STATISTICAL MECHANICS

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Licensing

A detailed breakdown of this resource's licensing can be found in ***Back Matter/Detailed Licensing***.

CHAPTER OVERVIEW

1: The Properties of Matter in Bulk

- 1.1: What is Statistical Mechanics About?
- 1.2: Outline of Book
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1.1: What is Statistical Mechanics About?

Statistical mechanics treats matter in bulk. While most branches of physics. . . classical mechanics, atomic physics, quantum mechanics, nuclear physics. . . deal with one or two or a few dozen particles, statistical mechanics deals with, typically, about a mole of particles at one time. A mole is 6.02×10^{23}, considerably larger than a few dozen. Let's compare this to a number often considered large, namely the U.S. national debt. This debt is (2014) about 18 trillion dollars, so the national debt is about thirty trillionth of a mole of dollars.[1] Even so, a mole of water molecules occupies only 18 ml or about half a fluid ounce. . . it's just a sip.

The huge number of particles present in the systems studied by statistical mechanics means that the traditional questions of physics are impossible to answer. For example, the traditional question of classical mechanics is the time-development problem: Given the positions and velocities of all the particles now, find out what they will be at some future time. This problem has has not been completely solved for three gravitating bodies. . . clearly we will get nowhere asking the same question for 6.02×10^{23} bodies! But in fact, a solution of the time-development problem for a mole of water molecules would be useless even if it could be obtained. Who cares where each molecule is located? No experiment will ever be able to find out. To make progress, we have to ask different questions, question like “How does the pressure change with volume?”, “How does the temperature change upon adding particles?”, “What is the mean distance between atoms?”, or “What is the probability for finding two atoms separated by a given distance?”. Thus the challenge of statistical mechanics is two-fold: first find the questions, and only then find the answers.

[1] In contrast, the Milky Way galaxy contains about 0.3 or 0.6 trillionth of a mole of stars. The entire universe probably contains fewer than a mole of stars.

1.2: Outline of Book

This book begins with a chapter, *the properties of matter in bulk*, that introduces statistical mechanics and shows why it is so fascinating.

It proceeds to discuss the *principles of statistical mechanics*. The goal of this chapter is to motivate and then produce a conceptual definition for that quantity of central importance: entropy. In contrast to, say, quantum mechanics, it is not useful to cast the foundations of statistical mechanics into a mathematically rigorous “postulate, theorem, proof” mold. Our arguments in this chapter are often heuristic and suggestive; “plausibility arguments” rather than proofs.

Once we have defined entropy and know a few of its properties, what can we do with it? The subject of thermodynamics asks what can be discovered about substance by just knowing that entropy exists, without knowing a formula for it. It is one of the most fascinating fields in all of science, because it produces a large number of dramatic and unexpected results based on this single modest assumption. This book’s chapter on thermodynamics begins begins by developing a concrete operational definition for entropy, in terms of heat and work, to complement the conceptual definition produced in the previous chapter. It goes on to apply entropy to situations as diverse as fluids, phase transitions, and light.

The chapter on *ensembles* returns to issues of principle, and it produces formulas for the entropy that are considerably easier to apply than the one produced in chapter 2. Armed with these easier formulas, the rest of the book uses them in various applications.

The first three applications are to the classic topics of classical ideal gases, quantal ideal gases, including Fermi-Dirac and Bose-Einstein statistics, and harmonic lattice vibrations or phonons.

The subject of ideal gases (i.e. gases of non-interacting particles) is interesting and often useful, but it clearly does not tell the full story. . . for example, the classical ideal gas can never condense into a liquid, so it cannot show any of the fascinating and practical phenomena of phase transitions. The next chapter treats *weakly interacting fluids*, using the tools of perturbation theory and the variational method. The correlation function is introduced as a valuable tool. This is the first time in the book that we ask questions more detailed than the questions of thermodynamics.

Finally we treat *strongly interacting systems and phase transitions*. Here our emphasis is on magnetic systems. Tools include mean field theory, transfer matrices, correlation functions, and computer simulations. Under this heading fall some of the most interesting questions in all of science. . . some answered, many still open.

The first five chapters (up to and including the chapter on *classical ideal gases*) are essential background to the rest of the book, and they must be treated in the sequence presented. The last four chapters are independent and can be treated in any order.

1.3: Fluid Statics

I mentioned above that statistical mechanics asks questions like "How does the pressure change with volume?". But what is pressure? Most people will answer by saying that pressure is force per area:

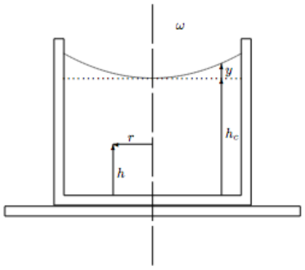
$$\text{pressure } = \frac{\text{force}}{\text{area}}. \tag{1.3.1}$$

But force is a vector and pressure is a scalar, so how can this formula be correct? The aim of this section is to investigate what this formula means and find out when it is correct.[2]

1.3.1 Problems

1.1 (I) The rotating water glass

A cylinder containing a fluid of mass density ρ is placed on the center of a phonograph turntable and rotated with constant angular velocity ω. After some initial sloshing of the fluid, everything calms down to a steady state.



a. The pressure is a function of height h and distance from the axis r. Show that the variation of pressure with radial distance is

$$\frac{\partial p(r,h)}{\partial r} = \rho\omega^2 r, \tag{1.3.2}$$

while the variation with vertical distance is

$$\frac{\partial p(r,h)}{\partial h} = -\rho g. \tag{1.3.3}$$

(Where g is the acceleration of gravity.)

b. The pressure at the surface of the fluid at the center of the cylinder (r = 0, $h = h_c$) is of course atmospheric pressure pa. Integrate the differential equations of part (a.) to show that, at any point in the fluid,

$$p(r,h) = p_a + \frac{1}{2}\rho\omega^2 r^2 - \rho g\left(h - h_c\right). \tag{1.3.4}$$

c. Show that the profile of the fluid surface is given by

$$y(r) = \frac{\omega^2}{2g} r^2. \tag{1.3.5}$$

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[2] As such, the aim of this section is quite modest. If you want to learn more about the interesting subject of fluid flow, see the "Resources" section of this chapter.

1.4: Phase Diagrams

Too often, books such as this one degenerate into a study of gases. . . or even into a study of the ideal gas! Statistical mechanics in fact applies to all sorts of materials: fluids, crystals, magnets, metals, polymers, starstuff, even light. I want to show you some of the enormous variety of behaviors exhibited by matter in bulk, and that can (at least in principle) be explained through statistical mechanics.

Because the axes of a phase diagram are pressure and temperature, the misconception arises that phase diagrams plot pressure as a function of temperature. No. Pressure and temperature are independent variables. For example, volume is a function of pressure and temperature, $V(T, p)$. Instead, the lines on a phase diagram mark the places where there are cliffs in the function $V(T, p)$.

End with the high Tc phase diagram of Amnon Aharony discussed by MEF at Gibbs Symposium. Birgeneau.

Resources

The problems of fluid flow are neglected in the typical American undergraduate physics curriculum. An introduction to these fascinating problems can be found in the chapters on elasticity and fluids in any introductory physics book, such as

> F.W. Sears, M.W. Zemansky, and H.D. Young, *University Physics*, fifth edition (Addison-Wesley, Reading, Massachusetts, 1976), chapters 10, 12, and 13, or
>
> D. Halliday, R. Resnick, and J. Walker, *Fundamentals of Physics*, fourth edition (John Wiley, New York, 1993), sections 16–1 to 16–7.

More idiosyncratic treatments are given by

> R.P. Feynman, R.B. Leighton, and M. Sands, *The Feynman Lectures on Physics* (Addison-Wesley, Reading, Massachusetts, 1964), chapters II-40 and II-41, and
>
> Jearl Walker *The Flying Circus of Physics* (John Wiley, New York, 1975), chapter 4.
>
> Hansen and McDonald

An excellent description of various states of matter (including liquid crystals, antiferromagnets, superfluids, spatially modulated phases, and more) extending our section on "Phase Diagrams" is

> Michael E. Fisher, "The States of Matter—A Theoretical Perspective" in W.O. Milligan, ed., *Modern Structural Methods* (The Robert A. Welch Foundation, Houston, Texas, 1980) pp. 74–175.