Chapter 1

The Failure of Classical Mechanics

Classical mechanics, erected by Galileo and Newton, with enormous contributions from many others, is remarkably successful. It enables us to calculate celestial motions to great accuracy, and triumphed in the precision of the unmanned space program (with some detailed refinements from General Relativity, which is still essentially classical). Yet, fundamentally, classical physics is not correct.

Let us start by discussing some of the indications known in the 19th century that something was amiss in the theoretical framework. First we discuss a thermodynamic problem. Probably you recall that at a definite absolute temperature T the energy of a system having one degree of freedom in thermal equilibrium is

$$E = \frac{1}{2}kT, \tag{1.1}$$

where k = Boltzmann's constant = 1.38×10^{-16} erg/K. (See Appendix for a derivation.) If a system has n degrees of freedom, and is in thermal equilibrium, it has this much energy per degree of freedom, or

$$E = \frac{1}{2}nkT. \tag{1.2}$$

Consider a monatomic gas (a noble gas, such as He, Ar, Ne) consisting of N atoms. Since there are three directions of space in which each atom can move, the energy of the gas is

$$E_m = 3N\frac{1}{2}kT, \tag{1.3}$$

and then the specific heat (at constant volume), the amount of energy required to raise the temperature of the gas by 1 K, is

$$c_m = \frac{dE}{dT} = \frac{3}{2}Nk. \tag{1.4}$$

Experimentally, this is very nearly true.

What about diatomic molecules, such as H_2, O_2, N_2, which consist of molecules with two atoms each? Now each atom has

- 3 translational degrees of freedom,

- 2 rotational degrees of freedom (you must specify the direction of the axis of rotation, which takes two numbers), and

- 2 vibrational degrees of freedom, which like a spring have quadratic terms in the energy corresponding to kinetic and potential energy:

$$E = \frac{1}{2}mv^2 + \frac{1}{2}kx^2, \tag{1.5}$$

  where v is the relative radial velocity of the atoms, and x is the relative coordinate.)

That is, there are seven (quadratic) degrees of freedom in all. Thus we expect the energy of the gas, and its specific heat, to be

$$E_d^{\text{th}} = \frac{7}{2}NkT, \quad c_d^{\text{th}} = \frac{7}{2}Nk. \tag{1.6}$$

But experimentally, we typically find something more like $c_d^{\text{exp}} \approx \frac{5}{2}Nk$. More precisely, the situation is something like that sketched in Fig. 1.1. At very low temperatures, it is a though only the translational degrees of freedom come in, at room temperature, translational and rotational motion are present, and only at very high temperatures does vibration play a role. This "freezing out" of degrees of freedom cannot be understood classically. In the 19th century, this failure of theory gave people grave concern whether atoms existed.

As a second example, consider a crystal, where every atom is arranged in a definite geometrical structure—a three-dimensional lattice. Each atom is held in a definite position—if an atom is disturbed, it experiences a restoring force and vibrates about its equilibrium position. Thus each atom has

- 3 translational (kinetic energy) degrees of freedom,

- 3 potential energy (x, y, and z) degrees of freedom.

Thus, the atom has 6 quadratic degrees of freedom. The energy, and specific heat, for a crystal with N atoms is

$$E_{\text{crystal}} = 6N\frac{1}{2}kT = 3NkT, \quad c = 3Nk, \tag{1.7}$$

which is seen empirically, as the law of Dulong and Petit (except that $c \to 0$ at low temperature).

What about a metal such as copper? The atoms are still held in a crystal lattice, but some of the electrons are free to migrate in a good conductor (no restoring forces for the conducting electrons). So we expect for the specific heat

$$c_{\text{metal}}^{\text{th}} = 3kN_{\text{atoms}} + \frac{3}{2}kN_{\text{electrons}}. \tag{1.8}$$
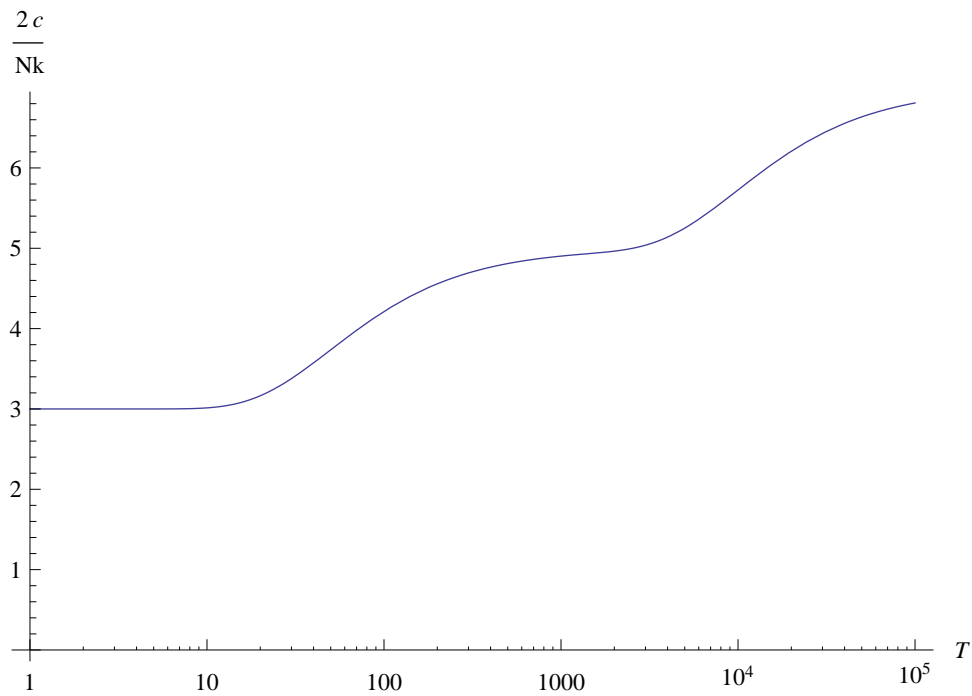
Figure 1.1: Sketch of the behavior of the specific heat at constant volume as a function of absolute temperature for a diatomic gas. At low temperature only the translational degrees of freedom play a role; at room temperature, the rotational degrees of freedom contribute, but the vibrations are frozen out.

For a good conductor, there is of the order of 1 conduction electron per atom,

$$N_{\text{electrons}} \sim N_{\text{atoms}}, \tag{1.9}$$

so

$$c_{\text{metal}}^{\text{th}} \sim \frac{9}{2}kN_{\text{atoms}}. \tag{1.10}$$

Bu, in fact, under normal conditions we don't see the electronic contribution to the specific heat.

These examples show that classical mechanics and thermodynamics fail, in an apparently unpredictable manner. The question is, how to erect a new set of rules that do work in the atomic realm, without destroying the success of classical physics. Perhaps the clearest indication that atomic physics cannot be correct was provided by the apparent establishment of the nuclear atom by Rutherford, Geiger, and Marsden (1910), who scattered alpha paricles (He nuclei) off nuclei and observed large deflections. In this picture, the atom consisted of a massive nucleus with light electrons orbiting it. But this model is unstable, since the electrons are always accelerated, and should therefore radiate electromagnetic energy. As they lose energy, the electrons should spiral in, and fall into the nucleus. How long would be required for this to happen?

The power radiated by a nonrelativistic accelerated charge is given by the Larmor formula (Gaussian electromagnetic units),

$$P = \frac{2}{3}\frac{e^2}{c^3}a^2, \tag{1.11}$$

where the charge of the particle is e. For an electron of mass m moving in a circle of radius r, orbiting a nucleus of charge $-e$, the acceleration is

$$a = \frac{e^2}{mr^2}, \tag{1.12}$$

assuming the orbit is always circular. P is the rate at which the electron loses energy, so if E is the energy of the electron,[1]

$$P = -\frac{dE}{dt} = -\frac{1}{2}\frac{dV}{dt}, \tag{1.13}$$

where V is the potential energy, $V = -e^2/r$. Putting these together we get

$$\frac{1}{2}\frac{d}{dt}\frac{e^2}{r} = \frac{2}{3}\frac{e^2}{c^3}\frac{e^4}{m^2r^4}, \tag{1.14}$$

or

$$-\frac{dr}{r^2}r^4 = \frac{4}{3}\frac{e^4}{m^2c^3}dt. \tag{1.15}$$

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[1]This uses the virial theorem: for a circular orbit the force on the electron is $mv^2/r = e^2/r^2$, which means that the energy is $E = mv^2/2 - e^2/r = -e^2/2r = V/2$. This is true on the average even if the orbit is not circular.

We integrate this from some intial radius R down to the origin, that is, the position of the nucleus,

$$\frac{1}{3}R^3 = -\int_R^0 dr\, r^2 = \frac{4}{3}\left(\frac{e^2}{mc^2}\right)^2 ct = \frac{4}{3}r_0^2 ct, \tag{1.16}$$

for the time t required for the electron to spiral into the nucleus. Here we have used the abbreviation

$$r_0 = \frac{e^2}{mc^2} = 2.8 \times 10^{-13}\,\text{cm}, \tag{1.17}$$

which is the so-called classical radius of the electron (in fact, as we now know to high precision, the electron has no size). Thus

$$t = \frac{R^3}{4r_0^2 c} = \frac{(10^{-8}\,\text{cm})^3}{4(3 \times 10^{-13}\,\text{cm})^2(3 \times 10^{10}\,\text{cm/s})} \approx 10^{-10}\,\text{s}, \tag{1.18}$$

if the initial distance of the electron from the nucleus is $R = 10^{-8}$ cm, a typical atomic dimension. If this were true, matter would have disappeared long ago! If fact, atoms are incredibly stable—they have been around since the big bang, some 13.7 billion years, and we can deduce much longer lifetimes for atomic stability. On the other hand, we know that accelerated electrons do radiate in the manner given by Maxwell's equations—electron synchrotrons, in which electrons move in circles, produce copious radiation which is used, for example, to study material properties. What's different about electrons in atoms?

1.1 Appendix

The equipartition theory says for any "quadratic" degree of freedom, the corresponding average energy is $\frac{1}{2}kT$. By quadratic degree of freedom, we mean it contributes to the energy proportional to the square of the coordinate or velocity, as in Eq. (1.5). Consider the kinetic energy due to the motion of an atom in one direction. Accoring to Boltzmann, the average value of this kinetic energy is given in terms of integrals over the velocity distributions:

$$\langle \frac{1}{2}mv^2 \rangle = \frac{\int_{-\infty}^{\infty} dv\, \frac{1}{2}mv^2\, e^{-\beta mv^2/2}}{\int_{-\infty}^{\infty} dv\, e^{-\beta mv^2/2}} = -\frac{\partial}{\partial\beta}\ln Z, \tag{1.19}$$

where $\beta = 1/kT$ and the partition function is

$$Z = \int_{-\infty}^{\infty} dv\, e^{-\beta mv^2/2} = \sqrt{\frac{2}{\beta m}}\int_{-\infty}^{\infty} dx\, e^{-x^2} = \sqrt{\frac{2\pi}{m\beta}}, \tag{1.20}$$

so

$$\langle \frac{1}{2}mv^2 \rangle = \frac{1}{2}\frac{\partial}{\partial\beta}\ln\beta = \frac{1}{2\beta} = \frac{1}{2}kT. \tag{1.21}$$