

Lecture 2: Review and preview

Let us begin with a review of undergraduate statistical physics, looking back at what you have already learnt in your first course on statistical physics.

Both Newtonian mechanics and its quantum counterpart, the Heisenberg-Schrodinger wave-mechanics are inherently deterministic theories. Consider for instance, the Hamiltonian formulation of Newton's laws

$$\begin{aligned}\frac{d\mathbf{p}}{dt} &= -\frac{\partial H(\mathbf{p}, \mathbf{q})}{\partial \mathbf{q}} \\ \frac{d\mathbf{q}}{dt} &= \frac{\partial H(\mathbf{p}, \mathbf{q})}{\partial \mathbf{p}}\end{aligned}\tag{1}$$

In these equations, knowing the initial condition $(\mathbf{p}(t=0), \mathbf{q}(t=0))$ fixes behaviour for all $t > 0$. The situation is similar in quantum mechanics. Consider Dirac's formulation of Schrodinger's equation

$$i\frac{d|\psi(t)\rangle}{dt} = \mathcal{H}|\psi\rangle\tag{2}$$

Knowing initial state $|\psi(t=0)\rangle$ fixes behaviour for all $t > 0$ given the system Hamiltonian \mathcal{H} .

Now, given the success of Newtonian mechanics (or its relativistic generalizations) in treating the behaviour of classical few-body systems and the corresponding success of the Schrodinger equation in the quantum realm, it might perhaps be natural to implicitly assume that the behaviour of large *macroscopic bodies*—their macroscopic properties, internal structure and dynamics—could all be understood *at least in principle* by an application of these deterministic laws to *all the* $\sim 10^{23}$ *atoms* that make up the macroscopic body.

However, the great insight which forms the foundation of Statistical Physics is that such an approach is *neither feasible nor relevant!* The first point is that it is simply not feasible to follow trajectories of $\sim 10^{23}$ electrons in a crystal or $\sim 10^{23}$ atoms in a gas. The second, more fundamental point is that this information on the trajectories of all the particles, or the time evolution of the many-body wavefunction, does *not help us understand* the *microscopic significance* of macroscopic notions like “temperature”, “hotness” vs “coldness” etc, which are key ingredients in our description of macroscopic systems.

These key ingredients are assembled to form the science of *thermodynamics*: As we know, thermodynamics starts with operational definitions for a

few key quantities, the so-called “thermodynamic variables” that characterize the state of a macroscopic body. These include the degree of “disorder” and quantity of heat, quantified by the thermodynamic entropy S , the hotness or coldness of macroscopic bodies, characterized by the absolute temperature T , the quantity of “available” energy, characterized by the free energy F , the internal energy U , and so on.

The predictive power of thermodynamics derives from a few simple properties these thermodynamic variables are postulated to satisfy. For instance, heat always flows from body A to B when in contact if $T_A > T_B$. S either increases or remains constant with time. And S goes to zero as $T \rightarrow 0$, and so on.

Now, as remarked earlier, it is by no means obvious at all where these properties like entropy and absolute temperature are “hiding” in the trajectories of $\sim 10^{23}$ atoms in a gas, or the evolution of the many-body wavefunction in a hilbert space of dimension $\sim 10^{23}$. And the central insight of statistical physics is the realization that these thermodynamic properties are *emergent* and *statistical* in nature.

The emergent aspect has to do with the fact that it makes no sense to say a single atom is “hot” or “cold”, or ascribe temperature T to it. But one mole of the corresponding gas in equilibrium can be described by thermodynamics, and does have a well-defined temperature at least in equilibrium. Likewise, there is no precise sense in which there is a sensibly defined entropy for a system of few atoms. Entropy, and the Third Law of thermodynamics both reflects the properties and behaviour of macroscopically large collections of atoms. Similarly, there is no sense in which a few atoms of Helium are in a superfluid state. Superfluidity (and we will have much more to say about it later) is a property of a macroscopically large collection of Helium atoms.

The statistical aspect is another facet which again reflects the key role played by the “thermodynamic limit”, *i.e.* the limit of macroscopically large system sizes (formally defined by keeping the density fixed and finite, but sending the volume to infinity). It has to do with the fact that thermodynamic laws can be violated by rare fluctuations in small systems. Thus, if you insist on using the operational definitions of thermodynamics to measure the entropy of very tiny systems, say a few dozen molecules bound together to form a polymer chain, you will find that the third law of thermodynamics can be disobeyed by rare fluctuations in the behaviour of the system.

Consequently, our microscopic understanding of thermodynamic properties has a statistical flavour that you are already familiar with. For the sake

of completeness, we provide a quick review: The basic idea is to start with the Gibbs distribution function, which postulates that a macroscopic system of N particles in fixed volume V is in eigenstate $|m\rangle$ with probability

$$\begin{aligned} P_m &= \frac{1}{Z} \exp(-E_m(V, N)/k_B T) \text{ where} \\ Z &= \sum_m \exp(-E_m(V, N)/k_B T) \end{aligned} \quad (3)$$

Here, Z is the *canonical partition function* of the system. An interesting aspect of this statistical description is that T , an emergent property of a macroscopic system, enters in the *relative probabilities* of various m .

With this starting point, one defines

$$U = \sum_m E_m P_m \quad (4)$$

$$F \equiv U - TS = -k_B T \log(Z) \quad (5)$$

where F is the Helmholtz free energy and U the internal energy. The temperature T , the internal energy U , the entropy S (defined implicitly in the above by subtracting the first equation from the second) and the free energy F defined in this manner are then argued to be possessed of all the properties one expects of the corresponding quantities defined operationally in thermodynamics. This provides an *a posteriori* justification of the Gibbs distribution function.

This framework generalizes readily if one wants a more general prescription that allows for number fluctuations. One starts with a larger space of states which considers all possible values of the total number N , and postulates the grand-canonical distribution function

$$\begin{aligned} P_{m,N} &= \frac{1}{Z_{GC}} \exp(-(E_m(V, N) - \mu N)/k_B T) \\ Z_{GC} &= \sum_{m,N} \exp(-(E_m(V, N) - \mu N)/k_B T) \end{aligned} \quad (6)$$

Z_{GC} , the grand-canonical partition function depends on the *chemical potential* μ , which can be thought of as the energy cost of adding a particle. Note that μ is an “intensive” variable, which can be thought of as a “Lagrange-multiplier” that fixes the mean number of particles to equal what we expect

for a system of that average density. From the grand-canonical partition sum, one obtains another thermodynamic potential

$$\Omega = -k_B T \log Z_{GC} \quad (7)$$

known as the Gibbs Free energy.

If appropriate for the experimental situation at hand, one can also work with a distribution function that allows for a variable volume

$$\begin{aligned} P_{m,V} &= \frac{1}{Z_P} \exp(-(E_m(V, N) + PV)/k_B T) \\ Z_P &= \sum_m \int dV \exp(-(E_m(V, N) + PV)/k_B T) \end{aligned} \quad (8)$$

Here Z_P is the partition function at fixed pressure P —again, the intensive pressure variable can be thought of as a “Lagrange-multiplier” that fixes the mean volume, and the corresponding thermodynamic potential

$$H = -k_B T \log(Z_P) \quad (9)$$

is the thermodynamic enthalpy.

Thus, the Gibbs distribution provides a statistical way of “understanding” the underlying rationale for the macroscopic laws of thermodynamics, and provides a clear calculational prescription for macroscopic concepts like temperature, free or available energy, entropy etc. Undergraduate treatments of statistical physics thus end on the following triumphant note:

Macroscopic phenomena are governed by thermodynamics. Since statistical mechanics provides the rationale for thermodynamics, all these phenomena can *in principle* be derived from statistical mechanics. At this point in our discussion, it is therefore worth asking: Really? Is this really true?

More precisely, let us list some phenomenological facts, drawn from everyday experience and a study of undergraduate physics, and ask: Where is all this lurking inside the Gibbs distribution function?

- Matter exists in several different phases:

Crystalline solid, liquid, gaseous phases of H_2O ; ferromagnetic and paramagnetic metals, insulators...

These phases are separated by phase transitions, accessed by changing pressure, temperature, magnetic field...

- Some of these phases are “distinctly” different from other phases:
Atoms in a crystal have a very “ordered” arrangement. Not so in a liquid
- Some phase transitions are “first order” with latent heat of phase change.
- Other transitions are accompanied by large scale fluctuations
e.g. as evidenced by the phenomenon of critical opalescence at liquid-gas critical point.

None of these follow in any automatic way from the basic prescription of Gibbs. They are all *emergent* properties of macroscopic aggregates of constituent particles, and require new ways of thinking to understand them well. One actually needs another layer of new concepts needed to “efficiently” think about these macroscopic phenomena. Here, we list them by way of preview, and discuss them in some detail in the next lecture:

- Spontaneous breaking of symmetry.
- Phases distinguished by long-range order.
- Order parameters.
- Rigidity.
- Broken ergodicity.
- Gapless elementary excitations related to the underlying rigidity.

More on this in the next lecture...