02.10.14

Statistical Physics Tutorial

Topics:

1.) From the microcanonical ensemble to the thermodynamic entropy

a) $S = k_B \log \omega(E) \equiv$ entropy from theory of heat

b) $S = k_B \log \omega(E) \underset{\substack{\uparrow \\ \text{in thermodyn. limit}}}{=} k_B \log \Phi(E)$

c) "Deviations" of thermodyn. limit $\longleftrightarrow$ fluctuations

2.) Equivalence of the microcanonical & canonical ensemble

1.) Microcanonical ensemble $\rightarrow$ Entropy

a) In the context of the microcanonical ensemble, we defined

$$\Phi(E) := \Lambda_N \int_{\mathcal{H}(p,q)<E} dp\,dq \quad , \quad \Lambda_N = \frac{1}{N!\, h^{3N}}$$

and

$$\underset{\substack{\uparrow \\ \text{volume of microcanonical ensemble.}}}{\omega(E)} := \Phi(E+\delta E) - \Phi(E) = \frac{d\Phi(E)}{dE}\,\delta E \, .$$

The entropy can then be defined as

$$S = k_B \cdot \log \omega(E) \, .$$

Question: Is this the entropy known from thermodynamics?

Answer: Yes (in the thermodynamic limit)

We need to show

↳ S is extensive

↳ S satisfies 2^{nd} law of termodyn.

Divide system into two subsystems : $\boxed{N_1, V_1 \,|\, N_2, V_2}$

↳ $S_i(E_i, V_i) = k_B \cdot \log \omega_i(E_i)$

↳ $\mathcal{H}(p,q) = \mathcal{H}_1(p_1,q_1) + \mathcal{H}_2(p_1,q_1)$

Consider microcanonical ensemble of total system:

$$E \leq (E_1 + E_2) \leq E + \delta E$$

$$\Rightarrow \quad \omega(E) = \sum_{i=0}^{E/\delta E} \omega_1(E_i)\, \omega_2(E - E_i) \qquad E_i = \delta E \cdot i$$

Let $\bar{E}_1 \in [0, \delta E, \dots, E]$ s.t. $\omega_1(\bar{E}_1)\, \omega_2(E - \bar{E}_1) = \max_{E_i} \omega_1(E_i)\, \omega_2(E - E_i)$.

$$\Rightarrow \quad \omega_1(\bar{E}_1)\omega_2(E - \bar{E}_1) \leq \omega(E) \leq \left(\frac{E}{\delta E} + 1\right) \omega_1(\bar{E}_1)\omega_2(E - \bar{E}_1)$$

$$\Leftrightarrow \underbrace{k_B \log(\bar{E}_1) + k_B \log \omega_2(E - \bar{E}_1)}_{\propto N} \leq k_B \log \omega(E) \leq \underbrace{k_B \log\left(\frac{E}{\delta E} + 1\right)}_{\propto \log(N)} + \underbrace{k_B \log \omega_1(\bar{E}_1) + k_B \log \omega_2(E - \bar{E}_1)}_{\propto N}$$

$$\Rightarrow \quad S(E) = S_1(\bar{E}_1, V_1) + S_2(E - \bar{E}_1, V_2) + \mathcal{O}(\log N)$$

i.e., for $N \to \infty$ (thermodyn. limit)

↳ S is extensive

↳ $\underbrace{\text{S is maximized}}$

} S is indeed thermodyn. entropy

↳ leads to temperature as equilibrium parameter (see lecture)

b) <u>Claim</u>: $S = k_B \log \omega(E) \underset{\substack{\uparrow \\ \text{in thermodyn. lim.}}}{=} k_B \log \Phi(E)$

<u>Pf:</u> Same idea as before:

$$\Phi(E) = \sum_{i=0}^{E/\delta E - 1} \omega(E_i) = \sum_{i=0}^{E/\delta E - 1} \Phi(E_i + \delta E) - \Phi(E_i)$$

$$\omega(\bar{E}) \leq \Phi(E) \leq \frac{E}{\delta E}\, \omega(\bar{E}) \quad , \quad \omega(\bar{E}) = \max_{E_i} \omega(E_i)$$

$$\Leftrightarrow k_B \log \omega(\bar{E}) \leq k_B \log \Phi(E) \leq k_B \log \left(\frac{E}{\delta E}\right) + k_B \log \omega(\bar{E})$$

$$\Leftrightarrow \underbrace{k_B \log \omega(\bar{E})}_{S(\bar{E}, V)} = k_B \log \Phi(E) + \mathcal{O}(\log N)$$

$S(\bar{E}, V)$ is maximal for $\bar{E} = E$ because $\frac{\partial S(E,V)}{\partial E} \equiv \frac{1}{T} \geq 0$ $\square$

$\rightsquigarrow$ For ideal gas the calculation is done more explicitly in the script.

c) "Deviations" from the thermodynamic limit & fluctuations:

So far we have seen, that the entropy of a bipartite system is dominated by a small region of phase space, corresponding to having a well-defined energy for both subsystems:

$$S(E) = S(\bar{E}_1) + S(E - \bar{E}_1) + \text{corrections.}$$

Let's now consider deviations in energy about this maximum

$$f(E, \varepsilon) := S_1(\bar{E}_1 + \varepsilon) + S_2(E - \bar{E}_1 - \varepsilon)$$

and expand f in ε:

$$f(E,\varepsilon) = S(E) + \Bigg(\underbrace{\frac{\partial S_1}{\partial E_1}\Bigg|_{E_1=\bar{E}_1}} - \underbrace{\frac{\partial S_2}{\partial E_2}\Bigg|_{E_2=E-\bar{E}_1}} \Bigg) \cdot \varepsilon + \frac{1}{2}\left(\frac{\partial^2 S_1}{(\partial E_1)^2} + \frac{\partial^2 S_2}{(\partial E_2)^2} \right)\varepsilon^2 + \text{higher orders}$$

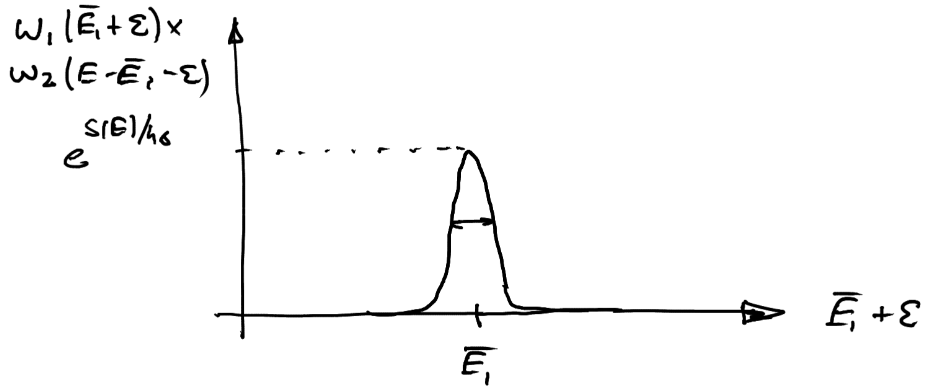
$$\frac{1}{T_1} = \frac{1}{T} = \frac{1}{T_2}$$

$$\approx S_1(\bar{E}_1) + S_2(E-\bar{E}_2) + \frac{\varepsilon^2}{2}\underbrace{\left(\frac{\partial T_1^{-1}}{\partial E_1} + \frac{\partial T_2^{-1}}{\partial E_2} \right)}_{-\frac{1}{T^2}\frac{1}{C_1} - \frac{1}{T}\frac{1}{C_2}}$$

heat capacity $\propto N$

$$= S(E) - \frac{\varepsilon^2}{2}\frac{1}{T^2}\left(\frac{1}{C_1} + \frac{1}{C_2} \right)$$

$$\Leftrightarrow \omega_1(\bar{E}_1+\varepsilon)\cdot\omega_2(E-\bar{E}_1-\varepsilon) = e^{S(E)/k_B}\cdot e^{-\frac{\varepsilon^2}{2k_BT^2}\left(\frac{1}{C_1}+\frac{1}{C_2}\right)}$$



$$\sigma^2 = k_B T^2\left(\frac{1}{C_1} + \frac{1}{C_2} \right) \propto \frac{1}{N}$$

Two important observations:

- ↳ as $N \to \infty$ (thermodyn limit) the distribution f approaches a δ-distribution
- ↳ Subleading orders of the entropy as $N\to\infty$ are related to response fct's (⇝ see Discussion about fluctuations later in the course)

Further remarks:

↳ Condition for equilibrium (maximization of entropy) leads to equilibrium parameter of thermodynamics (temperature)

↳ this will hold similarly for
- number of particles <-> chemical potential
- volume <-> pressure

2.) Equivalence of microcanonical & canonical ensembles

(This part has significant overlaps with the chapter about fluctuations in the script)

The aim is to show that even thout the canonical ensemble contains contributions of all energies, the corresponding contributions have all the same energy. This is why, in the formalism of statistical mechanics, the canonical and microcanonical ensembles are the same.

There are (at least) two ways to show this:

i) Consider $\langle \mathcal{U}^2 \rangle - \langle \mathcal{U} \rangle^2 \propto C_V \propto N$

ii) Consider contributions (w.r.t. to energy) to the partition function

i) see script

ii) partition function:

$$Z = \Delta_N \int dp\, dq\, e^{-\beta \mathcal{U}(p,q)} \quad , \quad \beta = \frac{1}{k_B T}$$

probability dist:

$$\rho(p,q) = \frac{1}{Z} e^{-\mathcal{U}(p,q)/k_B T}$$

Now write

$$Z = \mathcal{N}_N \int dp\,dq\; e^{-\beta \mathcal{H}(p,q)} = \int_0^\infty dE\, \omega(E)\, e^{-\beta E}$$

$$= \int_0^\infty dE\; e^{-\beta E + \log \omega(E)} = \int_0^\infty dE\; e^{\beta(T S(E) - E)}$$

(entropy from microcanonical ensemble)

and expand (as before):

$$S(E) = S(\bar{E}) + \underbrace{\left.\frac{\partial S}{\partial E}\right|_{E=\bar{E}}}_{\frac{1}{T}} (E-\bar{E}) + \frac{1}{2} \underbrace{\left.\frac{\partial^2 S}{\partial E^2}\right|_{E=\bar{E}}} (E-\bar{E})^2 + \text{higher orders}$$

$$\hookrightarrow T S(E) - E \approx T S(\bar{E}) + (E-\bar{E}) + \frac{1}{2} T \underbrace{\left.\frac{\partial^2 S}{\partial E^2}\right|_{E=\bar{E}}}_{-\frac{1}{T^2}\frac{1}{C_V}} (E-\bar{E})^2 - E$$

$$= T S(\bar{E}) - \bar{E} - \frac{1}{2 T C_V} (E-\bar{E})^2$$

Coming back to

$$Z = \int_0^\infty dE\; e^{\beta(T S(E) - E)} \approx e^{\beta(T S(\bar{E}) - \bar{E})} \underbrace{\int_0^\infty dE\; e^{-\frac{1}{2 k_B T^2 \cdot C_V}(E-\bar{E})^2}}_{\sqrt{2\pi k_B T^2 C_V}}$$

we find for the free energy

$$F = -\frac{1}{\beta} \log Z = TS - U \underbrace{- \frac{1}{2} k_B T \log(2\pi k_B T^2 C_V)}$$

$$= TS - U + \mathcal{O}(\log N)$$

$\rightsquigarrow$ For $N \to \infty$, the entropy defined in either the canonical or microcanonical ensemble are the same.

Final remark:

The vanishing of mean square fluctuations (as for the entropy) has an broader range of application:

For any observable quantity A, we need that

$$\frac{\langle A^2\rangle - \langle A\rangle^2}{\langle A\rangle^2} \xrightarrow[\text{limit}]{\text{thermodyn.}} 0 \,, \qquad \langle A\rangle := \frac{\int dp\,dq\; A(p,q)\,\rho(p,q)}{\int dp\,dq\; \rho(p,q)} .$$

If this would not hold, then different averages (such as the ensemble average and the most probable value for A) could give different results, which would pose a serious problem for the interpretation of this quantities in statistical mechanics.