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Excerpt
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PART I

ATOMIC AND MESOSCOPIC VIEWPOINT

1 Introduction

Summary[1]

- Science is an empirical endeavor.
- The world in which we live seems to permit microscopic, mesoscopic, and macroscopic descriptions.
- The macroscopic description is in terms of observables and concepts meaningful at the scale of our daily lives.
- The microscopic description is in terms of particles and fields that underlie our world.
- We see why atoms and molecules are so small compared to us. Thus, the law of large numbers is crucial to relate the macro and micro worlds.
- The mesoscopic description describes fluctuations deviating from the law of large numbers.
- The study of large deviation is the key to understanding fluctuations.

Key words[2]

three levels of description: microscopic, mesoscopic, macroscopic

Everybody knows that the materials we see around us are made of atoms and molecules. We could even see them, for example, with the aid of atomic force microscopes. However, only 50 years ago no one could see atoms. About 100 years ago the existence of atoms was still disputed.[3]

1 "**Summary**" at the beginning of each chapter highlights the chief topics in the section. The notations may not be defined or technical terms may not be explained. It serves as a preview before reading the chapter, and will be a checklist of the important topics after finishing the chapter.

2 The terms in "**Key words**" are those the reader should be able to explain to her lay friends.

3 **Mach and atomism** It is often said E. Mach (1838–1916) attacked atomism, but his criticism was nuanced; he opposed imagining atoms as ordinary (macroscopic) balls. See Brush, S. G. (1968a). On Mach's atomism. *Synthese* **18**, 192–215. P. Frank's comment quoted in this paper reads, "Also, strange as it was, in Vienna the physicists were all followers of Mach and followers of Boltzmann . . . All were more or less followers of Mach in the philosophical sense: Einstein, Heisenberg, and probably also Bohr." The author feels that there are two Machs (like two Kuhns): a critically rational Mach and his not-so-consistent brother.

1.1 Atomisms, Ancient and Modern

The idea that the world is made of indivisible and unchanging minute particles (atomism[4]) is, however, not a very unique idea. After all, it seems that there are only two choices: (i) the world is infinitely divisible and continuous or (ii) the world is made of indivisible units separated by void (we ignore various easy combinations of these ideas here).[5]

Leucippus (fifth century BCE) is usually credited with inventing atomism in Greece.[6] His disciple Democritus (*c*. 460–370 BCE) systematized his teacher's theory. The early atomists tried to account for the formation of the natural world by means of atoms and void alone. The void space is described simply as nothing, or the negation of body. Atoms are, by their nature, intrinsically unchanging, but can differ in size, shape, spatial position (and orientation), etc. They move in the void and can temporarily make clusters according to their shapes and surface structures.[7] The changes in the world of macroscopic objects were understood to be caused by rearrangements of the atomic clusters. Thus, atomism explains changes in the macroscopic world without creating new substance. All the macroscopic phenomena are naturally ephemeral.[8]

The most decisive difference between the modern atomism and the ancient atomism is that the latter is devoid of dynamics. The ancient atomism allowed motions to displace atoms and to change their aggregate states, but no special meaning was attached to the movements themselves (quite contrary to the modern thermal motion).

1.2 What was beyond Philosophers' Grasp?

The idea that everything is made of irreducible units is, as we have just argued, rather natural; if not infinitely divisible, there must be the smallest units. However, it is hard to identify without empirical information what the actual units are. Recall that no one ever imagined that we are made of cells, even though cell theory is one of the two pillars of

4 atom ← *atomos*: *a* = "not," *tomos* = "cutting"

5 We must note that what was really unique/creative was to ask a question that led them to such an idea.

6 See, e.g., Berryman, S. (2011). Ancient Atomism. In *The Stanford Encyclopedia of Philosophy* (Winter 2011 Edition), ed. E. N. Zalta.

7 **No interaction across the void** No "interatomic" forces were conceived. That is, they seemed to have imagined interactions between contacting bodies (atoms), but they never thought about forces through the void space. Interactions without contact (through void) seem to be a Newtonian novelty as we will see in Chapter 2.

8 **Atomism and humanism** Since atomism understands that the world orders emerge from rearrangements of atoms, we human beings are also understood as special arrangements of atoms. Consequently, ancient atomists were critically against the usual religions; atomism and secular humanism are rather harmonious as can be seen in Epicurus (341–270 BCE). In Lucretius' *On the Nature of Thing*, whose only single manuscript survived the Middle Ages, "narrowly escaping destruction by bigots, Lucretius feels towards Epicurus as towards a savior, and applies language of religious intensity to the man whom he regards as the destroyer of religion." quoted from chapter XXVII of Russell, B. (1945). *A History of Western Philosophy*. London: Simon and Schuster.

It is often criticized that, although the ancient atomism may have been able to give explanations of various daily phenomena, it never attempted to predict new phenomena nor to invent new methods to control Nature. The most important application of ideas may be, however, to change our Weltanschauung.

biology (the other is Darwinism). This indicates the limitation of philosophers who are not empirical enough. The lack of the idea of "molecule" in the ancient atomism is also an example of this limitation. Perhaps, it is a sign of progress to recognize that the world does not have the structures we "naturally" expect. Kepler's discovery that the circular orbit is not natural may be an example; this was never accepted by Galileo.

Mechanics was also beyond philosophers' grasp. Therefore, modern atomism was beyond the reach of any philosopher. We must respect empirical facts. Science is an empirical endeavor. At the same time, however, as the reader recognizes from the works of Newton, Maxwell, Darwin, and others, 'pure empiricism' is not enough at all to do good science.

1.3 How Numerous are Atoms and Molecules?

How many water molecules are there in a tablespoonful (15 cm^3) of water? Although we should discuss how to determine the size or mass of an atom empirically before discussing the question (see Chapter 9), let us preempt the result.

Suppose one person removes one molecule of water at a time from the tablespoonful of water, and another person uses the tablespoon to scoop out the ocean's water to the outer space (although no one would dare to start scooping out water of even a 50 m swimming pool). If they perform their operations synchronously, starting simultaneously, which person will finish first? The second person. However, the number of molecules in a spoonful of water is comparable to the amount of ocean water measured in tablespoons (the ratio is about 5; the number of molecules wins).

1.4 Why are Molecules so Small?

Molecules are numerous. They are numerous because they are tiny. Why is an atom so tiny? Because we are so big. Thus, the title question properly understood is: why is the size ratio between atoms and us so big? Do not forget that we human beings are products of Nature. To compare us with atoms does not necessarily imply that we subscribe to anthropocentric prejudices.

Large animals are often constructed with repetitive units such as segments. The size of the repeating unit is at least about one order (base 10) larger than the cell size. Consequently, the size of "advanced" organisms must be at least 2–3 orders as large as the cell size.

Thus, the problem is the cell size. Since we are complex systems,[9] the crucial information and materials required to build us come from the preceding generation. Since there is no ghost in the world, information must be carried by a certain thing (we should call

[9] See, e.g., chapter 5 of Oono, Y. (2013). *The Nonlinear World*, Tokyo: Springer.

this *no ghost principle*). Stability of the thing requires that information must be carried by polymers. What polymer should be used? Such a question is a hard question, so we simply imagine something like DNA. The "no ghost principle" tells us that organisms require a certain minimal DNA length. This seems to be about 1 mm $\sim$ 1 m (notice that the question is almost a pure physics question; to answer this we must understand the amount of the needed information as physicists, since physics can explain the atom size: 0.1–0.2 nm). As a ball its radius is about $0.1 \sim 1\ \mu$m. This implies that our cell size is $\sim 10\ \mu$m ($= 10^{-5}$ m).[10]

Thus, the segment size is about 1 mm, and the whole body size is at least about 1 cm (this is actually about the size of the smallest vertebrates). If we require good eyesight, the size becomes easily one to two orders more, so intelligent creatures cannot be smaller than $\sim$ 1 m. That is, the atom size must be 10^{-10} as large as our size.

We have, at least roughly, understood why atoms are small.

1.5 Our World is Lawful to the Extent of Allowing the Evolution of Intelligence

We have discussed, with the aid of atomism and the cell theory, that science is an empirical endeavor. We observe the world and are making science, so we must be at least slightly intelligent. To be intelligent we need to be at least $10^9 \sim 10^{10}$ times as large as the atom (in linear length). A large size is not enough, however. The world must have allowed intelligence to evolve.

If there is no lawfulness at all, or in other words, there is no order in the world,[11] then intelligence is useless. We use our intelligence to guess what happens next from the current knowledge we have. If organisms' guesses with the aid of their intelligence were never better than simple random choices (say, following a dice), then intelligence would not evolve. Random grading would not give an incentive for students to study. Recall that the human brain is the most energy consuming very costly organ.[12] This means that the macroscopic world (the world we observe directly at our space-time scale) must be at least to some extent lawful with some regularity. This is consistent with our superstitiousness, because mistaking correlation as causality is an important ingredient of superstition.

However, if the law or regularity is too simple, then again no intelligence is useful. If the world is dead calm, no intelligence is needed. The world must be "just right." The macroscopic world we experience is neither violent nor dull for most of the time (though it is punctuated by catastrophes that do not contribute to our evolution except for resetting the stage).

[10] We may safely claim that the lower bound of the cell size is determined by the amount of DNA.
[11] "Order" may be understood as redundancy in the world; knowing one thing can tell us something about other things, because everything is not totally unrelated.
[12] Its weight is 2% of the body weight, but it consumes about 20% of the whole body energy budget.

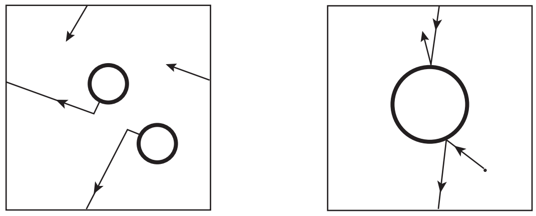

Fig. 1.1 Sinai billiard: (a) a motivation. Two hard elastic disks (pucks) are running around on the table with a periodic boundary condition (if a disk disappears from one edge, it reappears from the opposite edge with the same velocity), colliding from time to time with each other. This is a toy model of a confined gas. (b) If the dynamics of the center of mass (CM) of one disk is observed from the CM of the other disk, the former may be understood as a ballistic motion of a point mass with occasional collisions with the central circular obstacle. This is called the *Sinai billiard*, and is known to be maximally chaotic.

1.6 Microscopic World is Unpredictable

In contrast, we know the world of atoms and molecules (the microscopic world) is a busy and bustling world. They behave quite erratically and unpredictably. Atoms and molecules are believed to be rigorously governed by (quantum) mechanics. If we consider classical approximation for simplicity, there are at least two reasons for unpredictability: chaos and external disturbances. Quantum mechanically, the situation might be better intrinsically, since there is no real chaos in quantum mechanics. Still, extreme difficulties in the fundamental experiments to verify quantum effects attest eloquently to the fragile nature of intrinsic quantum mechanical evolution of the system.

Maxwell clearly recognized that molecules behave erratically due to collisions. Perhaps the simplest model to illustrate the point is the *Sinai billiard*. A hard ball (or rather, imagine an ice hockey puck) is moving without friction on a flat table, which has a circular obstacle on it. The ball hits the obstacle and is bounced back specularly (see Fig. 1.1(b)). Roughly speaking, a small deviation of the direction of the particle is doubled upon specular reflection by the central circle, so, for example, to predict the direction of the particle after 100 collisions is prohibitively hard.[13] Imagine what happens if there are numerous such particles colliding with each other. Predictions would be absolutely impossible. Worse still, it is very hard to exclude the effects of the external world, where we do not know what is going on at all. Notice that we cannot even breathe if we wish to study the “intrinsic behavior” of a collection of atoms in front of us.

1.7 Why our Macroscopic World is Lawful: the Law of Large Numbers

The world at the scale of atoms is full of (apparently) unpredictable behaviors. We know our scale is quite remote from the atomic scale. The time scales are also disparate; the

[13] It is convenient to remember that $2^{10} \simeq 10^3$, so $2^{100} \simeq 10^{30}$.

time scale required to describe molecular dynamics is $0.1 \sim 1$ fs (1 fs $= 10^{-15}$ s), but the shortest time span we can recognize must be much longer than 1 ms $= 10^{-3}$ s, because our lowest audible frequency is about 20 Hz. Lawfulness must come from suppression of unpredictability. Our size is crucial to this; even if molecules in a small droplet undergo quite erratic movements, their effect would not be detected easily in the droplet motion as a whole. This statement may be formally expressed as follows.

Let us consider a collection of numerous ($N \gg 1$) random variables.[14] X_n is the nth among them. Then,[15]

$$\sum_{n=1}^{N} X_n = Nm + o[N], \tag{1.1}$$

where m is the average value of X_n. This is the *law of large numbers*, the most important pillar of probability theory and the key to understanding the macroscopic world (Chapter 4). Imagine outcomes of coin tossing as an example: $X_n = 1$ if the nth outcome is a head; otherwise, $X_n = 0$. By throwing a coin N times, we get a 01 sequence of length N, say, $0100101101110101\cdots001$. We guess the sum is roughly $N/2$, if N is large enough. This is the law of large numbers. We clearly see the importance of being big (relative to atoms).

1.8 We Live in a Rather Gentle World

The reader might object, however, that being big may not be enough; we know about violent phenomena in the macroscopic world like turbulence or perhaps the cores of galaxies. If the variances are too big, perhaps we might not be able to expect the expectation value to settle down within a reasonable narrow range. Also even if the expectation value eventually converges, the needed N in (1.1) should not be too big; if we can recognize the regularity of the world only after averaging the observations during 1000 generations, probably the law of large numbers cannot favor intelligence very much. Thus, as already discussed, the world in which intelligence can emerge cannot be too violent. We have emerged in the world in which the law of large numbers holds rather easily at large scales to allow macroscopic laws. We live in the world whose space-time scale is not only quite remote from the microscopic world of atoms and molecules, but also whose "extent of nonequilibrium" is not too large.[16]

[14] **Random variables** We will discuss what we wish to mean by "random variables" more carefully later (Chapter 3), but here, the reader has only to understand them as variables that take various values within a certain range in an unpredictable fashion.

[15] **Landau symbol *o*** This standard symbol o means higher order small quantities. In the limit being discussed, if $X/Y \to 0$, then we write $X = o[Y]$, which is read as: compared with Y, X is a higher order small quantity in the limit being discussed. This does not mean X and Y themselves are infinitesimal. For example, $N^{0.99}$ is $o[N]$, if N is large (in the $N \to \infty$ limit), because $N^{0.99}/N = N^{-0.01} \to 0$ in this limit.

[16] We need stable and simple laws for feeble minds to work (recall the intelligence must evolve).

1.9 Thermodynamics, Statistical Mechanics, and Phase Transition

The macroscopic world close to equilibrium[17] is a world governed by the law of large numbers. It can be described *phenomenologically* by *thermodynamics* (Chapters 11–16). Here, "phenomenologically" implies that what we observe directly can be organized into a single theoretical system without assuming any entities beyond direct observations. Thermodynamics is distilled from empirical facts observable at our scale, so it is one of the most reliable theoretical systems we have in physics. Thus, thermodynamics will be explained through the basic facts; they are used to construct the key concept: entropy (roughly, a measure of diversity of microstates compatible with a macroscopic situation; Chapter 13). Its microscopic interpretation by Boltzmann, which is the key ingredient of statistical mechanics, will also be explained based on thermodynamics (Chapter 17) following Einstein's logic. It is quite advantageous to understand entropy intuitively in terms of information, so information theory and its relevance to thermal physics will be outlined (Chapters 21, 22).

We will learn that if we know a "thermodynamic potential," we can compute any equilibrium properties of a macroscopic system. In particular, the Helmholtz free energy A is a convenient thermodynamic potential (Chapter 16). Once A is known, for example, we can compute the amount of work we can obtain from a system. However, thermodynamics cannot give A; we need a more microscopic approach to obtain it. Thus, we need a bridge between the microscopic and the macroscopic worlds called statistical mechanics. Statistical mechanics gives the following expression of the Helmholtz free energy A (Chapter 18):

$$A = -k_B T \log Z, \tag{1.2}$$

where k_B is the Boltzmann constant, T is the absolute temperature, and Z is the (canonical) *partition function*

$$Z = \sum e^{-H/k_B T}. \tag{1.3}$$

Here, H is the system Hamiltonian and the summation is over all the *microstates* (microscopically described states of the system distinguishable by mechanics). Each term $e^{-H/k_B T}$ is a smooth function of T (> 0), so if the number of terms summed in (1.3) is finite, nothing very singular can happen for A as a function of T. However, if the system is very big (ideally, infinitely big, in the so-called *thermodynamic limit*), A can lose its smoothness as a function of T. Thus, *phase transitions* can occur, if the system is large enough (Chapters 31–36).

[17] Intuitively, the reader may regard a system to be close to equilibrium, if all the rapid changes in it have subsided.

1.10 The Mesoscopic World

What does the world look like if we observe it at the scale intermediate between the microscopic and the macroscopic scales? In (1.1) the $o[N]$ term becomes unignorable. That is, *fluctuation* cannot be ignored. This is the world where *Brownian motion* dominates, where unicellular organisms live, and where the cells making our bodies function. Intelligence is useless, because fluctuation is still too large and prevents agents from predicting what would happen. Often the best strategy is to wait patiently for a "miracle" to happen, and if it happens, to cling to it. Many molecular machines such as ribosomes follow just this strategy. We will discuss Brownian motion and will give an informal discussion of transport phenomena in Chapters 8–10. The study of Brownian motion substantiates the reality of atoms.

1.11 Large Deviation and Fluctuation

In the mesoscopic world, the average of what we observe is consistent with our macroscopic observation results. However, if we observe individual systems, observables fluctuate a lot around the expected macroscopic behaviors. What is the natural framework to understand the mesoscopic world, or $o[N]$ in (1.1)? It is the *large deviation principle* (Chapter 10) that refines the law of large numbers in the following form:

$$P\left(\frac{1}{N}\sum_{i=1}^{N} X_i \in v(x)\right) \approx e^{-NI(x)}, \tag{1.4}$$

where $\approx$ means that the ratio of the logarithms of the both sides is unity asymptotically for large N, $v(x)$ denotes the volume element around x, P is the probability (Chapter 3) of the event in the parentheses, and I is called the *large deviation function* (or *rate function*). I may be approximated by a quadratic function when x is close to the true expectation value m:

$$I(x) \simeq \frac{1}{2V}(x-m)^2. \tag{1.5}$$

Here, V is a positive constant (corresponding to the variance) and m is the expectation value. If N is large, the probability is positive only if x is very close to m: $I(m) = 0$ implies the law of large numbers. Equation (1.5) means that mesoscopic noise is usually Gaussian. That is, with the aid of a Gaussian noise ν whose average is zero and whose variance is V/N, we can write

$$\frac{1}{N}\sum_{i=1}^{N} X_i = m + \nu + o[1/\sqrt{N}]. \tag{1.6}$$

As we will see later (Chapter 26), I is related to the decrease of entropy from equilibrium due to fluctuations. Applying the idea of large deviation to Brownian motion allows us to study time dependence in the mesoscopic world (Chapters 10, 26).

To understand thermal physics is to understand the interrelationships among three levels of description of our world: the macroscopic, the mesoscopic, and the microscopic descriptions.

Problems

Q1.1 Big Numbers

(1) How many cells in a human body?
(2) How many atoms in a cell?
(3) How many seconds in 1 billion years?
(4) How many stars in the Universe?

Find the reader's own natural and interesting examples of big numbers relevant to the topics of this book.

Solution

(1) There are about 3.7×10^{13} of our own cells in our body.[18] We have about 1.5 kg of symbiotic prokaryotes (bacteria and archaea), whose number of cells is about the same as the total number of our own cells.[19] Therefore, we have at most 10^{14} cells. Now the world population is 7.4×10^9. This means that there are less than 1 mole ($= 6.022 \times 10^{23}$) of human cells on the Earth.
(2) There are about 2×10^{14} atoms in a cell; about a few 10^9 atoms in *Escherichia coli*. Thus cells are definitely mesoscopic.
(3) There are 3.1536×10^{16} seconds in 1 billion years = 1 Ga. By the way, 1 billion seconds is about 32 years. Such time-scale discrepancies are crucial to understanding nonequilibrium phenomena as we will see in Chapter 10.
(4) Our Milky Way is estimated to have about 10^{11} stars; the total Universe is said to have 10^{29} stars. This is about the same as the number of prokaryotes produced in the oceans in a year. The total number of electrons in our body is also of this order.

Q1.2 Atoms

At the beginning of this section, we read, "We could even see them, for example, with the aid of atomic force microscopes. However, only 50 years ago no one could see atoms." Are we really sure we can see them today? The reader should think over what we mean when we say we see something.

[18] There is a website called Bionumbers (the database of useful biological numbers) http://bionumbers.hms.harvard.edu/default.aspx.
[19] The latest may be: Sender, R., Fuchs, S., and Milo, R. (2016). Are we really vastly outnumbered? Revisiting the ratio of bacterial to host cells in humans. *Cell*, **164**, 337–340.