Notes for Lecture 7

Semi-classical statistical mechanics

We have covered some basics regarding the Boltzmann equation, the Boltzmann H theorem, and the Poincaré recurrence. These are all dynamical properties. Now, we will draw our attention to the statistical mechanics. We will not, by design, worry too much about how the equilibrium is brought about. Rather, we will merely assert that the main hypothesis of the statistical physics, and draw the probabilistic consequence from it. This does not mean that we should not worry about how the dynamical laws actually bring about these statistical phenomena. It just means that, in statistical mechanics, we are more interested in the probabilistic aspect of the problem.

Right from the beginning, let me emphasize that the so-called classical statistical mechanics really does not exist, with the benefit of hindsight. It is from this perspective that we call the theory here the "semi-classical" statistical mechanics. This is because statistical mechanics is concerned with microscopic behavior, and at microscopic levels, energy, action, and particle all behave quantum mechanically, not classical mechanically. The so-called classical statistical mechanics is called that since it is concerned with the high temperature regime where the Newtonian mechanics is a good approximation to describe the energetics. However, as we shall see below, basic quantum ideas for energy, action, and particle form the important foundation even at high temperatures. So, let us not be apologists for the classical statistical mechanics, but call the theory a semi-classical statistical mechanics, which is really what it is.

7.1 Microcanonical ensemble

For a closed system, the energy (E) and the "volume" (x) are conserved. The collection of states that we consider under this condition are called a *microcanonical*

ensemble.

7.1.1 Probability

The central postulate of the statistical mechanics is that in equilibrium

$$P_{E,x}(\mu) \;=\; \frac{1}{\Omega(E,x)}\,\delta_{H(\mu),E} \tag{7.1}$$

where δ here is the Kroncker delta symbol and Ω is the number of all accessible/possible microstates $\{\mu\}$.

NOTE ✎ The symbol μ is used for two things in the textbook. One for ''micro-state'' (so μ makes some sense). Unfortunately, the symbol μ is a universal symbol for the chemical potential, too. To avoid confusion, I use μ for a microstate, in my note. ✎

Here, μ represents one unique state in the phase space. I.e., it corresponds to a unique set of initial conditions for $\vec{\mathbf{p}}(0)$ and $\vec{\mathbf{q}}(0)$ and the unique phase space trajectory from it. Namely, μ is equivalent to $(\vec{\mathbf{p}}(t), \vec{\mathbf{q}}(t))$. Thus, μ is a $6N$ dimensional vector, as each bold vector is defined as a $3N$ dimensional vector. Since what we are doing is really semi-classical statistical mechanics, it is quite appropriate to keep in mind that a microstate in quantum mechanics is the total many body wave function for the N body system.

What is $\Omega(E,x)$? It is the total *number* of microstates that meets the specs (energy E and "volume" x). Remember the fluid analogy used with the Liouville theorem? How we can consider the phase space dynamics as a flow of "particles"? Now it's time to think more seriously what this "particle" really means. If we figure it out, then $\Omega(E,x)$ is the number of that particle. Similar to what we mean by a real fundamental particle, this particle in phase space can be thought of as the indivisible unit in that phase space. Such unit, classical mechanics can never come up with.

It *can* be deduced in semi-classical mechanics, through the Bohr-Sommerfeld quantization condition

$$\oint p dq \;=\; (n+\gamma)h \qquad\qquad n = \text{integer},\ \gamma = \text{problem dependent const.} \tag{7.2}$$

Note that we can define $S_n \equiv \oint p dq$ where S_n is the area in the two dimensional (p,q) plane. It follows that $\Delta S_n = h$. Namely, the adjacent semi-classical orbits differ in area by h. So, each orbit in the phase space *owns* an area/action quantum, which is precisely h.

The above Bohr-Sommerfeld result can be re-interpreted as follows and then be generalized to the many particle case to suit our need. The above result is not surprising, since we knew that there is an indivisible area in the two dimensional phase space (p, q) due to the Heisenberg uncertainty principle $\Delta p \Delta q \geq \hbar/2$. So, it was to be expected that a quantum action in the two dimensional phase space is on the order of $\hbar$. What Bohr-Sommerfeld quantization condition does is to give that area quantum precisely. As each pair of canonically conjugate variables give rise to a factor of h, we can then conclude that a "particle" in the $6N$ dimensional space occupies a volume h^{3N}. Thus, we arrive at the following.

$$\Omega(E, x) \;=\; \frac{\text{volume in phase space}}{h^{3N}} \tag{7.3}$$

Now, you may notice that there is a slight problem here. If the energy is really precisely defined, then the volume is simply zero. However, keep in mind that the energy really precisely well-defined in classical mechanics simply means a finite energy uncertainty given by the energy step in quantum mechanics. So, as we are thinking about the semi-classical physics here, it is quite reasonable to invoke a small width in energy $\Delta E \equiv 2\Delta$. We shall see that this width plays no essential role in computation of thermodynamic quantities.

Another problem is that the above counting does not take into account the identical particle nature of the N particles. If they come within a small distance to interact with each other (like in gas), then they can no longer be considered as non-identical. We need to divide by $N!$ to account for the multiple counting in classical mechanics.

$$\Omega(E, x) \;=\; \frac{\text{volume in phase space}}{h^{3N}\, N!} \qquad \text{for identical particles} \tag{7.4}$$

7.1.2 Primary state function – entropy

The entropy of the system is defined as

$$S(E, x) \;=\; k_B \log \Omega(E, x) \tag{7.5}$$

and plays the primary role in characterizing a microcanonical ensemble.

Let us calculate the entropy for a monatomic ideal gas. In this case, the total energy is given by $E = \sum_{i=1}^{N} \frac{p_i^2}{2m}$. So, if the energy uncertainty is 2Δ, then the volume in phase space is $S_{3N} \cdot (2mE)^{3N/2-1} \cdot V^N \cdot \sqrt{2m}\frac{\Delta}{\sqrt{E}}$. Here, S_d is the total *solid* angle in d-dimensions ($S_1 = 2$, $S_2 = 2\pi$ and $S_3 = 4\pi$). It can be obtained by $I_d \equiv \left(\int_{-\infty}^{\infty} dx e^{-x^2}\right)^d = \pi^{d/2}$. Since the integral expands to $S_d \int_0^\infty dr r^{d-1} \exp(-r^2) =$

$S_d \frac{1}{2}\int_0^\infty dr t^{d/2-1}\exp(-t) = S_d\,(d/2-1)!/2$, we get $S_d = 2\pi^{d/2}/(d/2-1)! = 2\pi^{d/2}/\Gamma(d/2)$. Thus, from Eq. 7.4,

$$\Omega(E,x) \;=\; \frac{2\pi^{3N/2}}{(3N/2-1)!}\cdot(2m)^{(3N-1)/2}\cdot E^{(3N-3)/2}V^N\Delta\cdot\frac{1}{h^{3N}N!} \tag{7.6}$$

The entropy is (ignoring such terms as $\log 2$, $\log E$ or $\log\Delta$,

$$S(E,x) \;\approx\; k_B\left[\frac{3N}{2}\log(2m\pi E/h^2) - \log(3N/2-1)! + N\log V - \log N!\right] \tag{7.7}$$

Using the Stirling's formula (Eq. 5.10), $\log N! \approx N\log N - N + O(\log N)$, we get

$$S(E,x) \;\approx\; k_B N\left[\frac{3}{2}\log\left(\frac{4m\pi E}{3h^2N}\right) + \log\frac{V}{N} + \frac{5}{2}\right] \tag{7.8}$$

This is the so-called *Sackur-Tetrode equation*. This is a beautiful expression in that (1) it is extensive (i.e. when E, N, V are scaled by λ, S also scales as λS) and (2) it does not suffer from any unknown constant of order N. The fact (1) owes it to the consideration of the identical particle (the $1/N!$ factor) in Eq. 7.4, while the fact (2) owes it to the identification of h as the quantum of action in the same equation. However, note that this entropy is clearly incorrect as T goes to zero, as it does not approach a constant. To correct *this* deficiency, the semi-classical physics is not enough and one needs to do the full quantum statistics.

In relation to point (1) just made, consider the following. Suppose there are two different gases at the same temperature. N_1, V_1 characterizes the first gas and N_2, V_2 characterizes the second gas. Imagine that they are initially separated by a thin hard wall, which is suddenly removed. When the two are mixed, the gases are then spread to the total volume $V = V_1 + V_2$, the final entropy increases. This increase in entropy can be calculated from Eq. 7.8 as (noting that E/N is a function of only T for an ideal gas)

$$\begin{aligned}\Delta S_{mix,inh} \;&=\; k_B N_1\log\frac{V}{N_1} + k_B N_2\log\frac{V}{N_2} - k_B N_1\log\frac{V_1}{N_1} - k_B N_2\log\frac{V_2}{N_2}\\ &=\; k_B N_1\log\frac{V}{V_1} + k_B N_2\log\frac{V}{V_2}\end{aligned} \tag{7.9}$$

However, if the two gases are identical, then

$$\Delta S_{mix,hom} \;=\; k_B N\log\frac{V}{N} - k_B N_1\log\frac{V_1}{N_1} - k_B N_2\log\frac{V_2}{N_2} \tag{7.10}$$

These are the mixing entropy formulae for ideal gas. In particular, consider the case when the initial densities are identical with the final density $N_1/V_1 = N_2/V_2 = N/V$.

The homogeneous mixing entropy is zero, in this case, according to Eq. 7.10, while the inhomogeneous mixing entropy is always positive. This is of course the correct result.

Had we stuck to the purely classical statistics where the identical particle nature of gas molecules when they come into contact is ignored, then we would have gotten a finite mixing entropy even for the homogeneous gases of the same density. This is called the "Gibbs paradox" for the historical reason.

7.1.3 Laws of thermodynamics

Once the entropy concept is firmly established, one can go ahead and make connections with the thermodynamics.

Suppose two systems with energy E_1 and E_2 constitute a total system, which is a closed system. Assuming that they interact weakly, we have the total energy $E = E_1 + E_2$. The total number of states

$$\Omega(E) = \sum_{E_1+E_2=E} \Omega_1(E_1)\Omega_2(E_2) \tag{7.11}$$

where we leave out the volume parameters, x_1 and x_2, and $x = x_1 + x_2$, assuming that all of them are constant. So, the energy exchange between the systems is not through any mechanical work. Here, the sum can be considered as the sum over E_1, which has *discrete* values with an energy step given by 2Δ as we defined in Section 7.1.1.

Note that both Ω_1 and Ω_2 are exponentially large numbers. Let us say that the product is maximized at a certain value of $E_1 = E_1^*$ and the corresponding value of $E_2 = E_2^* = E - E_1^*$. Then, by the rule of large numbers, we conclude that

$$\log \Omega(E) \;=\; \log \Omega_1(E_1^*) + \log \Omega_2(E_2^*) \tag{7.12}$$

Multiplying by k_B, we conclude, nicely, that the entropy is extensive

$$S_{tot}(E) \;=\; S_1(E_1^*) + S_2(E_2^*) \tag{7.13}$$

The *fundamental hypothesis* of the statistical mechanics is that the system will approach this maximum entropy state as time progresses if the system was initially in a state where $\Omega_1\Omega_2$ is not the maximum possible. If the system is already in the maximum entropy state, then it will remain there. Thus the maximum entropy state defines the equilibrium state. This is the formulation of the 2nd law of thermodynamics in terms of the statistical mechanics.

Note that the above formulation does not really answer the question of "how." That must be answered by dynamical laws, and we are still awaiting a competent first-principle answer to the "how" question.

Note also that the above formulation is a statistical argument and thus does not preclude rare events in which the entropy does decrease. The issue is how likely such a rare event occurs. One can view the Poincaré cycle as the time scale in which such rare events occur. And so the answer is "meaninglessly long for a macroscopic sample."

In addition, the zeroth law and the first law can be nicely formulated from the point of view of the micro-canonical ensemble (section T4.2).

7.2 Canonical ensemble

For a system that is in contact with a big heat reservoir kept at a constant temperature, then the system is constrained to have a constant temperature T. Assuming that no work is exchanged between the reservoir and the system, the "volume" of the system, x, is also constant.

The ensemble of states under the constant T and the constant x is called the *canonical ensemble*.

7.2.1 Probability

As derived in class,

$$p(\mu) = \frac{\exp(-\beta H(\mu))}{Z} \tag{7.14}$$

$$Z = \sum_{\mu} \exp(-\beta H(\mu)) \tag{7.15}$$

where Z is the partition function, which is the normalization constant for the probability distribution for the canonical ensemble. On change of variable from μ to $\mathcal{E}$ (energy), we get (as shown in class),

$$p(\mathcal{E}) = \frac{\exp(-\beta \mathcal{F}(\mathcal{E}))}{Z} \tag{7.16}$$

$$Z = \sum_{\mathcal{E}} \exp(-\beta \mathcal{F}(\mathcal{E})) \tag{7.17}$$

$$\mathcal{F}(\mathcal{E}) \equiv \mathcal{E} - TS(\mathcal{E}) \tag{7.18}$$

7.2.2 Primary state function – Helmholtz free energy

The macroscopic Helmholtz free energy, F, is the value of $\mathcal{F}$ that maximizes the summand of Eq. 7.17 and it can be written as[1]

$$F \equiv E - TS = -k_B T \log Z \tag{7.19}$$

Another quantity that can easily be derived from Z is the energy and its cumulants. Here is a derivation. Note that Z can be formally thought of as a function of β. We form a rather artificial but extremely useful function

$$c(\beta, \gamma) \equiv \frac{Z(\beta)}{Z(\gamma)} \tag{7.20}$$

We can write

$$\langle E^n \rangle = \frac{\sum_{\mu} (H(\mu))^n \exp(-\beta H(\mu))}{Z} \tag{7.21}$$

$$= \frac{1}{Z} \frac{\partial^n Z}{\partial (-\beta)^n} \tag{7.22}$$

$$= \left. \frac{\partial^n c(\beta, \gamma)}{\partial (-\beta)^n} \right|_{\gamma=\beta} \tag{7.23}$$

Recalling that $\langle x^n \rangle = \frac{\partial^n \tilde{p}(k)}{\partial (-ik)^n}$, we see that $c(\beta, \gamma) = \tilde{p}(k = -i\beta)$ as long as we consider γ another independent variable, which we put $\gamma = \beta$ only after all necessary differentiations with respect to β are completed. With this rule, we can regard c as the characteristic function with a complex $k = -i\beta$. Then, $\log c$ is the second characteristic function that generates cumulants. Namely, $\langle E^n \rangle_c = \left. \frac{\partial^n c(\beta,\gamma)}{\partial (-\beta)^n} \right|_{\gamma=\beta}$, from which we arrive at a very useful relation

$$\langle E^n \rangle_c = \left. \frac{\partial^n \log Z}{\partial (-\beta)^n} \right|_x \tag{7.24}$$

In particular, this means that

$$\langle E^2 \rangle_c = \left. \frac{\partial \langle E \rangle_c}{\partial (-\beta)} \right|_x \tag{7.25}$$

$$= \frac{dT}{d(-\beta)} \left. \frac{\partial E}{\partial T} \right|_x \tag{7.26}$$

$$= k_B T^2 C_x \tag{7.27}$$

Thus, the uncertainty in energy is given by

$$\Delta E = \sqrt{\langle E^2 \rangle_c} = T \sqrt{k_B C_x} \tag{7.28}$$

In particular, this means that ΔE is of order $\sqrt{N}$, since E and C_x are of order N. In the thermodynamic limit, $\Delta E / E \to 0$ as $O(1/\sqrt{N})$.

[1] Again, we use the rule of large numbers, here.

7.2.3 Which ensemble to choose?

As we just found out, the canonical ensemble for which we allowed the energy value to adjust to keep temperature constant ends up attaining a unique energy value in the thermodynamic limit. Thus, for a given physical system of interest, we could either choose the microcanonical ensemble *or* the canonical ensemble. For computing the thermodynamic variables and their interrelations, it does not matter which one to choose. Or, any other ensemble discussed later on in this note will do fine too. It is the convenience of the calculation whereby a particular ensemble is chosen.

7.2.4 Equipartition principle, ideal gas

The partition function for a monatomic ideal gas is easily calculated as

$$Z = \int \frac{\prod_i d^3\vec{p}_i d^3\vec{q}_i}{N! h^{3N}} \exp\left(-\beta \sum_{i=1}^{N} \frac{\vec{p}^2}{2m}\right) \tag{7.29}$$

Using $\int dx \exp(-\beta x^2/(2m)) = \sqrt{\pi}\sqrt{2mk_BT}$, we get

$$Z = \frac{V^N}{N!}\left(\sqrt{\frac{2\pi m k_B T}{h^2}}\right)^{3N} \tag{7.30}$$

Define

$$\lambda(T) \equiv \frac{h}{\sqrt{2\pi m k_B T}} \tag{7.31}$$

which may be defined as the thermal Debye wavelength as it is on the order of the De Broglie wavelength for the thermal energy $3k_BT/2$. Note that the applicability of Newton's laws in semi-classical statistical mechanics means that $\lambda(T)^3 N/V \ll 1$. Using λ, and we get

$$Z = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N \tag{7.32}$$

From this, F and E can be readily obtained using $F = -k_BT \log Z$ and $E = -\frac{\partial \log Z}{\partial \beta}\Big|_x$. And, then, S can be obtained, with the identical result as in Section 7.1.2 (left for your exercise to verify it!). In addition, the pressure can be obtained as

$$P = -\frac{\partial F}{\partial V}\Big|_T = k_BT \frac{\partial \log Z}{\partial V}\Big|_T = \frac{Nk_BT}{V} \tag{7.33}$$

establishing the equation of state.

Now, let us look at the energy more closely: $E = -\frac{\partial \log Z}{\partial \beta}\Big|_x$ applied to Eq. 7.30 gives $E = 3Nk_BT/2$, since $Z \propto \beta^{-3N/2}$. The origin of this dependence on β is the fact that there are $3N$ degrees of freedom $(\vec{p}_1, ..., \vec{p}_N)$ that contribute to the quadratic energy of the form Ap^2 where A is positive. Now, suppose that our gas consists of O_2 molecules. The above partition function considers the monatomic gas, and thus considers only the center of mass motion of each oxygen molecule. However, there are internal motions per each molecule and they must be included in the partition function as well. This is simple to do within the Harmonic approximation, i.e. assuming that the inter-atomic motion within a molecule is governed by the Hooke's law. Then the inter-oxygen potential energy is of the form Ar^2 where r is the inter-oxygen distance minus the bond length. This r is another degree of freedom for the problem to be included in the partition function. In addition, there will be an internal kinetic energy term of the form Bp_r^2 where B involves the reduced mass. The involved integrals are the same integrals that we already performed above, and so this problem of including the internal degrees of freedom is pretty straightforward. In particular, the energy is very simple. This is because every degree of freedom that gives rise to the quadratic function in energy will contribute to one power of $\beta^{-1/2}$ to the partition function. This means that the total energy is given by

$$E = \frac{Q_d}{2} k_B T \tag{7.34}$$

where Q_d is the quadratic degrees of freedom. This is the **equipartition theorem**. In the O_2 example, we get $Q_d = (3 + 2 + 2)N = 7N$, where the last two is from the rotational motion. The discrepancy between the equipartition theorem and the experiment was a great impetus to the birth of quantum mechanics.

7.3 Grand canonical ensemble and Gibbs canonical ensemble

If one considers the system in contact with a reservoir that not only keeps the temperature constant but also maintains the "force" J, then what is the probability distribution for the system?

Doing like in the derivation of the probability distribution of the canonical ensemble, but now allowing the x value to fluctuate, we see that the probability of the system to have E_S and x_S is proportional to $\Omega_R(E_{tot} - E_S, x_{tot} - x_S)$, where E_{tot}, x_{tot} are conserved quantities for the combined system consisting of the reservoir and the

system.

$$\log p(\mu_S) = \text{const} + \log \Omega_R(E_{tot} - E_S, x_{tot} - x_S) \tag{7.35}$$

$$= \text{const} + \frac{1}{k_B} S_R(E_{tot} - E_S, x_{tot} - x_S) \tag{7.36}$$

$$= \frac{1}{k_B}\left(S_R(E_{tot}, x_{tot}) - \left.\frac{\partial S_R}{\partial E}\right|_x E_S - \left.\frac{\partial S_R}{\partial x}\right|_E x_S \right) + ... \tag{7.37}$$

Recognizing that $\left.\frac{\partial S_R}{\partial E}\right|_x = 1/T$ and $\left.\frac{\partial S_R}{\partial x}\right|_E x_S = -J/T$, we get, by collecting only those terms that depend on the system and then dropping the subscript S,

$$p(\mu) \propto \exp\left(-\beta[E(\mu) - Jx]\right) \tag{7.38}$$

7.3.1 Grand canonical ensemble

This is the case when $J = \mu$ and thus $x = N$. So, in a grand canonical ensemble T and μ are fixed while E, S and N are allowed to fluctuate. Note that if another volume variable such as V or M exists, then it is considered fixed as in the canonical ensemble.

$$p(\mu) = \frac{\exp\left(-\beta\left[E(\mu) - \mu N\right]\right)}{\mathcal{Q}} \tag{7.39}$$

$$\mathcal{Q} = \sum_{\mu} \exp\left(-\beta\left[E(\mu) - \mu N\right]\right) \qquad \text{grand partition function} \tag{7.40}$$

$$\mathcal{G} = E - TS - \mu N = -k_B T \log \mathcal{Q} \qquad \text{grand potential} \tag{7.41}$$

$$\langle N^n \rangle_c = \frac{1}{\beta^n} \frac{\partial^n \log \mathcal{Q}}{\partial \mu^n} \tag{7.42}$$

The grand canonical ensemble comes handy when the calculation becomes much easier by allowing particle numbers unrestricted. This is often the case in quantum statistics. It follows from the last equation above that $\Delta N = \sqrt{\langle N^2 \rangle_c} = \sqrt{\frac{1}{\beta}\frac{\partial N}{\partial \mu}} = O(\sqrt{N})$ and so $\Delta N/N \to 0$ in the thermodynamic limit.

7.3.2 Gibbs canonical ensemble

This is the case when J and x are mechanical variables (i.e. anything other than μ and N: $-P, V$ or H, M will do). So in a Gibbs canonical ensemble, T and J are fixed

by the reservoir.[2]

$$p(\mu) = \frac{\exp\left(-\beta\left[E(\mu) - Jx\right]\right)}{\mathcal{Z}} \tag{7.43}$$

$$\mathcal{Z} = \sum_{\mu} \exp\left(-\beta\left[E(\mu) - Jx\right]\right) \qquad \text{Gibbs partition function} \tag{7.44}$$

$$G = E - TS - Jx = -k_B T \log \mathcal{Z} \qquad \text{Gibbs free energy} \tag{7.45}$$

$$\langle x^n \rangle_c = \frac{1}{\beta^n} \frac{\partial^n \log \mathcal{Z}}{\partial J^n} \tag{7.46}$$

$$\langle H^n \rangle_c = \frac{\partial^n \log \mathcal{Z}}{\partial(-\beta)^n} \qquad H = E - Jx = \text{enthalpy} \tag{7.47}$$

(7.48)

[2]Note that, except for the grand canonical ensemble, N for the system is considered a fixed number for all the ensembles considered so far.