Theo. 4. Statistical Physics.

Lecture 15.

Felix Yu

December 10, 2023.

Last time: Shannon entropy, information
Third law, Gibbs entropy

Today: Thermodynamic potentials, constraints.
[Maxwell's equations (next time).]
Enthalpy, Helmholtz free energy, Gibbs free energy

We have now studied (well enough for an introductory course) the question of how ~~sys~~ isolated systems time-evolve towards equilibrium. In summary, the system time-evolves to thermal equilibrium from some given initial state, and in the process, the entropy of the system maximizes. No work energy, heat, or particle exchange occurs for such an isolated system with its environment.

Such a system is characterized by a microcanonical ensemble, and since one macrostate is reached, we can evaluate the entropy by $S = k_B \ln \Omega$.

The equilibrium condition, however, can be modified ~~once~~ once we start allowing free exchange of heat, work, or number of particles with the environment. As an analogy, consider the force balance in a rest frame versus an accelerating frame (in classical mechanics).

Being in an accelerating frame still allows us to calculate in a center of mass frame, where the external force providing acceleration causes the center of mass + all of the system's components to accelerate together. At the same time, the system in the CoM frame can be stable + not fly apart because of the external force. As a simple example, we are stationary in the Earth CoM frame but moving (rotating) around the Sun. We can think of such a situation as steady-state in the accelerating frame.

In a similar way, we have many scenarios where systems are not completely isolated from their enviroment and so they will reach a different type of steady state behavior as a result.

The first scenario to consider is a system that has no heat exchange but is in mechanical equilibrium with a constant external force. Recall mechanical equilibrium is when two ~~potentials~~ forces are equated, such as a mass m hanging vertically from a spring k in gravity. We have $\frac{d}{dx}\left(\frac{1}{2}kx^2 - mgx\right) = 0 \Rightarrow x_{eq} = \frac{mg}{k}$.

More generally, the potential energy of the system $U(x)$ gives an internally generated force $F_{int} = -\frac{dU}{dx}$ that balances the external force F at the equilibrium point.

For a given set of displacements $\vec{x}$, the external generalized forces $\vec{J}_{ext}$ perform work on the system as $đW \leq \vec{J} \cdot d\vec{x}$. Given $đQ = 0$ by assumption, then

$$H \equiv E - \vec{J} \cdot \vec{x} \quad \text{has} \quad \delta E \leq \vec{J} \cdot \delta \vec{x}$$

by the first Law and so $\delta H \leq 0$. The notation of "δ" for "δE", for example, indicates that the variation of E is done as the system is approaching equilibrium & thus the parametric dependence of the variation is a parameter that is not a function of state.

In contrast, in equilibrium, the enthalpy H is extremized since the system E energy responds to the external work $\vec{J} \cdot \vec{x}$ to achieve equilibrium by extremizing $H \equiv E - \vec{J} \cdot \vec{x}$. When equilibrium is achieved, we can characterize the system by functions of state (as usual), and

$$\begin{aligned} dH &= dE - d(\vec{J} \cdot \vec{x}) \\ &= T\,dS + \vec{J} \cdot d\vec{x} - \vec{x} \cdot d\vec{J} - \vec{J} \cdot d\vec{x} \\ &= T\,dS - x \cdot d\vec{J}. \end{aligned}$$

Given the differential of H only involves differentials of S and $\vec{J}$, the "natural" variables for the functional form of H are S and $\vec{J}$, i.e. $H(S, \vec{J})$. We recognize that

$$T = \left(\frac{\partial H}{\partial S}\right)\Big|_{\vec{J}} \quad \text{and} \quad \vec{x}_i = -\left(\frac{\partial H}{\partial \vec{J}_i}\right)_{S,\, J_{j \neq i}}$$

give equilibrium displacements.

In words, the system's internal dofs displace themselves in response to the externally applied force. An analogy is the ~~reacting~~ rearrangement of the electrons around a nucleus when placed in an electric field. Normally, the electrons are symmetric and screen the long distance charge of the nucleus. When in an electric field, however, the electrons find a dipole configuration with the nucleus to exert a force against the chemical bonds, since the dipole configuration helps minimize the total potential energy. This is the origin of polarization and polarized materials.

The next thermodynamic potential is the Helmholtz free energy, which is applicable when heat is exchanged via an isothermal transformation but no mechanical work is performed

We know $đQ \leq T\delta S$ in the process of approaching equilibrium, and $\delta E = đQ + đW \leq T\delta S$, giving

$$\delta F \leq 0 \quad \text{for} \quad F \equiv E - TS,$$

with F as the Helmholtz free energy. We have

$$dF = dE - d(TS) = TdS + \vec{J}\cdot d\vec{x} - SdT - TdS$$
$$= -SdT + \vec{J}\cdot d\vec{x},$$

so the natural formal form of F is $F(T, \vec{x})$.

The equilibrium forces and entropy are $J_i = \left.\frac{\partial f}{\partial x_i}\right|_{T, x_{j\neq i}}$ and $S = -\left.\frac{\partial F}{\partial T}\right|_{\vec{x}}$.

If we now combine mechanical work with isothermal transformations, then we have the thermodynamic potential called Gibbs free energy.

Construction: $đW \leq \vec{J}\cdot d\vec{x}$, $đQ \leq T\delta S$,

and $\delta E \leq T\delta S + \vec{J}\cdot\delta\vec{x}$, so

$\delta G \leq 0$ where $G \equiv E - TS - \vec{J}\cdot\vec{x}$.

Calculate $dG = dE - d(TS) - d(\vec{J}\cdot\vec{x})$

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

gives $G(T, \vec{J})$.

H, F, & G are examples of Legendre transforms to change variables to the best / most suited set of coordinates to study a given situation.

Note H, F & G are all functions of state, in that they are constructed ~~from~~ as mathematical combinations of thermodynamic coordinates that all have units of energy. These three are relevant, however, in contrast to the infinite possibilities of other fcns, because their extremization condition denotes an equilibrium condition. (more intuitively called steady state).

A final thermodynamic potential is the grand potential, when there is no mechanical work but instead chemical work affecting numbers of constituents. $\mathcal{G} = E - TS - \vec{\mu}\cdot\vec{N}$,

$d\mathcal{G} = -SdT + \vec{J}\cdot d\vec{x} - \vec{N}\cdot d\vec{\mu}$.

We have seen that many of these thermodynamic potentials have "natural" choices of functional dependence on extrinsic (S, x, N) and intrinsic (T, J, μ) variables at the same time. We will study further how this is precisely useful for systems in equilibrium and the mathematical structure underlying this fact, known as Maxwell's relations, next time. We will also briefly discuss the stability requirement of such thermodynamic potentials beyond simple extremization.