Theo. 4. Statistical Physics. 1/5

Lecture 22.

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Last time: Gibbs canonical ensemble

Grand canonical ensemble.

Today: Legendre transforms briefly

Interacting models

From before, we have seen that in the different ensembles, the input of heat, work, and/or chemical energy into the system motivates the study of a new functional (thermodynamic potential) that carries different variable dependence than before, in comparision to the system energy for the microcanonical ensemble. In the textbooks, this transformation is motivated "intuitively" by noting that the natural variables of $E_{sys}(S, \vec{x})$ [following $dE = T\,dS + \vec{J}\cdot d\vec{x}$] are using, in particular, the entropy S, which is not as tractable as other (conjugate) variables such as temperature, pressure, chemical potential μ. In other words, it is easier to conceptualize of coupling the system to a reservoir of const. T, P, or μ.

The formal mathematics of these transformations are the realm of Legendre transforms, where particular convex functions share a functional relationship:

$$G(m) = F(x(m)) - x \cdot m.$$

This should already be familiar from the classical mechanics topics of Hamiltonians & Lagrangians. We can emphasize it again for E_{sys} and Helmholtz free energy, $F = E - TS$.

Using $E(S, \vec{x})$, we have $dE = T\,dS + \vec{J}\cdot d\vec{x}$.

Note extensivity & intensitivity of $(S, \vec{x})$ and $(T, \vec{J})$, respectively.

The total $dF = dE - (dT)S - T\,dS$

$$= \vec{J}\cdot d\vec{x} - S\,dT,$$

so $\vec{J} \equiv \left(\frac{\partial F}{\partial \vec{x}}\right)_T$ and $S \equiv -\left(\frac{\partial F}{\partial T}\right)_{\vec{x}}$.

In general, with functionals (especially energy functionals), we ignore constants in E and F, so knowing the "natural" variables via derivative definitions lets us recreate F in its entirety. Namely, have $F(T, \vec{x})$ vs. $F(T, \vec{x}, S)$ is redundant: the second functional does not treat S independently in any practical application. The use of Legendre transforms is also key to the validity of Maxwell relations, since the commutation of mixed second derivates allows an equality of first derivatives when we replace by intermediate arguments:

$$-\left(\frac{\partial S}{\partial x}\right)_T = \left(\frac{\partial J}{\partial T}\right)_x.$$

There are many further properties of Legendre transforms, but they are more applicable to an applied mathematical math course.

The only one we will emphasize (at the end of the course) will be the connection back to extensive & intensive variables and the characterization of phase transitions via heat capacities and the more general study of derivative properties critical exponents, critical phenomena, and scaling relations.

Having discussed the principles of statistical mechanics (probabilities of microstates are prop. to Boltzmann factors of the relevant amount of heat energy, work energy, or chemical energy needed to obtain a second microstate with energy diff. than the first), we have used this principle to analyze & calculate in closed form the partition function (the distribution of microstates as a function of macrostate variables).

Unfortunately, the partition function is only calculable in limited circumstances because, intuitively, the stat. mech. approach works in regimes outside the thermodynamic limit ($N \to \infty$), and in particular, in regimes where $T \to 0$ and interactions become important and $N \to$ small, $V \to$ small where quantization effects are important.

Therefore, we now consider interacting statistical systems, followed by (idealized) quantum stat. systems.

non-interacting & interacting

To be fair, the variety of systems becomes much more varied & rich, and we will not have time to study all systems or classes of systems in detail.

Examples: Phonons in solids, Einstein model
Photons / Ultrarelativistic gases w/ & w/o mass
Lasers
Van der Waals gas ("realistic" gas)

[NB: we may study some systems in HW.]

Basic idea for including interactions in stat. mech.

$$H_N = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \mathcal{U}(\vec{q}_1, \ldots, \vec{q}_N)$$

where $\mathcal{U}$ provides interparticle interactions

$$\Rightarrow Z(T,V,N) = \frac{1}{N!} \int \prod_{i=1}^{N} \left(\frac{d^3\vec{p}_i\, d^3\vec{q}_i}{h^3} \right) \exp\left(-\beta \sum_i \frac{\vec{p}_i^{\,2}}{2m} \right) \cdot \exp\left(-\beta \mathcal{U}(\vec{q}_1, \ldots, \vec{q}_N) \right)$$

$$= Z_0(T,V,N) \left\langle \exp\left(-\beta \mathcal{U}(\vec{q}_1, \ldots, \vec{q}_N) \right) \right\rangle^0$$

where $Z_0 = \left(\frac{V}{\lambda^3}\right)^N \frac{1}{N!}$ is ideal gas part. fcn. +

$\langle \mathcal{O} \rangle^0$ is exp. value of $\mathcal{O}$ computed using prob. dist. of non-interacting system.

We can observe that this relates the desired part. fcn. Z to the "known" part. fcn. Z_0 via cumulants of U:

$$\ln Z = \ln Z_0 + \sum_{\ell=1}^{\infty} \frac{(-\beta)^\ell}{\ell!} \langle U^\ell \rangle_c^0 .$$

U only has position dependence, positions are uniformly & independently distributed in volume V, so moments are

$$\langle U^\ell \rangle^0 = \int \left(\prod_{i=1}^{N} \frac{d^3\vec{q}_i}{V} \right) U(\vec{q}_1, \ldots, \vec{q}_N)^\ell$$

Can also calculate perturbatively,

$$\langle \mathcal{O} \rangle = \frac{1}{Z} \frac{1}{\lambda^{3N} N!} \int \prod_{i=1}^{N} \left(d^3\vec{p}_i \, d^3\vec{q}_i \right) \exp\left[-\beta \sum_i \frac{\vec{p}_i^{\,2}}{2m} \right] \exp[-\beta U] \cdot \mathcal{O}$$

$$= \frac{\langle \mathcal{O} \exp[-\beta U] \rangle^0}{\langle \exp[-\beta U] \rangle^0}$$

$$= i \frac{\partial}{\partial k} \ln \langle \exp[-ik\mathcal{O} - \beta U] \rangle^0 \Big|_{k=0}$$

This is $\ln \equiv \sum_{\ell,\ell'=1}^{\infty} \frac{(-ik)^{\ell'}}{\ell'!} \frac{(-\beta)^\ell}{\ell!} \langle \mathcal{O}^{\ell'} * U^\ell \rangle_c^0$

and $\langle \mathcal{O} \rangle = \sum_{\ell=0}^{\infty} \frac{(-\beta)^\ell}{\ell!} \langle \mathcal{O} * U^\ell \rangle_c^0 .$

This defines cumulant expansion, which we will discuss more next time.