial derivative satisfies the following identities.

$$\frac{\partial y}{\partial x} \bigg|_z \frac{\partial x}{\partial y} \bigg|_z = 1 \quad \frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}.$$

In the first identity, we think of the functions as $y(x, z)$ and $x(y, z)$. By keeping z constant, we are simply reduced to the single-variable case $y(x)$ and $x(y)$, and the result follows from the ordinary chain rule. The second identity shows that partial derivatives commute.

Exercise 3. For a function $f(x, y)$ with differential

$$df = f_x dx + f_y dy$$

prove that the identity

$$\frac{\partial f_x}{\partial y} \bigg|_x = \frac{\partial f_y}{\partial x} \bigg|_y$$

must be satisfied. Conversely, if you are given a differential that doesn't satisfy this, you can be sure that it's not the differential of *any* function. For an ideal gas, write down the differential dQ in terms of dT and dV , and use it to prove that Q is not a state function.

Exercise 4. Starting from the differential $dU = -PdV + TdS$, show that

$$-\left.\frac{\partial P}{\partial S}\right|_V = \left.\frac{\partial T}{\partial V}\right|_S.$$

This is an example of a Maxwell relation.

Problem 2 (BB 12.2). Consider a gas with the equation of state $PV = f(T)$. Show that

$$\left.\frac{\partial P}{\partial T}\right|_V = \frac{1}{V} \frac{df}{dT}, \quad \left.\frac{\partial V}{\partial T}\right|_p = \frac{1}{p} \frac{df}{dT}.$$

Also show that

$$\left.\frac{\partial Q}{\partial V}\right|_P = C_P \left.\frac{\partial T}{\partial V}\right|_P, \quad \left.\frac{\partial Q}{\partial P}\right|_V = C_V \left.\frac{\partial T}{\partial P}\right|_V.$$

In an adiabatic process, we have $dQ = 0$. By taking the differential with respect to dp and dV , show that PV^γ is constant, thus generalizing the rule for adiabatic processes for ideal gases.

2 The Second Law

The entropy S is defined by

$$dS = \frac{dQ}{T} \text{ for a reversible process.}$$

Explicitly, dS is the increase in entropy of a body at temperature T that receives heat dQ . It can be shown that S is a state function, so we can write dS . For a proof, see Fermi or chapter 13 of Blundell and Blundell. This definition means adiabatic processes hold entropy constant.

Idea 3: Second Law

The second law of thermodynamics takes several equivalent forms, which are all useful.

- For an isolated system, $dS > 0$ for any spontaneous process.
- Clausius: no process is possible whose sole result is the transfer of heat from a colder to a hotter body.
- Kelvin: no process is possible whose sole result is the complete conversion of heat into work.
- Carnot: of all heat engines working between two given temperatures, none is more efficient than a Carnot engine.

Exercise 5. Verify that the second law of thermodynamics allows heat to flow from a hot body to a cold one, but not vice versa. In particular, note that it doesn't forbid the entropy of the hot body from decreasing, only the total entropy.

Exercise 6. Some systems, such as gravitationally bound systems of particles, and black holes have negative heat capacities.

- (a) What happens if a system with a negative heat capacity is placed in thermal contact with a slightly cooler system with a positive heat capacity?
- (b) What if the other system also has a negative heat capacity?

Some other systems, such as lasers, have negative temperatures and positive heat capacities.

- (c) What happens if such a system is placed in thermal contact with a system with positive temperature and heat capacity?

Exercise 7. Consider the free expansion of an ideal gas. No work is done, and the internal energy U does not change. However, the entropy increases since the process is irreversible. On the other hand, the First Law states

$$dU = TdS - dW$$

so there appears to be a contradiction. What is wrong with this argument?

Exercise 8. Derive the efficiency of a Carnot engine operating between reservoirs of temperatures $T_H > T_C$ by using the fact that the Carnot cycle is reversible, and after a complete Carnot cycle, the entropy of the engine itself returns to its original value. Verify that the operation of a Carnot cycle does not increase the total entropy of the engine and reservoirs.

Problem 3. Consider two objects of heat capacities C_1 and C_2 at temperatures T_1 and T_2 . A reversible heat engine is run between the two objects until they are at the same temperature T_f . Find T_f and the work done by the heat engine. (Hint: think of the process as a combination of infinitesimal Carnot cycles.)

Problem 4. ⌚ USAPhO 2014, problem A2.

Problem 5. ⌚ USAPhO 2017, problem A2. Once you're done, see problem 13.9 of Blundell and Blundell. There's an important lesson to be drawn from this.

Problem 6. Consider n moles of a monatomic ideal gas in a volume V with temperature T . The gas is allowed to freely expand into a volume αV . This is a complicated nonequilibrium process, so we cannot compute the increase of the entropy directly. Instead, it can be computed using the fact that entropy is a state function, i.e. the change depends only on the final state of the gas and not how it got there. Find a set of reversible processes that get to the same final state, and use them to find the change in the entropy.

Problem 7. Show that the entropy of an ideal gas obeys

$$S = C_V \log(PV^\gamma) + \text{constant}.$$

The integration constant cannot be determined by classical thermodynamics, which only concerns changes in the entropy. From this expression we can immediately see that PV^γ is constant for an adiabatic process.

Next, we'll apply the Second Law to some more exotic systems.

Exercise 9. A black hole has an entropy of

$$S = \frac{A}{4}$$

where A is the area of its event horizon. The radius of an uncharged, unrotating black hole is

$$R = 2M.$$

In these equations, \hbar , c , and G have all been set to one; you do not need to restore these factors. Compute the temperature and heat capacity of such a black hole.

Exercise 10. Two uncharged, unrotating black holes begin very far apart from each other, then merge into a single black hole, emitting gravitational waves in the process; assume there is no initial angular momentum, so the final black hole is nonrotating as well. Find the maximum possible efficiency of this process, defined as the fraction of the initial energy that is converted into gravitational waves, for any set of initial black hole masses.

Exercise 11. Planck's law states that the power output by an ideal blackbody at temperature T at frequency f , per unit frequency, is

$$\frac{dP}{df} = \frac{2f^2}{c^2} \frac{hf}{e^{hf/k_B T} - 1}.$$

The second factor comes from statistical mechanics, as you derived last week, because a standing wave with frequency f can have any integer number n of photons, and hence the energy levels are $E = nhf$. The first factor accounts for the number of standing wave solutions per unit frequency.

In a nonideal blackbody we instead have

$$\frac{dP}{df} = \frac{2f^2}{c^2} \frac{hf}{e^{hf/k_B T} - 1} e(f)$$

where $e(f)$ is called the emissivity. Also, a nonideal blackbody absorbs only a fraction $a(f)$ of incident radiation with frequency f , where a is called the absorptivity. Using simple thought experiments, show that $a(f) = e(f)$, a result known as Kirchoff's law.

Problem 8 (Kardar). Conceptual questions about the second law. The solar system originated from a dilute gas of particles, sufficiently separated from other such clouds to be regarded as an isolated system. Under the action of gravity the particles coalesced to form the sun and planets.

- (a) The motion and organization of planets is much more ordered than the original dust cloud. Why does this not violate the second law?
- (b) The nuclear processes of the sun convert protons to heavier elements such as carbon. Does this further organization lead to a reduction in entropy?
- (c) The evolution of life and intelligence requires even further levels of organization. Why does this not violate the second law?

For a discussion of these issues, see section 36.7 of Blundell and Blundell.

3 Quantum Statistical Mechanics and the Third Law

Idea 4: Third Law

The entropy of any thermodynamic system approaches zero as the temperature goes to zero.

The third law of thermodynamics is a bit of a black sheep. Unlike the other laws, it is inherently quantum mechanical, and comes from the statistical definition of entropy.

Idea 5

If it is only known that an isolated system is in one of Ω quantum states, then all of the states are equally likely, and the entropy is

$$S = k_B \log \Omega.$$

This may be regarded as the true, fundamental definition of entropy. Under this viewpoint, the equation $dS = dQ/T$ is not a definition of entropy, but actually a definition of temperature! The Third Law follows from this postulate because, at temperature $T = 0$, all systems settle into their ground state, so $\Omega = 1$ and $S = 0$.

Exercise 12. Show that the Third Law is not compatible with the classical expression for the ideal gas entropy. This implies that the ideal gas law *must* break down in quantum mechanics.

Exercise 13. Show that the Third Law requires the specific heat C to approach zero as the temperature approaches zero.

The assertion that all states are equally likely may sound a bit confusing, because last week we were using the Boltzmann distribution, which stated that higher-energy states were less likely to be occupied. The difference is that for the Boltzmann distribution, we assumed the system was inside an environment at temperature T . In fact, all quantum states of the system and environment together remain equally likely in this context, but lower-energy states of the system correspond to more energy in the environment, and hence (usually) more possible environment states. Thus, if we ignore what's going on in the environment, lower-energy states of the system are more likely. In the following problem, you'll see how this works.

Problem 9. Consider a set of N atoms, each of which may be in the ground state, with zero energy, or in an excited state with energy E_0 . Suppose it is only known that the total energy of the system is $\alpha N E_0$.

(a) For large N , Stirling's approximation applies,

$$\log N! \approx N \log N - N.$$

Using Stirling's approximation, show that the entropy of the system is

$$S = Nk_B \left(\alpha \log \frac{1}{\alpha} + (1 - \alpha) \log \frac{1}{1 - \alpha} \right).$$

(b) Show that the system has a temperature of

$$T = \frac{E_0}{k_B} \frac{1}{\log(1 - \alpha) - \log \alpha}.$$

Sketch the temperature as a function of α . In particular, what temperature do you need to get $\alpha = 1/2$? How about $\alpha = 1$?

- (c) Show that the Third Law of Thermodynamics is satisfied.

Now consider just a single one of the N atoms, where the total energy of the system is $\alpha N E_0$ as before. If we look at this atom alone, we can regard the rest of the system as a thermal bath of temperature T , and hence use the Boltzmann distribution.

- (d) Show that the Boltzmann equation yields the correct probability that the atom is excited.