Theo. 4. Statistical Physics

Lecture 18.

Felix Yu

January 8, 2024.

Last time: Thermodynamic stability

Revisiting the microcanonical ensemble.

Today: Non-interacting classical systems from stat. physics

Two-level systems

Ideal gas

In this lecture, we use stat. mech. ~~[illegible]~~ techniques to ~~[illegible]~~ analyze two types of (solvable) non-interacting systems.

Two level system:

Such systems are, as the name suggests, have two energy levels, $E=0$ and $E=\epsilon$, which are characterized by occupation numbers $\{n_i\}$, with $n_i = 0$ or 1 if the i^{th} site is in the ground or excited state. A physical system that realizes such a two-level system is a series of N impurity atoms trapped in a solid (crystal) matrix, where each impurity can be excited independently.

Thus, the microstates are the set of occupation numbers, $\{n_i\}$, with $i = 1, \ldots, N$. (Essentially, an N-vector with each entry as 0 or 1.). Obviously, the total energy is

$$H(\{n_i\}) = \epsilon \sum_{i=1}^{N} n_i \equiv \epsilon N_1 \text{ with}$$

N_1 the total number of excited impurities.

Thus, $E = \epsilon N_1$ and N_1 denote macrostates of the system.

The microcanonical probability $p(\{n_i\}) = \frac{1}{\Omega(E,N)} \delta_{\epsilon \sum_i n_i, E}$

There are $N_1 = \frac{E}{\epsilon}$ excited impurities,

we calculate Ω as the number of ways of choosing N_1 excited levels among the N sites, giving a binomial coefficient

$$\Omega(E,N) = \frac{N!}{N_1!\,(N-N_1)!}$$

As usual, $S = k_B \ln \Omega = k_B \ln\left(\frac{N!}{N_1!\,(N-N_1)!}\right)$

Using Stirling's formula, for $N_1, N \gg 1$,

$$S(E,N) \simeq -N k_B \left[\frac{N_1}{N} \ln \frac{N_1}{N} + \frac{N-N_1}{N} \ln \frac{N-N_1}{N}\right]$$

$$= -N k_B \left[\left(\frac{E}{N\epsilon}\right) \ln\left(\frac{E}{N\epsilon}\right) + \left(1-\frac{E}{N\epsilon}\right) \ln\left(1-\frac{E}{N\epsilon}\right)\right]$$

This also lets us calculate the equilibrium temperature, $\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_N$

$$= -N k_B \left[\frac{1}{N\epsilon} \ln\left(\frac{E}{N\epsilon}\right) + \left(\frac{E}{N\epsilon}\right) \cdot \frac{N\epsilon}{E} \cdot \frac{1}{N\epsilon} + \left(\frac{-1}{N\epsilon}\right) \ln\left(1-\frac{E}{N\epsilon}\right) - \frac{1}{N\epsilon}\right]$$

$$\frac{1}{T} = -\frac{k_B}{\epsilon} \ln\left(\frac{E}{N\epsilon - E}\right)$$

We can also solve for internal energy E as a fcn. of T:

$$\frac{1}{T} = \frac{k_B}{\epsilon} \ln\left(\frac{N\epsilon - E}{E}\right)$$

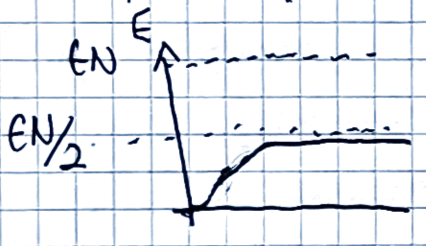
$$\frac{1}{T} = \frac{k_B}{\epsilon} \ln\left(\frac{N\epsilon}{E} - 1\right)$$

$$\frac{\epsilon}{k_B T} = \ln\left(\frac{N\epsilon}{E} - 1\right)$$

$$\frac{N\epsilon}{E} = \exp\left(\frac{\epsilon}{k_B T}\right) + 1$$

$$E(T) = \frac{N\epsilon}{\exp\left(\frac{\epsilon}{k_B T}\right) + 1}$$

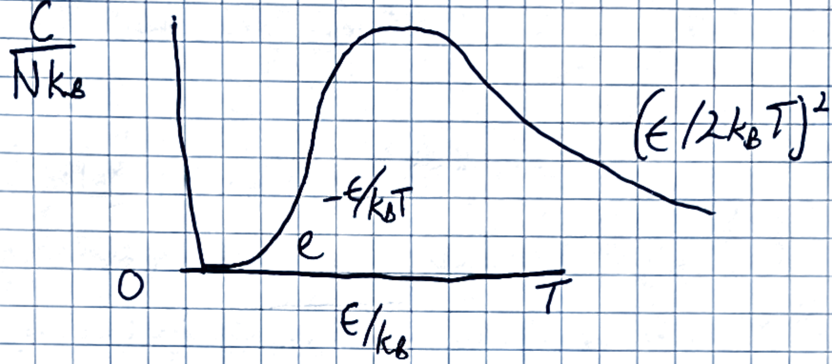
So, $E(0) = 0$ and $E(T \to \infty) = \frac{N\epsilon}{2}$.



These systems can also start with energies larger than $\frac{N\epsilon}{2}$, which essentially translates to negative temperature (as an equivalent eq. T), and this makes sense because you decrease the number of microstates as T increases given an upper bound on the energy. (All excited is $N\epsilon$.) Coupling the system with any reservoir, though, will lead to the system equilibrating at a positive T.

The heat capacity is always the change in energy per unit temperature, $C = \frac{dE}{dT} = \frac{N k_B \left[\left(\frac{\epsilon}{k_B T}\right)^2 \exp\left(\frac{\epsilon}{k_B T}\right)\right]}{\exp\left[\left(\frac{\epsilon}{k_B T}\right)+1\right]^2}$

Sketch:



C goes to 0 at both high & low T.

At low T, the gap in the system is characteristic of vanishing C.

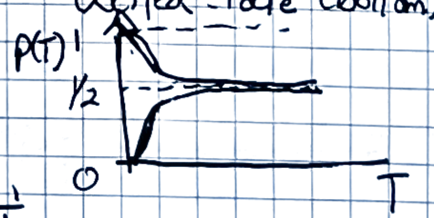
At high T, the system ~~is~~ experiences saturation.

For probabilities, unconditional prob. for exciting a particular impurity is

$$p(n_1) = \sum_{\{n_2,\dots,n_N\}} p(\{n_i\})$$

$$= \frac{\Omega(E-n_1\epsilon, N-1)}{\Omega(E,N)}$$

Sketch: prob. to find a single impurity in ground state (top), excited state (bottom).



$$p(n_1=0) = \frac{\Omega(E, N-1)}{\Omega(E,N)} = 1 - \frac{N_1}{N}$$

and $p(n_1=1) = 1 - p(n_1=0) = \frac{N_1}{N}$.

$$\Rightarrow p(0) = \frac{1}{1+\exp\left(\frac{-\epsilon}{k_B T}\right)}, \quad p_1 = \frac{\exp\left(\frac{-\epsilon}{k_B T}\right)}{1+\exp\left(\frac{-\epsilon}{k_B T}\right)}$$

Ideal gas. (Non-interacting)

Here, the phase space is 6N-dimensional, with microstates $\mu \equiv \{\vec{p}_i, \vec{q}_i\}$ for $i = 1, \ldots, N$.

We have
$$\mathcal{H} = \sum_{i=1}^{N} \left[\frac{\vec{p}_i^{\,2}}{2m} + U(\vec{q}_i) \right]$$

where $U(\vec{q})$ is the potential imposed by a box of volume V.

The joint PDF for a microstate is
$$p(\mu) = \frac{1}{\Omega(E,V,N)} \begin{cases} 1 & \text{for } \vec{q}_i \in \text{box} \ \& \ \sum_i \frac{p_i^2}{2m} = E \pm \Delta_E \\ 0 & \text{otherwise.} \end{cases}$$

The allowed phase space is a product of V^N from coordinates and the surface area of a 3N-dimensional sphere of radius $\sqrt{2mE}$ from momenta. (or shell with thickness $\Delta_R = \sqrt{2m/E}\ \Delta E$). Area is $A_d = S_d R^{d-1}$, with S_d solid angle.

Can solve for S_d using Gaussian integrals:
$$S_d = \frac{2\pi^{d/2}}{(d/2 - 1)!} \qquad \text{(exercise)}$$

Get
$$\Omega(E,V,N) = V^N \frac{2\pi^{3N/2}}{(3N/2 - 1)!} (2mE)^{(3N-1)/2} \Delta_R$$

We immediately calculate entropy:
$$S \simeq N k_B \ln\left[V \left(\frac{4\pi e m E}{3N} \right)^{3/2} \right]$$

+ this gives
$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_{N,V} = \frac{3}{2} \frac{N k_B}{E}$$

This gives both $E = \frac{3}{2} N k_B T$

and $C_V = \frac{3}{2} N k_B$, and equation of state

$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_{N,E} = \frac{N k_B}{V} \Rightarrow PV = N k_B T.$$

Finally, calculating joint PDFs leads to the Maxwell-Boltzmann distribution:

$$p(\vec{p}_1) = \frac{1}{(2\pi m k_B T)^{3/2}} \exp\left(- \frac{\vec{p}_1^{\,2}}{2 m k_B T} \right)$$

Next time:

Mixing entropy & Gibbs paradox.