Theo. 4. Statistical Physics.

Lecture 17.

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Last time: Maxwell's relations.

Today: Stability requirements.

The microcanonical ensemble revisited

Previously, we studied new types of thermodynamic potentials that arose when a system is not completely isolated but instead can exchange heat, work, or both (or also particles) with a reservoir. These new thermodynamic potentials extremized in steady state behavior:

	$\delta Q = 0$	const. T
$\delta W = 0$	$\delta S \geq 0$	$\delta F \leq 0$
const. $\vec{J}$	$\delta H \leq 0$	$\delta G \leq 0$

(Remark: in this language, S is maximized for system in isolation + acts as a thermodynamic potential for $\delta W = 0$ + $\delta Q = 0$.)

So each of enthalpy H, Helmholtz free energy F, & Gibbs free energy G are all minimized in equilibrium with the external source. We will now briefly discuss the stability requirement of such systems.

In general, a potential (energy) is (meta)stable when there exists a local minimum in some neighborhood of x_0: $\left.\frac{dU}{dx}\right|_{x_0} = 0$ and $\left.\frac{d^2U}{dx^2}\right|_{x_0} > 0$.

Given an external force J, we have now tilted the potential to become enthalpy $H = U - Jx$.

If there are more mechanical coordinates, then the stability requirement generalizes to

$$\sum_{i,j} \frac{\partial^2 U}{\partial x_i \partial x_j} \delta x_i \, \delta x_j > 0$$

Recognizing that $\delta J_i = \delta\left(\frac{\partial U}{\partial x_i}\right) = \sum \frac{\partial^2 U}{\partial x_i \partial x_j} \delta x_j$,

we rewrite that stability requirement to

$$\sum_i \delta J_i \, \delta x_i > 0.$$

Allowing for thermal and chemical couplings, we should now generalize to

$$\delta T \delta S + \sum_i \delta J_i \delta x_i + \sum_\alpha \delta \mu_\alpha \delta N_\alpha > 0.$$

This is the general stability condition.

Can also be derived from studying equilibrium exchange of two halves A & B of a total system and matching variations at leading order (Kardar, p. 24).

This also leads to the mathematical concept of quadratic forms, which are general ways to study the geometry of hypersurfaces characterized by stability requirements in higher dimensional surfaces.

We would also use the opportunity to illustrate more specific aspects of thermodynamics in systems other than an ideal gas. These include an elastic rod, which can stretch from thermal expansion, a liquid on a surface (droplet),

and paramagnets. For paramagnets, it is convenient to analyze them using complete control with statistical physics, but an introductory version with magnetic dipoles can be found in Blundell + Blundell.

We now transition to statistical physics and demonstrate how many aspects of thermodynamics are understood from a modern view of equilibrium properties of statistical physics.

We start with the microcanonical ensemble again, which is applicable for systems with total energy fixed. Each microstate has the same energy, and the time evolution of the points in phase space are governed by a Hamiltonian. Since Hamiltonians conserve energy, all microstates form a (manifold) surface of $\mathcal{H} = E$ in phase space.

As we know, the starting point is that the equilibrium probability distribution is given by

$$P_{(E,\vec{x})}(\mu) = \frac{1}{\Omega(E,\vec{x})} \begin{cases} 1 & \text{for } \mathcal{H} = E \\ 0 & \text{otherwise.} \end{cases}$$

(μ: microstate)

The normalization factor $\Omega(E,\vec{x})$ is the area of the surface of constant energy in phase space. Because constructing densities in phase space that are non-zero only on a surface is mathematically difficult ("holes" inhibit differentiability), it will be convenient to define the microcanonical ensemble as a shell with thickness 2Δ around the surface of energy E.

and we allow $E-\Delta \leq H(\mu) \leq E+\Delta$. It is possible to show that the correction to $\ln \Omega$ is not strongly sensitive to $\frac{\Delta}{E}$, given $\frac{\Delta}{E} < 1$. (See Pathria, p. 20-22.)

We have the entropy of the uniform probability distribution as

$$S(E, \vec{x}) = k_B \ln \Omega(E, \vec{x}).$$

Given that compositions of systems are products of individual Ω_i, the corresponding entropies are additive, as required by extensitivity.

Recall that we showed the emergence of the equilibrium notion of temperature & the 0th law of thermodynamics previously. To recap, two microcanonical systems can be brought into contact to exchange energy but not work. The combined system has $E = E_1 + E_2$, and the new microstate is $\mu = \mu_1 \otimes \mu_2$, and $H(\mu_1 \otimes \mu_2) = H_1(\mu_1) + H(\mu_2)$.

In equilibrium, the joint system has

$$p_E(\mu_1 \otimes \mu_2) = \frac{1}{\Omega(E)} \begin{cases} 1 & \text{for } H_1(\mu_1) + H_2(\mu_2) = E \\ 0 & \text{otherwise} \end{cases}$$

The total allowed phase space is

$$\Omega(E) = \int dE_1 \, \Omega_1(E_1) \Omega_2(E - E_1)$$

$$= \int dE_1 \exp\left(\frac{S_1(E_1) + S_2(E - E_1)}{k_B} \right)$$

We know that the numbers involved in Ω_1 & Ω_2 are exponentially large, so we can use a saddle point method on S_1 & S_2 to obtain the maximum value of the integrand at $E_1^* + E_2^* = E - E_1^*$.

This gives the total entropy $S(E) = k_B \ln \Omega(E)$

$$\approx S_1(E_1^*) + S_2(E_2^*)$$

and the extremization condition requires

$$\left.\frac{\partial S_1}{\partial E_1}\right|_{\vec{x}_1} = \left.\frac{\partial S_2}{\partial E_2}\right|_{\vec{x}_2} \quad \text{at equilibrium,}$$

which is again the requirement that temperature is equilibrated $\left.\frac{\partial S}{\partial E}\right|_{\vec{x}} = \frac{1}{T}$.

We can also see the first law emerge, from considering variations of $S(E,\vec{x})$ via reversible coordinate changes by $\delta\vec{x}$. This is a change of the system energy by $đW = \vec{J}\cdot\delta\vec{x}$, with $E \to E + \vec{J}\cdot\delta\vec{x}$. The first order change in entropy is

$$\begin{aligned}\delta S &= S(E+\vec{J}\cdot\delta\vec{x},\ \vec{x}+\delta\vec{x}) - S(E,\vec{x}) \\ &= \left(\left.\frac{\partial S}{\partial E}\right|_{\vec{x}}\vec{J} + \left.\frac{\partial S}{\partial \vec{x}}\right|_{E}\right)\cdot\delta\vec{x}\end{aligned}$$

This change in entropy occurs spontaneously, evolving the system into a more probable state, unless the parenthesis term vanishes. We have

$$\left.\frac{\partial S}{\partial x_i}\right|_{E,x_{j\neq i}} = -\left.\frac{\partial S}{\partial E}\right|_{x_i}\cdot J_i = -\frac{J_i}{T}$$

We can now construct the total differential of $S(E,\vec{x}) \Rightarrow$

$$dS(E,\vec{x}) = \left.\frac{\partial S}{\partial E}\right|_{\vec{x}} dE + \left.\frac{\partial S}{\partial x_i}\right|_{E,x_j\neq i} dx_i$$

$$dS = \frac{dE}{T} - \frac{\vec{J}}{T}\cdot d\vec{x}$$

$$\Rightarrow dE = TdS + \vec{J}\cdot d\vec{x}.$$

The heat input is thus $TdS = đQ$.

Finally, we remark that the equilibrium energies (E_1^*, E_2^*) are characterized by the condition that they give a larger number of accessible states compared to any starting point, so

$$\Omega_1(E_1^*, \vec{x}_1)\,\Omega_2(E_2^*, \vec{x}_2) \geq \Omega_1(E_1, \vec{x}_1)\,\Omega_2(E_2, \vec{x}_2)$$

As a result, entropy increases:

$$\delta S = S_1(E_1^*) + S_2(E_2^*) - S_1(E_1) - S_2(E_2) \geq 0.$$

We also observe that the increase in entropy directs heat flow from hotter to colder systems.

Next time: Further (non-interacting) systems analyzed exactly using statistical physics.