

1. Introduction

The Chapters which follow describe statistical methods that are used to describe macroscopic assemblies of matter. To set this discipline into perspective we start by summarizing some methods used to treat matter in general. This discussion will be very brief and is intended only to distinguish statistical physics within physics more generally.

1.1. Approaches used to describe matter

Newtonian mechanics, also called classical mechanics, assumes the world consists of a collection of point particles that interact with each other through specified forces that affect their subsequent motion according to his second law. In principle, this framework allows the prediction of the positions, $q_i(t)$, and momenta, $p_i(t)$, of all those particles at all future times (with arbitrary precision), if their values are precisely known at some earlier instant in time. This approach is limited to velocities small compared to that of light and distances large compared to atomic dimensions, and with these restrictions is highly successful, particularly in celestial mechanics. However, it quickly becomes impracticable, even with the largest computers (existing or proposed), for large assemblies of particles.

A different formalism, *Quantum mechanics*, governs the behavior of particle assemblies at the microscopic level. Particle positions and momenta are then replaced by a complex *amplitude*, also called the *wavefunction*, which depends on the particle positions together with the time and is typically written as $\Psi(q_1, q_2 \dots; t)$. The certainty of particle positions associated with Newtonian mechanics is then replaced by a probability which is proportional $|\Psi(q_1, q_2 \dots; t)|^2$. Accompanying this description is the Heisenberg uncertainty principle which places limits on the precision which the coordinates and momentum q_i and p_i can be simultaneously measured. Internal *electronic* degrees of freedom associated with atoms and molecules must always be treated with this formalism, although molecular vibrations and rotations can sometimes be treated classically. Translational motion is largely treated classically at all but the very lowest temperatures. The so called measurement problem, in which the wavefunction “collapses”, and particles instantly acquire specific positions, remains controversial (as exemplified by the Schroedinger cat problem).

Continuum mechanics is an approach used to describe properties of macroscopic particle assemblies at length and time scales where individual particle positions can be “smoothed over”.

One then has volume elements containing many particles that are assigned positions and, when in motion, velocities. Some macroscopic systems can be classified as fluids, either liquids or gasses, and others as solids, although the boundaries between these classifications are not always sharp (as exemplified by liquid crystals, plastics, biomaterials and geological soils).

Macroscopic materials in equilibrium typically resist a reduction in their volume, as measured by a *compressibility*. The defining property of a solid is that it also resists a shape change, as measured by a *shear modulus*. Relating such distortions to the external forces (stresses) that act on a material is the subject of *elasticity*. The Newtonian dynamics arising from these elastic forces in solids and fluids leads to oscillatory motions, sound waves, which are the subject of *acoustics*.

The static properties of fluids, materials for which the shape can be continuously changed, are the subject of *hydrostatics* (e.g., Archimedes principle). Fluids in motion are the subject of *hydrodynamics* (which incorporates Newton's laws).

Thermodynamics is an experimentally based science that describes some aspects of the near-static response of macroscopic matter in terms of a small number of so called *thermodynamic variables*, such as pressure and temperature (in addition to volume and shape), that do not immediately connect with the particle positions and velocities of mechanics. It relies on the property that blocks of matter, if left undisturbed, will approach an *equilibrium state*, about which we will say more as our discussion develops. Slow changes in certain properties of that state can then be described in terms of the thermodynamic (more correctly called *thermostatic*) variables; the laws governing these changes can be accurately established experimentally (leading to the first and second laws of thermodynamics). Many aspects of thermodynamics can be smoothly integrated into continuum mechanics (hydrodynamics and elasticity) with variables such as temperature then accompanying the positions and velocities of small regions within the material.

Statistical physics seeks a description of matter that forms a bridge between a microscopic description, say (but not limited to) a mechanical system governed by Newton laws or Schrodinger's equation, and a near equilibrium macroscopic one, treated via thermodynamics or continuum mechanics. It relies on the property that, provided the underlying motions are not too chaotic, such that well defined averages can be defined, such a connection is to be expected based on everyday experience.

Special Relativity supercedes Newtonian mechanics when particle velocities approach that of light, and must be incorporated into statistical physics for some systems, particularly astronomical systems like white dwarfs and neutron stars. Curiously, the Universe as a whole (as opposed to various parts) appears to be in a non equilibrium state, and it is thought that this may be connected with gravitation and the *general theory of relativity*.

1.2. Molecular Dynamics

As noted above, if we are given a collection of particles, together with defined forces acting on and between them, we can *numerically* solve Newton's law and obtain their positions and velocities at all times t , provided we specify all values of these quantities at some chosen time. Ignoring quantum effects, and given the availability of a suitable computer, this way of describing a set particles works well provided the particle number N is small enough to make the computations tractable.

This powerful approach is now widely practiced for small systems ($\sim 10^4$ particles¹) and is termed *molecular dynamics*. It cannot be extended to macroscopic amounts of terrestrial condensed matter where one typically has 10^{22} particles per cm^3 . But in many cases the properties of bulk matter, e.g. water, can be accurately obtained by extrapolating the computational results to large samples. Complex small systems, such as the various conformations of a biological protein, are now being routinely calculated.

1.3. Fluctuations and the law of large numbers

Constructing a statistical description of matter rests on the so-called *law of large numbers* which governs how fluctuations in larger statistical samples of some quantity are suppressed relative to those in smaller ones. Suppose we have some system consisting of N parts. Here we might think of some large amount of a substance that we divide into parts which can be examined individually, each designated by an index i , allowing us to measure some property, f_i , of them (say their energy or density). Designating the value for the sum of these parts as F we can then write

$$F = \sum_{i=1}^N f_i . \quad (1.1)$$

¹ As examples of "particles" we may picture atoms, molecules, planets, stars

Now imagine the individual f_i fluctuate, say due to internal motions or “interactions” with a neighboring or external environment, and that we measure their average values, \bar{f}_i . The average for the system as a whole is then

$$\bar{F} = \sum_{i=1}^N \bar{f}_i. \quad (1.2)$$

We designate the difference, or fluctuation, between the *average* value for part i , \bar{f}_i , and that of an *individual measurement*, f_i , as $\Delta f_i = \bar{f}_i - f_i$. The fluctuation in F due to the fluctuations of its parts f_i is then

$$\Delta F = F - \bar{F} = \sum_{i=1}^N (f_i - \bar{f}_i) = \sum_{i=1}^N \Delta f_i. \quad (1.3)$$

On averaging ΔF we obtain

$$\begin{aligned} \overline{\Delta F} &= \overline{\sum_{i=1}^N f_i} - \sum_{i=1}^N \bar{f}_i \\ &= \sum_{i=1}^N \bar{f}_i - \sum_{i=1}^N \bar{f}_i = 0, \end{aligned} \quad (1.4)$$

as expected. Next we examine the *square* of the total fluctuation

$$(\Delta F)^2 = (F - \bar{F})^2 = \left(\sum_{i=1}^N (f_i - \bar{f}_i) \right)^2 = \left(\sum_{i=1}^N \Delta f_i \right)^2,$$

which on averaging is

$$\overline{(\Delta F)^2} = \overline{\left(\sum_{i=1}^N \Delta f_i \right)^2} = \sum_{i=1}^N \overline{\Delta f_i} \sum_{j=1}^N \overline{\Delta f_j} = \sum_{i,j=1}^N \overline{\Delta f_i \Delta f_j}. \quad (1.5)$$

If the parts are *statistically independent*, which we now assume, the terms with $i \neq j$ will tend to have random signs and hence cancel out. Retaining only the terms with $i = j$ we then have

$$\overline{(\Delta F)^2} = \sum_i^N \overline{(\Delta f_i)^2}. \quad (1.6)$$

For convenience we now assume each of the parts is, on average, the same size, \bar{f} , and (1.2) then becomes

$$\bar{F} = N\bar{f} . \quad (1.7)$$

Similarly we assume the fluctuations Δf_i , although random in sign, are similar in magnitude, $\bar{\Delta f}$, so that we can write

$$\sum_i^N (\overline{\Delta f_i})^2 = N(\overline{\Delta f})^2 \quad (1.8)$$

Using (1.6) – (1.8) we calculate the ratio

$$\begin{aligned} \frac{(\overline{(\Delta F)^2})^{1/2}}{\bar{F}} &= \frac{\sqrt{N} \bar{\Delta f}}{N \bar{f}} \\ &= \frac{1}{\sqrt{N}} \frac{\bar{\Delta f}}{\bar{f}} . \end{aligned} \quad (1.9)$$

Hence the square root of the mean square fluctuation (referred to as the *root-mean square* or rms fluctuation) for the system as a whole is smaller than that of its parts by the factor $N^{-1/2}$; this property is termed the *law of large numbers*.

For solid terrestrial matter there are typically $N \approx 10^{22}$ particles in a cubic centimeter of matter.² Hence under most circumstances the fluctuation in the number of molecules is of order $N^{1/2} \approx 10^{11}$. The fractional change would then be $N^{-1/2} \approx 10^{-11}$ which is exceedingly small when compared to typical measurement capabilities.³

Some Books on Statistical Physics

Statistical Physics, Part I, L. D. Landau and E. M. Lifshitz, Pergamon Press, 1980.

Statistical Mechanics and Thermodynamics, Claude Garrod, Oxford, 1995.

Statistical Mechanics, Dirk ter Haar, Butterworth-Heinemann, 1995.

Introduction to Statistical Physics, 2nd Edition, Kerson Huang, CRC Press, Boca Raton, 2009

² This follows from Avogadro's number which tells us that a mole of a pure substance contains $\mathcal{A}_0 = 6.022 \times 10^{23}$ molecules. A mole of water (H_2O) weighs 18 grams (1+1+16); with a density of 1 gram/cm³, a cubic centimeter would contain $6.022 \times 10^{23} / 18 = 3.34 \times 10^{22}$ molecules.

³ The law of large numbers is quite general in character. To calculate the actual magnitudes of the fluctuations of various thermodynamic quantities we must develop the overall formalism which will be discussed in Chapter 14.

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