Heat, Temperature and the First Law of Thermodynamics

Stephen R. Addison

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Introduction

The object of our studies is thermal physics. Thermal physics is a combination of two historic disciplines: thermodynamics and statistical mechanics.

Thermodynamics

Thermodynamics developed before the atomic nature of of matter was understood. Major developments occurred in the first half of the nineteenth century. The names Carnot, Clausius, W. Thompson (Kelvin) are major names associated with these developments. Tsallis is a notable current worker in this field. Thermodynamics is based on a small number of basic principles (the laws of thermodynamics.) These are deductions from and generalizations of a large number of the results of a large number of experiments on macroscopic systems. They are phenomological descriptions and are not based on microscopic structure at all. Thermodynamics uses exclusively macroscopic variables such as p, V, and T. Equations of state such as $pV = NkT = nRT$ are experimentally derived.

Statistical Mechanics

Statistical mechanics developed along with the understanding of the atomic nature of matter at the end of the nineteenth century and the beginning of the twentieth century. Names associated with these developments are Boltzmann, Maxwell, Ehrenfest, Gibbs, Planck, Fowler, Dirac, Bose, Einstein, Fermi, Rushbrooke, Onsager, and others on to today like Kadanoff and P.W. Anderson. There are both classical and quantum versions. In statistical mechanics macroscopic laws are derived from microscopic properties of matter.

Thermal Physics

The newly merged discipline incorporates probabilistic derivations into thermodynamics. We'll develop the entire theory with special interest in simple systems - gases, atomic magnets, simple solids and stars. Thermal physics is the study of the properties of macroscopic physical systems. Macroscopic systems are systems that contain a large number of atoms (molecules). Avogadro's number is $N_A = 6.022X10^{23}/mole$. Note that physicists are increasingly using SI units and so you'll see $N_A = 6.022X10^{26}/kmol$. With particle numbers of this order we can't obtain a complete microscopic (that is atomic) specification. Even if we could specify the configuration, we would be unable to follow its time evolution. However, macroscopic bodies follow definite laws that can be phrased in term of the macroscopic variables, p, V, and T etc. You've also seen that such expressions can be developed statistically. (You should have calculated the pressure in a gas in University Physics.)

Thermal Variables and Concepts

Temperature

Perhaps the basic concept, certainly the most familiar, and without doubt the most misunderstood concept in thermal physics is temperature. We won't be able to give a real definition for a few weeks. It will be useful to start with a practical definition: **Temperature is what you measure with a thermometer.**

We will use many definitions of this kind, its called an **operational definition**. Operational definitions are useful – they tell us how to measure things even if we can't define them in other ways. Realizing that two object in contact with each other eventually achieve a common temperature leads to the development of the zeroth law of thermodynamics. In formal terms we say: If two objects are placed in contact, energy flows from one to the other until temperature equalizes. The flow of energy is what called heat. When the flow of heat ceases the objects are said to be in *thermal equilibrium.* We can say that temperature is the thing that's the same for two object if they've been in contact long enough.

Equilibrium

We use the term *thermal equilibrium* to denote equality of temperature. Consider an isolated system – it could contain pressure differences, temperature gradients, density variations, etc. A system in such a state is not in equilibrium; the system will change over time: pressures will equalize, thermal conduction, diffusion, and other processes will occur will occur. When the system evolves to a state in which no further *macroscopically observable* changes take place, the system has achieved equilibrium. We say that it is in an equilibrium state. Nothing else will ever happen if the system remains isolated. This is the ultimate fate of a closed universe, we usually call it *the heat death of the universe.*

Equilibrium states

Equilibrium states can be described by and are fully determined by a small number of macroscopic variables. (It isn't necessary to specify $\rho(\mathbf{r})$,etc. These few variables then determine all other macroscopic variables. Such properties – properties that depend only on the state of the system, are called functions of state.

As an example, the state of a homogeneous fluid is determined by M, V, and p. Thus, we can write $T = f(p, V, M)$. Note that in thermodynamics we will prefer to write: $T = T(p, V, M)$ This equation is called the equation of state for the fluid. We could equally well write $p = p(M, V, T)$. Knowledge of a single equation of state does not constitute complete thermodynamic knowledge of a system – you need to know all the equations of state. Actually, you'll see that we'll reserve the term equation of state for more specialized equations. We'll worry about this later.

The Zeroth Law of Thermodynamics

This law of thermodynamics is due to R.H. Fowler. It provides a basis for thermometry. In a course on classical thermodynamics, we'd probably spend at least a week on this topic. We'll spend a few minutes on it. Let's begin with its statement.

If two objects are in thermal equilibrium with a third object, then they are in thermal equilibrium with each other.

This allows the development of thermometry based on a physical property of some material. Such scales use a pair of fixed points. Temperature scales developed from this law tend to agree only at the fixed points, and perhaps a few others. The theoretical development of absolute temperature scales depends on the second law.

Heat and Work

We have talked about temperatures equalizing, it is now time to discuss what changes when temperatures equilibrate. When objects in contact come to equilibrium, there is a *net transfer of energy* from one object to the other. It is this net transfer that we call *heat.* The term heat is an anachronism - it is a relic of an old theory known as *caloric.* Such a transfer requires no change in *external parameters.* Technically external parameters are those terms that appear in the Schrödinger equation for the system. On a more mundane level, they are things like volume. In fact you could readily name many.

The key point is that energy can be transferred in two way by heating (which includes cooling) and by changes in external parameters. We call energy transfer by changes in external parameters *work.*

Dilute Gases and Ideal Gases

Consider a real gas, at sufficiently low temperatures and pressures, we can write

$$pV = constant$$

at any temperature. This equation, which relates different states of the system at different temperatures, is called an *isotherm.*

An ideal gas is defined as a fluid for which this equation holds exactly for an isotherm. Thus ideal gases are extrapolations to zero pressure from real gases.

We can now make use of this to define the ideal gas temperature scale.

$$T \propto \lim_{p \to 0} pV$$

The scale is then determined if we fix a single point by definition. The chosen point is the triple point of water. The triple point is the point at which solid, liquid, and gas can coexist in equilibrium. The triple point of water occurs at a pressure of $4.58mm$ of mercury and a temperature of 0.01^0C. This fixed point was chosen because 1^0 is as close as possible to 1^0 on the Celsius scale. In 1954 $T_{tr} \equiv 237.16K$ was adopted by definition. Our use of K here anticipates that the thermodynamic temperature scale is identical to the thermodynamic temperature scale. The constant of proportionality is determined experimentally with a gas thermometer.

Basic Results for Ideal Gases

In lower level courses, you have met a variety of results that apply to ideal gases. I am not going to derive many of these results. Instead, we will list them and I will assign some of the derivations/justifications as homework problems. For 1 mole of an ideal gas $pV = RT$, where R is the ideal gas constant. ($R = 8.31\ Jmol^{-1}K^{-1}$.) For n moles of gas this becomes $pV = nRT$.

Frequently, in place of use the gas constant and the number of moles, we shall use the Boltzmann constant and the number of particles. In terms of these quantities, we write the ideal gas law as $pV = NkT$. In this expression N is the number of particles and k is the Boltzmann constant. ($k = 1.381 \times 10^{-23}$ J/K.) We can relate the number of moles to the number of particles through $n = N/N_A$,, where N_A is Avogadro's number. By inspection, we can see that $k = R/N_A$). Either of the results $pV = nRT$, $pV = NkT$ can be called the equation of state for an ideal gas. We also know that for an ideal gas $E = E(T)$ only. (The particles don't interact so there are no potential energy terms to worry about.)

Other equations you should have seen include:

$$\langle E \rangle = \frac{3}{2} NkT,$$

$$p = \frac{1}{3}\frac{N}{V}m\langle v^2\rangle = \frac{2}{3} \times \frac{1}{2}m\langle v^2\rangle\frac{N}{V},$$

and

$$pV^\gamma = constant.$$

We'll introduce other such relationships as we need them.