Lecture 1 **DRAFT**

The Laws of Thermodynamics

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Preface

Given this is the first lecture, I will briefly stop to discuss the direction and goal of these notes. As a student of physics myself, I am familiar with many of the pitfalls and confusions new students may have when approaching thermodynamics and statistical mechanics. My hope is that by pooling insights and explanations from various resources as well as clarifying confusions I have struggled with, these notes may be helpful for other students. My expectation is that these notes should be somewhere between the level of an undergraduate course and a introductory graduate course, and will hopefully grow to include all of the material covered in a one-semester statistical mechanics course.

Contents

1 What is Thermodynamics?

Before we discuss the laws of thermodynamics and their implications, we must delegate some time to discussing what exactly thermodynamics sets out to describe. **Thermodynamics** is a coarse-grained description of the *equilibrium* properties of very large systems. If a system has evolved to a terminal state, we say that it is in **equilibrium**. Although this is not a particularly rigorous definition of equilibrium, this is really the best we can do from a thermodynamics perspective. Additionally, equilibrium thermodynamics is a **time-independent** theory– systems at equilibrium appear independent of time and have no memory. Note, however, this does not mean that equilibrium states are unchanging or permanent. As we shall see in future lessons, thermodynamics and statistical mechanics is fundamentally the study of fluctuations away from these equilibrium states. Without these fluctuations, water wouldn't boil, the sky wouldn't be blue, and the dynamic processes underpinning life would cease. Thermodynamics and statistical mechanics present a formalism by which we can understand the timescales and magnitudes of these fluctuations.

Although we have explained that thermodynamics and statistical mechanics are effective tools for answering questions such as "Why is the sky blue?", we have not yet demonstrated its superiority over, say, classical mechanics. To this end, consider a box with $6 \cdot 10^{23}$ classical particles that can collide. Although we could solve for the position and momentum of each particle using Hamilton's equations, this would involve solving a hopelessly large number of coupled first order differential equations. Moreover, a lot of this microscopic information is generally not necessary to make experimentally verifiable predictions. Thermodynamics enables us to shrink this hopelessly large number of degrees of freedom down to just a few functions of state (ex. temperature, pressure, volume) in a way we shall soon make explicit. With this being said, we will now state the fundamental laws of thermodynamics and investigate their immediate implications.

2 First Law of Thermodynamics

Given the significance of the laws of thermodynamics, it should come as no surprise that there have been many different formulations of the first law over the past two centuries. A more general formulations is attributed to Planck in his seminal *Treatise on Thermodynamics*:

> "it is in no way possible, either by mechanical, thermal, chemical, or other devices, to obtain perpetual motion" - Max Planck

This statement has meaning for open systems, closed systems, and even systems that aren't in equilibrium. Most modern resources restrict this discussion to the first law of thermodynamics as it applies to closed systems. Here we shall follow a similar course, but studies of the first law of thermodynamics for open systems and systems out of equilibrium can easily be found elsewhere.

2.1. First Law For Closed Systems

The first law is usually stated as a conservation law — that is, if the energy of a system increases, either **work** was done *on* the system ($đW$) or **heat** had to flow *into* the system ($đQ$). Explicitly, we write

First Law of Thermodynamics

$$dE = đW + đQ$$

The reader should note that $đW$ and $đQ$ are **inexact differentials**. The integral of an exact differential (e.g. dE) along a transformation A → B depends entirely on the endpoints A and B of the transformation, not the path taken from A → B. By contrast, the integral of an inexact differentials depend on the specific path taken going from A to B. For the curious reader, we briefly discuss inexact differentials in appendix A.

We will further postulate that energy is **extensive**. If we have two subsystems with energies E_1 and E_2, the extensivity of energy would imply that the energy of the entire system obeys

$$E = E_1 + E_2 \tag{1}$$

If we double the size of the system keeping other things fixed, an extensive quantity will double. More generally, extensive properties scale linearly with the size of a system.

Although the first law, as stated above, appears to hold true for any transformation in a closed system, we must restrict the kinds of transformations we look at in order to make sense of this $đW$ term. To see why this is necessary, consider a rubber band under tension f. If we pull the band sufficiently slowly, the change in energy can be written as $\int_{L_i}^{L_f} f dL$. If it is pulled too abruptly, some of the work will be converted into kinetic energy and lost as the rubber band comes to rest. This is an example of a non *quasi-static* transformation.

Quasi-static transformations are transformations that happen so slowly that the system is always at equilibrium. For quasi-static transformations, it is generally possible to write the change in energy due to work as a product of generalized forces ($\vec{F}$) and generalized displacements ($\vec{X}$). In fact, this is only possible during quasi-static transformations, as the thermodynamic quantities associated with these generalized forces and displacements (ex. pressure and volume) are only defined at equilibrium. We can write

$$đW = \sum_{\alpha} F_{\alpha} \cdot dX_{\alpha} \tag{2}$$

In the case of only pressure-volume work, $đW = -PdV$ (note the sign convention!). However, we need not only consider hydrostatic work— we could instead consider magnetic field and magnetization, string tension and length, electric field and polarization, among many other pairs of forces and displacements.

2.2. New Directions

The first law on its own is not entirely sufficient to answer the questions that thermodynamics sets out to answer. As previously mentioned, one of the central goals of thermodynamics is to study small fluctuations of systems away from equilibrium. The second law of thermodynamics equips us with the tools necessary to answer these questions in a way we will make clear.

3 Second Law of Thermodynamics

Similar to the first law of thermodynamics, the second law of thermodynamics has seen many iterations and interpretations over the past two centuries. The formulation we will present here requires a brief discussion of entropy:

Axioms of Entropy

There exists a state function, **Entropy**, denoted S, that is defined for all equilibrium states such that

1. Entropy is a *state function* of the extensive variables
2. Entropy is *extensive*
3. Entropy is *differentiable* and *continuous*
4. S is a *monotonically increasing* function of Energy

Second Law of Thermodynamics

If a state B is *adiabatically* accessible from a state A, then

$$S_B \geq S_A$$

If we can run this process in reverse adiabatically, then state A is also adiabatically accessible from state B and $S_A \geq S_B$, so $S_A = S_B$. In general, we say this adiabatic process A $\rightleftarrows$ B is **reversible**. By the above argument, $dS = 0$ for any reversible process.

3.1. Obtaining a More Mathematical Statement

Since entropy is differentiable, it is possible to write its differential (dS) in the following form:

$$dS = \left(\frac{\partial S}{\partial E}\right)_{\vec{X}} dE + \sum_{\alpha} \left(\frac{\partial S}{\partial X_\alpha}\right)_{E, X_{i\neq\alpha}} dX_\alpha \tag{3}$$

Where $\left(\frac{\partial F}{\partial X}\right)_Y$ signifies the partial derivative of F with respect to X while holding Y constant.

For quasi-static reversible processes, we also have

$$dE = đQ_{rev} + \sum_{\alpha} F_\alpha \cdot dX_\alpha \tag{4}$$

Combining 3 and 4, we can write

$$dS = \left(\frac{\partial S}{\partial E}\right)_{\vec{X}} đQ_{rev} + \sum_{\alpha} \left[\left(\frac{\partial S}{\partial X_\alpha}\right)_{E, X_{i\neq\alpha}} + \left(\frac{\partial S}{\partial E}\right)_{\vec{X}} \cdot F_\alpha\right] \cdot dX_\alpha \tag{5}$$

As $dS = 0$ for reversible processes and $đQ = 0$ for any adiabatic process, we can rewrite (5) for any quasi-static adiabatic reversible process

$$0 = \sum_{\alpha} \left[\left(\frac{\partial S}{\partial X_\alpha}\right)_{E, X_{i\neq\alpha}} + \left(\frac{\partial S}{\partial E}\right)_{\vec{X}} \cdot F_\alpha\right] \cdot dX_\alpha \tag{6}$$

$$\left(\frac{\partial S}{\partial X_\alpha}\right)_{E, X_{i\neq\alpha}} = -\left(\frac{\partial S}{\partial E}\right)_{\vec{X}} \cdot F_\alpha \tag{7}$$

Note that this equality only depends on functions of state. In this way, (7) holds for any transformation between two states where these thermodynamic quantities are defined. As such, this equality holds whether the transformation is adiabatic or non-adiabatic (note that this is a subtle argument). **I need to make this clearer, I really dont get it tbh**

Our fourth axiom for entropy dictates that $(\partial S/\partial E)$ ¿ 0. We can rewrite this as $(\partial E/\partial S) \geq 0$. We can define

$$T \equiv (\partial E/\partial S) \geq 0 \tag{8}$$

In general, we will find later on that temperature is positive in all physically realistic systems. Temperature, defined in this way, *can* be negative if a system has a bounded energy, but this is a not a physically relevant situation and will not prove troublesome for this development. Using this new definition of temperature, we can write 7 as

$$(\partial S/\partial X_\alpha) = -F_\alpha/T \tag{9}$$

Plugging back into 5, we find

$$dS = \frac{1}{T}dE - \frac{1}{T}\sum_\alpha F_\alpha \cdot dX_\alpha \tag{10}$$

equivalently, we can write

$$dE = TdS + \sum_\alpha F_\alpha \cdot dX_\alpha \tag{11}$$

This is a more mathematical formulation of the second law. Note that if we only consider hydrostatic work, we recover the famous

$$dE = TdS - PdV \tag{12}$$

3.2. Studying Fluctuations

Previously, it was claimed that the second law was central to our goal of studying fluctuations. Strangely enough, we can approach this objective by studying what happens when we modify the constraints of a systems. In order to see why this is, imagine a system is at equilibrium in state A with a constraint (ex. a wall separating two parts of the system). After this constraint is removed, the system will relax to a new equilibrium state B. Once the system has relaxed, it is not possible generally to tell whether the new system was caused by a microscopic fluctuation or by a change in constraints. In this way, we can study the thermodynamics of fluctuations by studying how systems respond to various kinds of constraints. In the next lesson, we will investigate various conditions necessary for equilibrium, as well as how the zeroth law arises naturally from this formulation of the laws of thermodynamics.

Appendix A: Inexact Differentials

Generally speaking, inexact differentials are a specific type of differential form. In the context of thermodynamics, we use inexact differentials to denote differentials whose integrals are path dependent, that is,

$$\int_\gamma đX \neq \int_{\gamma'} đX \tag{13}$$

for distinct paths γ and γ'.
More generally, there is no state function f which satisfies the following relation

$$df \neq đX \tag{14}$$

There are no heat (Q) or work (W) state functions. After you perform work or add heat to a system, you can no longer tell whether it was mechanical work or heat that added energy to the system. Because there is no state function for these variables, there is no exact differential. Energy, on the other hand, is a state function (E), which has an exact differential dE.

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