Notes for Lecture 5

Kinetic theory of gases

In the previous class, we proved one of the most celebrated theorems of statistics. The central limit theorem. However, one must keep in mind that this theorem is valid only when correlations are absent or weak. Such problems are generally referred to as "normal" problems. However, an active array of research is where correlations are very strong. In those cases, the problem becomes exponentially hard, but both analytical methods and numerical methods are shedding light on such difficult problems.

Before we go on to the kinetic theory of gases, we have a bit of catchups to do for the probability theory.

5.1 Rules for large numbers

5.1.1 Summation

If $\varepsilon_i > 0$ and $\sim O(\exp(N\phi_i))$ where ϕ_i is a constant which does not depend on N, then

$$\mathcal{S} \equiv \sum_{i=1}^{\mathcal{N}} \varepsilon_i \ \sim \ \varepsilon_{max} \tag{5.1}$$

when N is a large integer, $\mathcal{N}$ is some polynomial of N, and ε_{max} is the maximum of ε_i.

Note the use of the symbol $\sim$ above. Usually, this symbol means "is on the order of." Here, its meaning is a bit looser, in pure mathematical terms: it means

"has a similar order of magnitude as." However, as we will discuss below, physically the usage of symbol $\sim$ here is as good as using the symbol $\approx$.

The proof is quite elementary. $\varepsilon_{max} \leq \mathcal{S} \leq \mathcal{N}\varepsilon_{max}$. Taking the logarithm, we get $\log \varepsilon_{max} \leq \log \mathcal{S} \leq \log \mathcal{N} + \log \varepsilon_{max}$. This means that $\log S \approx \log \varepsilon_{max}$ for large N, since $\log \varepsilon_{max} = N\phi_{i_{max}} \gg n \log N \gg \log \mathcal{N}$ ($n = m + 1$, where $\mathcal{N}$ is the m-th order polynomial of N). Thus, $\log S \approx \log \varepsilon_{max}$.

Now, since $\log S \approx \log \varepsilon_{max}$, it may be tempting to write $S \approx \varepsilon_{max}$. Such an expression would be something of a bad taste, in general, since the approximate equality of logarithms really ensures the approximate equality of the order of magnitude only. Indeed, a statement such as $N \exp(N) \approx \exp(N)$ for a large N would not make much sense since the difference between $N \exp(N)$ and $\exp(N)$ is about $N \exp(N)$, i.e. the relative error for the above statement is 100 %!

However, this mathematical point would be quite moot in most *real* physical cases when N is given by the number of particles or a related large number that is subject to a large fluctuation $\sim \sqrt{N}$ (which is nevertheless small, compared to N). In such a case, one *can* view $N \exp(N)$ and $\exp(N)$ as physically equivalent to each other, since the additional multiplicative factor due to the uncertainty $\sim \exp(\sqrt{N}) \gg N$ or any polynomial of N. Besides, consider also the fact that in characterizing the real systems, we always suffer from an uncertainty of the measurement. Such an uncertainty, which may be a finite fraction of N in typical situations, would introduce an even greater range of values for $\exp(N)$.

5.1.2 Integral

Consider the integral

$$\mathcal{J} \;=\; \int dx \exp(N\phi(x)) \tag{5.2}$$

when N is large

$$\mathcal{J} \;\sim\; \exp(N\phi(x_{max})) \tag{5.3}$$

where the symbol $\sim$ is used in the same meaning as in the previous section, and x_{max} is the x value at which the function $\exp(N\phi(x))$ is the maximum, or one of the (degenerate) maxima (as long as the number of degenerate maxima is of the polynomial order of N).

Note that the above statement is somewhat more disturbing than that of the last section, since, if x has a physical dimension, then $\mathcal{J}$ and $\exp(N\phi(x_{max}))$ are clearly

different in terms of their dimensions. However, we will see below that this does *not* pose any problem.

To prove the above statement, let us note that, if the integral exists, then it means that

$$\mathcal{J} \approx h \sum_{i=1}^{M} \exp(N\phi(x_i)) \tag{5.4}$$

Here, $h = (x_u - x_l)/M$, where x_u is the upper limit of integration and x_l is the lower limit of integration. Note that the original integral might have an infinite range of integration. Even then, the finite sum approximation is possible where x_u and x_l are finite numbers, for a sufficiently large M.

We do not know a priori what the value of M is. Here, we will simply assume that for a given value of N, M is of the order of polynomial of N at the most[1]. Then, by the result of the previous section, we have $\mathcal{J} \sim h \exp(N\phi(x_{max}))$.

Taking the log of $h \exp(N\phi(x_{max}))$ we get

$$\log h + N\phi(x_{max}) = \log(x_u - x_l) - \log M + N\phi(x_{max})$$

For a large N, the first two terms are of the order of $\log N$ at the most, by our assumption, and so they can be ignored, thus proving Eq. 5.3.

The last step of the proof also shows why even the unit of x does not matter. That is, the dimension mismatch between Eqs. 5.2 and 5.3 is *not* important, if we define the unit change transformation as $x = A10^p x'$, where p is a physically reasonable integer $|p| \lesssim 50$ and A is a real number with the property $|A| < 10$. By such a transformation, all that will happen above is $\log(x_u - x_l) \to p \log_{10} A + \log(x'_u - x'_l)$. Assuming that $p \ll N$ such a unit change will have no effect to our result here. Note that p is an integer whose magnitude is, at the most about 50, while usually on the order of 10 or 20, for all purposes that we can meaningfully discuss, while N is on the order of 10^{23} for a macroscopic sample. That is, $10^{10^{23}}$ seconds $\sim$ $10^{10^{23}}$ years $\sim$ $10^{10^{23}}$ ages of the Universe[2], if one notes that the age of the Universe is *merely* $\approx 4 \times 10^{17}$ seconds, and one year $\approx 3 \times 10^7$ seconds.

It is helpful to consider the above integral in more details, assuming that there is

[1] The grid on which finite sums are evaluated can be made logarithmic, also. This would be a sensible thing to do, if the above integral is evaluated numerically, in practice. The net result of such a sensible operation is a great reduction of the number of summands.

[2] Note that here, one can also say that $e^{10^{23}}$ seconds $\sim$ $e^{10^{23}}$ years $\sim$ $e^{10^{23}}$ ages of the Universe. Base e is more directly relevant to the current discussion, while the point made is the same no matter which base one uses.

only one maximum[3]. Now, consider the above integral as approximated as

$$\mathcal{J} \;=\; \int dx \exp\left(N\phi_m - \frac{N}{2}|\phi''_m| \cdot (x - x_{max})^2 + \frac{N}{2}\phi'''_m \cdot (x - x_{max})^3 + ... \right) \qquad (5.5)$$

where $\phi_m = \phi(x_{max}), \phi''_m = \phi''(x_{max})$, etc. Factoring out the first part outside the integral and ignoring all other terms give the approximation of Eq. 5.3. However, one can obtain a more systematic expansion by changing the variable to $y = \sqrt{\frac{N|\phi''_m|}{2}}(x - x_{max})$. Then, $\mathcal{J} = \exp(N\phi_m)\sqrt{\frac{2}{N|\phi''_m|}} \int dy \exp(-y^2 + \sum_{n=3}^{\infty} a_n y^n)$. An important point is that $a_n = O(N^{1-n/2})$.

$$\begin{aligned} \mathcal{J} \;&=\; \exp(N\phi_m)\sqrt{\frac{2}{N|\phi''_m|}} \int dy \exp\left(-y^2 + \sum_{n=3}^{\infty} a_n y^n \right) \\ &\approx\; \exp(N\phi_m)\sqrt{\frac{2}{N|\phi''_m|}} \int dy \exp(-y^2)\, \left(1 + a_3 y^3 + ...\right) \end{aligned}$$

Noting that the integral range is given by $y_{min} = -O(\sqrt{N})$ and $y_{max} = O(\sqrt{N})$, it can be thought of as $-\infty$ to ∞ due to the Gaussian function $\exp(-y^2)$. Since the integral $\int_{-\infty}^{\infty} dy \exp(-y^2) = \sqrt{\pi}$ and any integral $\int_{-\infty}^{\infty} dy \exp(-y^2) y^n$ is finite (in particular zero for any odd n due to parity), we get a very useful result

$$\mathcal{J} \;=\; \sqrt{\frac{2\pi}{N|\phi''_m|}}\, \exp(N\phi_m)\, \left(1 + O\left(\frac{1}{N}\right)\right) \qquad (5.6)$$

where the $O(1/N)$ term comes from the fact that a_4 is of that order, while the a_3 term integrates to zero due to parity.

5.1.3 Stirling's approximation

$$\begin{aligned} N! = \Gamma(N+1) \;&=\; \int_0^{\infty} dx x^N \exp(-x) \qquad (5.7) \\ &=\; \int_0^{\infty} dx \exp(N \log x - x) \qquad (5.8) \end{aligned}$$

[3]If there are multiple maxima, then one can break the integral into many finite pieces, when possible to do so. Our result here will apply to each maximum separately, and they will need to be summed up.

So, $\phi(x) = \log x - x/N$, which has the maximum $\log N - 1$ at $x = N$ and $\phi'' = -1/N^2$ at $x = N$. Applying Eq. 5.6

$$N! \;=\; \sqrt{2\pi N}\exp(N\log N - N)\left(1 + O\left(\frac{1}{N}\right)\right) \tag{5.9}$$

In other words,

$$\log N! \;=\; N\log N - N + \frac{1}{2}\log(2\pi N) + O\left(\frac{1}{N}\right) \tag{5.10}$$

which is the well-known "Stirling's formula" or "Stirling's approximation" for the factorial/gamma function.

5.2 Kinetic theory of gases

Here, we review some of the work that is carried out by Boltzmann for the most part. Boltzmann may be viewed as the father of modern statistical mechanics, much as Bohr is viewed as such for quantum mechanics. At the same time, the theories by these pioneers have this quality of "being shaky at places but still lovely" to them. They are not rigorous and they are flawed, but they work well in simple cases and they provide insights in complex cases. This is why they are still useful despite the fact that we have more the more rigorous theory, which we will discuss later on in this course.

Boltzmann pioneered the statistical mechanics by considering the dynamics of gas in microscopic terms and coming up with his "H theorem" and the celebrated Boltzmann equation. The Boltzmann entropy leads naturally to the Gibbs entropy, which is the standard entropy in statistical mechanics today.

The kinetic theory of gases refers to the ambitious project of deducing macroscopic properties of a very large number of particles, starting from first principles.

We will see later that there are nice quantum equivalents to the Boltzmann's work, which was purely classical as it was done long decades before the quantum mechanics was developed.

However, some words regarding the overall landscape are in order. The classical statistical mechanics that Boltzmann's theory gave rise to is quite an incomplete theory. An analogy with the Bohr-Sommerfeld theory is appropriate. Note that, while we know that the quantum mechanics is the correct method to use to calculate the atomic energy levels, it is not always the simplest or the most convenient to use.

The celebrated Bohr-Sommerfeld quantization condition $\oint dq\, p = nh$ is actually the quickest way to use for many problems[4]. However, note that this Bohr-Sommerfeld condition is something that you cannot prove rigorously, while it "makes sense." Its domain of existence is the gray area between classical mechanics and quantum mechanics, and so it is no wonder that it is not derivable from a rigorous theory. The classical statistical mechanics is a bit like it – it is a plausible theory that is fundamentally weak at the root of it since it *has to* make contact with the quantum theory. However, this does not mean that it is a bad theory. It is a theory of much good use even to this day. As the Bohr-Sommerfeld theory may be viewed as a more intuitive theory that explains certain physics better, the same kind of assessment can be made for the Boltzmann equation and the classical statistical mechanics. It is also often the case that a very long quantum calculation will give a certain result that is very quickly deduced, or reproduced, from the Boltzmann equation.

As we shall see, the "classical statistical mechanics" is littered with problems that only quantum mechanics can resolve. In this sense, perhaps the better name for "classical statistical mechanics" is the "semi-classical statistical mechanics."

5.3 Ensemble

In the Gibbs formalism of statistical mechanics, the concept of ensemble is central. It means the following. Consider a system consisting of N particles.

From the classical mechanics point of view, the system is completely specified by specifying the $6N$ initial conditions, generalized coordinates q_α and corresponding canonical momenta $p_\alpha = \frac{\partial L}{\partial \dot{q}_\alpha}$, where $i = 1, ..., 3N$, and L is the Lagrangian.

We call such a state a *microstate*. A microstate is the state of the system in which everything that needs to be specified is specified. Theoretically, any closed system can be characterized by a microstate.

A *macrostate* is the characterization of the system only in terms of macroscopic variables such as volume, pressure, energy, entropy, etc. Thus, in general many microstates correspond to one macrostate.

When a system is modeled as one *microstate*, we call such a state a *pure state*. When a system is modeled as a collection of many *microstates*, we call such a state a *mixed state*. Such a collection of microstates is called an *ensemble*, a *statistical*

[4]Here, the integral is over one period of classical motion, for which q is the generalized coordinate and p is its canonical momentum. $n = 1, 2, 3, ...$ The method becomes even more accurate if one uses the "greedy factor" γ, $\oint dq\, p = (n + \gamma)h$. For example, $\gamma = -1/2$ for a simple harmonic oscillator.

ensemble or a *thermodynamic ensemble*. Soon, we will see exactly how an ensemble is constructed.

The ensemble is the expression of a certain type of symmetry. And as such, it is based on the fact that experiments work reproducibly when materials are prepared under the same macroscopic conditions without any intent (or capability!) of controlling all parameters of the actual microstate.

In describing classical statistical mechanics, the phase space is a convenient place to start. It is the space where the coordinates are (q_α, p_α) where $\alpha = 1, ..., 3N$. We will often denote V_i as the phase space volume for a fixed particle index $i = 1, ..., N$. That is

$$dV_i \equiv d^3\vec{q}_i \, d^3\vec{p}_i \tag{5.11}$$

and the total infinitesimal volume ($d\Gamma$) of the phase space is given by

$$d\Gamma \;=\; \prod_i dV_i \tag{5.12}$$

Also, in this note, $\vec{\mathbf{q}} \equiv (q_1, ..., q_{3N})$ and $\vec{\mathbf{p}} \equiv (p_1, ..., p_{3N})$.

Suppose that we consider a total of $\mathcal{N}$ points in the phase space. $\mathcal{N}$ defines the size of our ensemble, and corresponds to the number of microstates. Suppose that, corresponding to $d\Gamma$, there are $d\mathcal{N}$ points. We can form a (properly normalized) probability distribution function $\rho(\vec{\mathbf{p}}, \vec{\mathbf{q}}, t)$ as

$$\rho(\vec{\mathbf{p}}, \vec{\mathbf{q}}, t)\, d\Gamma \;=\; \frac{d\mathcal{N}(\vec{\mathbf{p}}, \vec{\mathbf{q}}, t)}{\mathcal{N}} \tag{5.13}$$

Given this probability distribution function, the ***ensemble average*** of any dynamical quantity $O(\vec{\mathbf{p}}, \vec{\mathbf{q}})$ is given by

$$\langle O \rangle \equiv \int d\Gamma \, \rho(\vec{\mathbf{p}}, \vec{\mathbf{q}}, t)\, O(\vec{\mathbf{p}}, \vec{\mathbf{q}}) \tag{5.14}$$

5.4 Hamiltonian and Poisson bracket

The *canonical equation of motion* is given by

$$\begin{aligned} \frac{\partial H}{\partial p_\alpha} &= \dot{q}_\alpha \\ \frac{\partial H}{\partial q_\alpha} &= -\dot{p}_\alpha \\ \frac{dH}{dt} &= \frac{\partial H}{\partial t} \end{aligned} \tag{5.15}$$

where $H(\vec{\mathbf{p}}, \vec{\mathbf{q}}, t)$ is the so-called Hamiltonian function, defined as $\vec{\mathbf{p}} \cdot \dot{\vec{\mathbf{q}}} - L(\vec{\mathbf{q}}, \dot{\vec{\mathbf{q}}}, t)$, where L is the Lagrangian and $\vec{\mathbf{p}} \equiv \frac{\partial L}{\partial \dot{\vec{\mathbf{q}}}}$. It is equivalent to the Newtonian laws of motion.

This equation of motion can be derived from the Lagrangian equation of motion. However, in this course, one must become familiar with this canonical equation of motion enough to just recall and use it. Note also that in this course we will rarely consider the case when H is explicitly time dependent. However, note that certain properties (e.g. Liouville's theorem) are valid even if H is explicitly time-dependent. When H is not explicitly time dependent, then H is a conserved quantity, as the last of the three equations above shows.

The Poisson bracket of two general functions $g(\vec{\mathbf{p}}, \vec{\mathbf{q}}, t)$ and $h(\vec{\mathbf{p}}, \vec{\mathbf{q}}, t)$ is defined as

$$\{g, h\} \;=\; \sum_{\alpha} \left(\frac{\partial g}{\partial q_\alpha} \frac{\partial h}{\partial p_\alpha} - \frac{\partial g}{\partial p_\alpha} \frac{\partial h}{\partial q_\alpha} \right) \tag{5.16}$$

The following properties directly follow from the above definition and the canonical equations of motion (Eq. 5.15).

$$\{g, h\} \;=\; -\{h, g\} \tag{5.17}$$

$$\{g, g\} \;=\; 0 \tag{5.18}$$

$$\{g, G(g)\} \;=\; 0 \qquad G(g) \text{ is any function of } g. \tag{5.19}$$

$$\{q_\alpha, p_\beta\} \;=\; \delta_{\alpha,\beta} \tag{5.20}$$

$$\frac{dg}{dt} \;=\; \{g, H\} + \frac{\partial g}{\partial t} \qquad H \text{ is the Hamiltonian.} \tag{5.21}$$

Note that if we change $\{g, h\} \to -\frac{i}{\hbar}[g, h]$, then all of these properties are translated to those identities that are well-known for the *quantum mechanical* commutator $[g, h]$ *if* g, h were quantum mechanical operators.

5.5 Liouville's theorem

According to the canonical equation of motion written in the previous section, the time evolution in classical mechanics can be viewed as a mapping of a point $(\vec{\mathbf{p}}(t), \vec{\mathbf{q}}(t))$ to another point $(\vec{\mathbf{p}}(t + dt), \vec{\mathbf{q}}(t + dt))$, since $\vec{\mathbf{p}}(t + dt) \approx \vec{\mathbf{p}}(t) + dt\, \dot{\vec{\mathbf{p}}}$ and $\vec{\mathbf{q}}(t + dt) \approx \vec{\mathbf{q}}(t) + dt\, \dot{\vec{\mathbf{q}}}$ and since $\dot{\vec{\mathbf{p}}}$ and $\dot{\vec{\mathbf{q}}}$ are given by the canonical equation of motion.

Now, consider an arbitrary volume Γ in phase space whose points evolve in time as so. Liouville's theorem says that Γ may deform but its volume cannot change.

One can also interpret this result as follows. Consider the volume as consisting of a certain number of points, each of which occupies a small identical phase space volume element $\Delta\Gamma$. So, we can consider the flow of phase space volume as the flow of $\Gamma/\Delta\Gamma$ "particles" where each small volume element is christened as a particle. As the volume is invariant, this *fluid* acts as an *incompressible fluid*.

While there are many proofs of this theorem[5], the following proof[6] is the best in my opinion.

Consider the movement of the phase space volume as the motion of a fluid. By the continuity, we know that the density of the fluid must satisfy

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \vec{\mathcal{R}}} \cdot \left(\rho \vec{\mathcal{V}} \right) = 0 \tag{5.22}$$

Here, $\vec{\mathcal{R}} \equiv (q_1, ..., q_{3N}, p_1, ..., p_{3N})$ and $\vec{\mathcal{V}} \equiv \frac{d\vec{\mathcal{R}}}{dt}$. The above continuity equation is the consequence of observing that $\rho\vec{\mathcal{V}}$ is the current density of the fluid in the phase space. It is easily derived by considering the flow of particles in and out of a small fixed volume, without any sink or source for the particles.

We can expand the above equation as $\frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial \vec{\mathcal{R}}} \cdot \vec{\mathcal{V}} + \rho \frac{\partial}{\partial \vec{\mathcal{R}}} \cdot \vec{\mathcal{V}} = 0$. Now, note that the third term on the left side is zero, since $\frac{\partial}{\partial \vec{\mathcal{R}}} \cdot \vec{\mathcal{V}} = \sum_\alpha \left(\frac{\partial \dot{q_\alpha}}{\partial q_\alpha} + \frac{\partial \dot{p_\alpha}}{\partial p_\alpha} \right)$ and $\frac{\partial \dot{q_\alpha}}{\partial q_\alpha} = \frac{\partial^2 H}{\partial q_\alpha \partial p_\alpha} = -\frac{\partial \dot{p_\alpha}}{\partial p_\alpha}$ from the canonical equation (Eq. 5.15). Thus we we get is $\frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial \vec{\mathcal{R}}} \cdot \vec{\mathcal{V}} = 0$, which just means that $\frac{d\rho}{dt} = 0$, since $\rho = \rho(\vec{\mathcal{R}}, t)$. This means that the density of the fluid remains constant, proving the Liouville's theorem. Here are the four forms that need to be kept in mind.

$$\frac{d\rho}{dt} = 0 \tag{5.23}$$

$$\frac{\partial \rho}{\partial t} + \sum_\alpha \dot{q}_\alpha \frac{\partial \rho}{\partial q_\alpha} + \sum_\alpha \dot{p}_\alpha \frac{\partial \rho}{\partial p_\alpha} = 0 \tag{5.24}$$

$$\frac{\partial \rho}{\partial t} + \{\rho, H\} = 0 \tag{5.25}$$

$$d\Gamma(t) \equiv \prod_\alpha dq_\alpha(t) dp_\alpha(t) = d\Gamma(0) \equiv \prod_\alpha dq_\alpha(t=0) dp_\alpha(t=0) \tag{5.26}$$

The first two equations mean that the total time derivative of $\rho = \rho(\vec{\mathbf{q}}, \vec{\mathbf{p}}, t)$ is zero. The third equation has the same content as the second, and is the consequence of

[5] They can be found in standard texts such as Landau, Goldstein, Marion-and-Thornton, etc.

[6] The proof in the textbook on page 59 is a sketch, which is somewhat mathematically flawed. If you point out why the textbook proof is flawed, then you may enter my list of great readers. Incidentally, if you point out typos and such for my notes or the textbook, then the same will happen.

the first equation upon applying Eq. 5.21. Due to the conceptual advantage of the Poisson bracket, the third equation should be viewed as a better form of the second equation, while content-wise they are completely identical. The fourth equation also means the same thing as the other three. As we follow the fluid in a small volume element $d\Gamma$ containing our "particles" of interest, this volume element can deform in shape but its volume must be conserved, since the density of particles does not change.

Keep in mind that in this fluid analogy, the "particle" is actually a small volume of microstates of the real system. It should never be confused with a real particle, such as a gas molecule.

5.6 Basic assumption of statistical mechanics

From Eq. 5.14, we see that

$$\frac{d\langle O\rangle}{dt} = \int d\Gamma \frac{\partial \rho}{\partial t} O \tag{5.27}$$

This means that in equilibrium, we must have $\frac{\partial \rho}{\partial t} = 0$. What generic condition would satisfy it? Since $\frac{\partial \rho}{\partial t} + \{\rho, H\} = 0$ (Eq. 5.25) by the Liouville theorem, we see that the requirement would be met, if $\{\rho, H\} = 0$. By Eq. 5.19, we see that the condition $\rho = \rho(H)$ will do. A more general statement can be made if one notes that for any conserved quantity Q that is not explicitly dependent on time, $\{Q, H\} = 0$ by Eq. 5.21, and thus any function of Q will have a vanishing Poisson bracket with H. This means that ρ at equilibrium can be a function of that conserved quantity also. Thus, the following is the basic assumption regarding the equilibrium state.

$$\rho = \rho(H, L_1, L_2, ...) \qquad \text{at equilibrium} \tag{5.28}$$

where none of H, L_1, L_2 depends on t explicitly and L_1, L_2, ... are conserved quantities given by the Hamiltonian H. This means that, for a given set of conserved quantities, *all accessible states* are equally likely to occur.