

# 114036 - Statistical and Thermal Physics

Amit Keren

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## Abstract

## 1 Introduction

### History

- First, thermodynamics was developed, before atoms were known to exist.
- Statistical physics.
- Quantum physics.

In the course, the order is the opposite.

### 1.1

Suppose we have two balls of diameter  $d$ . If both are on the bottom, total energy is 0. If one is on the other, total energy is  $mgd$ .



Number of state	Degeneracy	Energy
0	3	0
1	3	$mgd$
2	0	$2mgd$

**Paramagnetism** Define magnetic moment as  $\vec{m} = I\vec{a}$ . For magnetic field energy is  $U = -\vec{B} \cdot \vec{m} = -\vec{B}\mu$ .

Suppose we have a system of a big amount of current loops, each of which can have one of two directions - clockwise or counterclockwise. For example



To calculate total magnetic momentum we just sum all of the moments, which are either  $\mu$  or  $-\mu$ . In upper example,  $M = \sum_i \mu_i = 2\mu$ .

The total number of possible states is  $2^N$ . The possible energy is  $M = (N - 2N_d)\mu$  where  $N_d$  is number of down-facing loops of current. Number of different states with sam energy is

$$\binom{N}{N_d} = \frac{N!}{N_d!N_u!}$$

Now, for even  $N$ , define

$$2S = N_u - N_d$$

Then

$$\binom{N}{N_d} = \frac{N!}{((\frac{1}{2}N - S)!((\frac{1}{2}N + S)!}$$

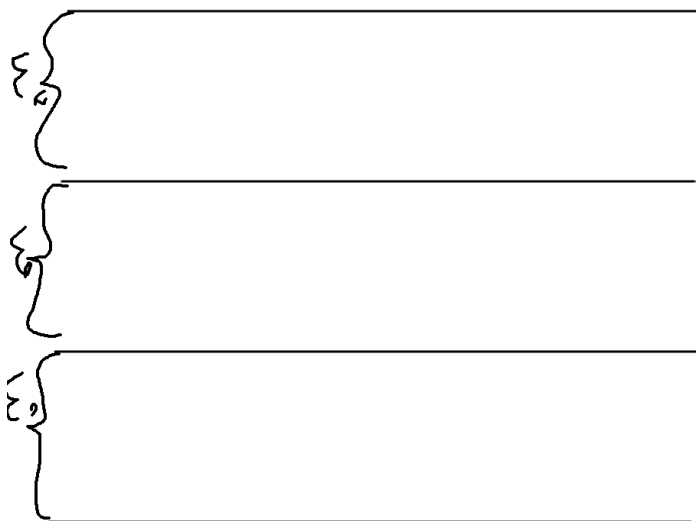
and the energy

$$U = -2S\mu B \Rightarrow S = -\frac{U}{2\mu B}$$

The degeneracy of the state thus is

$$g(N, S) = \frac{N!}{\left(\frac{1}{2}N - \frac{U}{2\mu B}\right)! \left(\frac{1}{2}N + \frac{U}{2\mu B}\right)!}$$

**Particles on shelves (quantum oscillator)** Suppose we have equally-distant shelves, and energy distance between two shelves is  $\epsilon_0$ :



Define  $n = \frac{U}{\epsilon_0}$  which is amount of energy we have (it comes in quantas is degeneracy? What is degeneracy? It is combinations of  $N$  out  $n$  with returns:

$$g(N, u) = \frac{(n + N - 1)!}{n!(N - 1)!} = \frac{\left(N + \frac{U}{\epsilon_0} - 1\right)!}{\left(\frac{U}{\epsilon_0}\right)!(N - 1)!}$$

**Particles on shelves with quadratic distances (particles in box)** Now suppose distances goes as square of number of shelf ( $\epsilon_0, 4\epsilon_0, \dots$ ). This problem doesn't have analytical solution. But we can find solution manually. For example, to find  $g(6, 18\epsilon_0)$ . The only option is 2 boxes on first energy level  $U = \epsilon_0$  and 4 on second energy level, thus

$$g(6, 18\epsilon_0) = \binom{6}{2} = 15$$

**1D box with particles** Now we want to calculate kinetic energy:

$$E = \frac{p^2}{2m}$$

Since we can't do much with continuous values (there is infinite number of options), let's divide both momentum and position into discrete intervals of size  $w$  and  $l$  correspondingly. Now, the position is independent on energy, but there are only two options for momentum -  $\pm\sqrt{2mE}$ . Thus degeneracy is

$$g(1, E) = 2 \frac{L}{l}$$

**2D box** We now divide position in momentum into intervals of length  $l$  and  $w$  in both directions. Position is still arbitrary, and momentum lies on a circle of radius  $2mE$ . However, it's hard to calculate.

Let's define instead  $S(1, E)$  - number of states with energy *less* than  $U$ . For 1-dimensional case

$$S(1, E) = \frac{L}{l} \cdot 2 \cdot \frac{\sqrt{2mE}}{w} = \frac{1}{lw} \int_{-\frac{l}{2}}^{\frac{l}{2}} ds \int_{-\sqrt{2mE}}^{\sqrt{2mE}} ds$$

In 2D we get, for box of area  $A$

$$S(1, E) = \frac{A}{l^2} \cdot \frac{2\pi mE}{w^2} = \frac{1}{l^2 w^2} \int_{-\frac{l}{2}}^{\frac{l}{2}} dx \int_{-\frac{l}{2}}^{\frac{l}{2}} dy \iint_{|p| < \sqrt{2mE}} d^2 p$$

$$S(1, E) = \frac{V}{l^3} \cdot \frac{4\pi(2mE)^{\frac{3}{2}}}{3w^3}$$

We denote  $h = lw$ . Now note that  $G(n, U) = \frac{\partial S(n, U)}{\partial U}$ .

**Two distinguishable particles in 1D** While positions are independent, there is dependence between  $p_1$  and  $p_2$ :

$$\frac{p_1^2}{2m} + \frac{p_2^2}{2m} + E$$

We can note that

$$S_{2D}(1, U) = S_{1D}(2, U)$$

**$N$  particles in  $D$  dimensions**

$$S_D(N, U) = \frac{1}{h^{DN}} \int_{\vec{x}_1 \in V} d^D x_1 \dots \int_{\vec{x}_n \in V} d^D x_n \int_{\sum_{i=1}^n \vec{p}_i^2 \leq 2mU} \dots \int d^D p_1 \dots d^D p_n$$

**Ball volume in dimension  $d$**  Define gamma function. For  $\alpha > 0$

$$\frac{1}{\alpha} = \int_0^\infty dx e^{-x\alpha}$$

Differentiating  $n$  times by  $\alpha$  (and dividing by  $(-1)^n$ ):

$$\frac{N!}{\alpha^{N+1}} = \int_0^\infty dx x^N e^{-x\alpha}$$

By substituting  $\alpha = 1$ :

$$N! = \int_0^\infty dx x^N e^{-x}$$

Thus define

$$\Gamma(N+1) = \int_0^\infty dx x^N e^{-x}$$

Define area of  $d$ -dimensional sphere of radius  $R$  as

$$A_d = S_d \cdot R^{d-1}$$

Define also

$$I_d = \left( \int_{-\infty}^{\infty} dx e^{-x^2} \right)^d$$

On one hand  $I_D = \pi^{\frac{d}{2}}$ , on the other hand

$$I_d = \int_{-\infty}^{\infty} dx_1 e^{-x^2} \int_{-\infty}^{\infty} dx_2 e^{-x^2} \dots \int_{-\infty}^{\infty} dx_n e^{-x^2} = \int_{-\infty}^{\infty} dx_1 dx_2 \dots dx_n e^{-\sum_{i=1}^n x_i^2}$$

For  $R = \sum_{i=1}^n x_i^2$ :

$$I_D = \int_0^{\infty} dR S_d R^{d-1} e^{-R^2}$$

(Note that when we perform integral over angular dimensions we acquire exactly  $S_d$  from Jacobean).

For  $y = R^2$ ,  $dy = 2R dR$ :

$$\int_0^{\infty} \frac{dy}{2\sqrt{y}} S_d y^{\frac{d-1}{2}} e^{-y} = \frac{S_d}{2} \int_0^{\infty} y^{\frac{d}{2}-1} e^{-y} dy = \frac{S_d}{2} \Gamma\left(\frac{d}{2}\right)$$

Thus

$$\frac{S_d}{2} \Gamma\left(\frac{d}{2}\right) = \pi^{\frac{d}{2}}$$

i.e.

$$S_d = \frac{2\pi^{\frac{d}{2}}}{\Gamma\left(\frac{d}{2}\right)}$$

Now the volume of  $d$ -dimensional ball

$$V_d = \int_0^R dr \frac{2\pi^{\frac{d}{2}}}{\Gamma\left(\frac{d}{2}\right)} r^{d-1} = \frac{\pi^{\frac{d}{2}}}{\Gamma\left(\frac{d}{2}\right)} \frac{r^d}{\frac{d}{2}} = \frac{\pi^{\frac{d}{2}} r^d}{\Gamma\left(\frac{d}{2} + 1\right)}$$

Back to our particles:

$$S_D(N, U) = \frac{1}{h^{DN}} \int_{\vec{x}_1 \in V} d^D x_1 \dots \int_{\vec{x}_n \in V} d^D x_n \int_{\sum_{i=1}^n \vec{p}_i^2 \leq 2mU} \dots \int d^D p_1 \dots d^D p_n = \frac{L^{DN} \pi^{\frac{DN}{2}} (2mU)^{\frac{DN}{2}}}{h^{DN} \Gamma\left(\frac{DN}{2} + 1\right)} = \left(\frac{L}{h}\right)^{DN} \frac{(2\pi m w)^{\frac{DN}{2}}}{\Gamma\left(\frac{DN}{2} + 1\right)}$$

Thus in our world

$$S_3(N, U) = \frac{V^N \pi^{\frac{3N}{2}} (2mU)^{\frac{3N}{2}}}{h^{3N} \Gamma\left(\frac{3N}{2} + 1\right)}$$

And

$$G_3(N, U) = \frac{\partial S_3(N, U)}{\partial U} = \frac{V^N \pi^{\frac{3N}{2}} (2mU)^{\frac{3N}{2}-1} \cdot \frac{3}{2} N \cdot 2m}{h^{3N} \Gamma\left(\frac{3N}{2} + 1\right)} = \frac{3V^N \pi^{\frac{3N}{2}} (2mU)^{\frac{3N}{2}-1} m N}{h^{3N} \Gamma\left(\frac{3N}{2} + 1\right)}$$

**Integral approximation with steepest descent** Suppose we want calculate

$$I = \int dx e^{N\phi(x)}$$

for some big  $N$  and  $x_{max}$  is maximum of  $\phi$ :

$$I \approx \int dx \exp \left[ N \left( \phi(x_{max}) - \frac{1}{2} |\phi''(x_{max})| (x - x_{max})^2 + \frac{1}{3!} \phi'''(x_{max}) (x - x_{max})^3 \right) \right]$$

Then, substituting  $y = \sqrt{N}(x - x_{max})$

$$I = e^{N\phi(x_{max})} \int \frac{dy}{\sqrt{N}} e^{-\frac{1}{2} |\phi''(x_{max})| y^2 + \frac{1}{3!} \phi'''(x_{max}) \frac{y^3}{\sqrt{N}}}$$

Since  $N$  is big,  $\frac{1}{3!} \phi'''(x_{max}) \frac{y^3}{\sqrt{N}}$  is negligible (and higher orders too):

$$I = e^{N\phi(x_{max})} \sqrt{\frac{2\pi}{N |\phi''(x_{max})|}}$$

**Example** Lets approximate  $n!$ :

$$\Gamma(n+1) = \int_0^\infty dx x^N e^{-x} = \int_0^\infty dx e^{N(\ln x - \frac{x}{N})}$$

Thus  $\phi(x) = \ln x - \frac{x}{N}$ , and

$$\phi'(x) = \frac{1}{x} - \frac{1}{N}$$

i.e.,  $x_{max} = N$ . And

$$|\phi''(x)| = \frac{1}{x^2}$$

$$\Gamma(n+1) = \int_0^\infty dx x^N e^{-x} = \int_0^\infty dx e^{N(\ln x - \frac{x}{N})} \cong e^{N(\ln N - 1)} \sqrt{\frac{2\pi}{N \frac{1}{N^2}}} = N^N e^{-N} \sqrt{2\pi N}$$

which is Stirling approximation. We usually want to take logarithm:

$$\ln(N!) \cong N \ln N - N + \frac{1}{2} \ln(2\pi N)$$

**Example** Back to example with up and down particles:

$$g(N, S) = \frac{N!}{N_\uparrow! N_\downarrow!}$$

where  $2S = N_\uparrow - N_\downarrow$  and  $N = N_\uparrow + N_\downarrow$

$$\ln g = \ln N! - \ln N_\uparrow! - \ln N_\downarrow!$$

$$\ln N! = \frac{1}{2} \ln 2\pi + (N+1) \ln N - \frac{1}{2} \ln N - N$$

Substituting

$$\ln N! = \frac{1}{2} \ln \frac{2\pi}{N} + \left( N_\uparrow + \frac{1}{2} + N_\downarrow + \frac{1}{2} \right) \ln N - (N_\uparrow + N_\downarrow)$$

in addition

$$\ln N_\uparrow! = \frac{1}{2} \ln 2\pi + \left( N_\uparrow + \frac{1}{2} \right) \ln N_\uparrow - N_\uparrow$$

$$\ln N_\downarrow! = \frac{1}{2} \ln 2\pi + \left( N_\downarrow + \frac{1}{2} \right) \ln N_\downarrow - N_\downarrow$$

so

$$\ln g = \frac{1}{2} \ln \frac{1}{2\pi N} - \left( N_\uparrow - \frac{1}{2} \right) \ln \frac{N_\uparrow}{N} - \left( N_\downarrow + \frac{1}{2} \right) \ln \frac{N_\downarrow}{N}$$

Now since

$$\ln \frac{N_\uparrow}{N} = \ln \left( \frac{1}{2} + \frac{2S}{2N} \right) = \ln \frac{1}{2} \left( 1 + \frac{2S}{N} \right) = \ln \frac{1}{2} + \ln \left( 1 + \frac{2S}{N} \right)$$

If  $S \ll N$

$$\ln \frac{N_\uparrow}{N} = -\ln 2 + \frac{2S}{N} - \frac{2S^2}{N^2}$$

similarly

$$\ln \frac{N_\downarrow}{N} = -\ln 2 - \frac{2S}{N} + \frac{2S^2}{N^2}$$

Thus

$$\ln g = \frac{1}{2} \ln \frac{1}{2\pi N} - \left( \frac{1}{2} N + S - \frac{1}{2} \right) \left( -\ln 2 + \frac{2S}{N} - \frac{2S^2}{N^2} \right) - \left( \frac{1}{2} N - S + \frac{1}{2} \right) \left( -\ln 2 - \frac{2S}{N} + \frac{2S^2}{N^2} \right)$$

i.e.,

$$\ln g = \frac{1}{2} \ln \frac{2}{\pi N} + N \ln 2 - \frac{2S}{N} + \mathcal{O}\left(\frac{S^3}{N^2}\right)$$

$$g(N, S) = \left( \frac{2}{\pi N} \right)^{\frac{1}{2}} 2^N e^{-\frac{2S^2}{N}}$$

And if use energy,

$$g(N, U) = \left( \frac{2}{\pi N} \right)^{\frac{1}{2}} 2^N e^{-\frac{2U^2}{(\mu B)^2 N}}$$

Now since number of configurations is  $2N$ ,

$$\rho(S) = \left( \frac{2}{\pi N} \right)^{\frac{1}{2}} e^{-\frac{2S^2}{N}}$$

Which is normal distribution with mean 0 and standard deviation  $\frac{\sqrt{N}}{2}$ . (This is immediate from CLT).

Lets check the standard deviation of actual  $S$ :

$$\langle (2S)^2 \rangle = \left\langle \left( \sum_i N_i \right)^2 \right\rangle = \left\langle \sum_{i,j} N_i N_j \right\rangle = \left\langle \sum_i N_i^2 + \underbrace{\sum_{i \neq j} N_i N_j}_{0 \text{ from independence}} \right\rangle = \left\langle \sum_i N_i^2 \right\rangle = N$$

Thus variance of  $2S$  is  $N$  and variance of  $S$  is  $\frac{N}{4}$ . Now, relative standard deviation

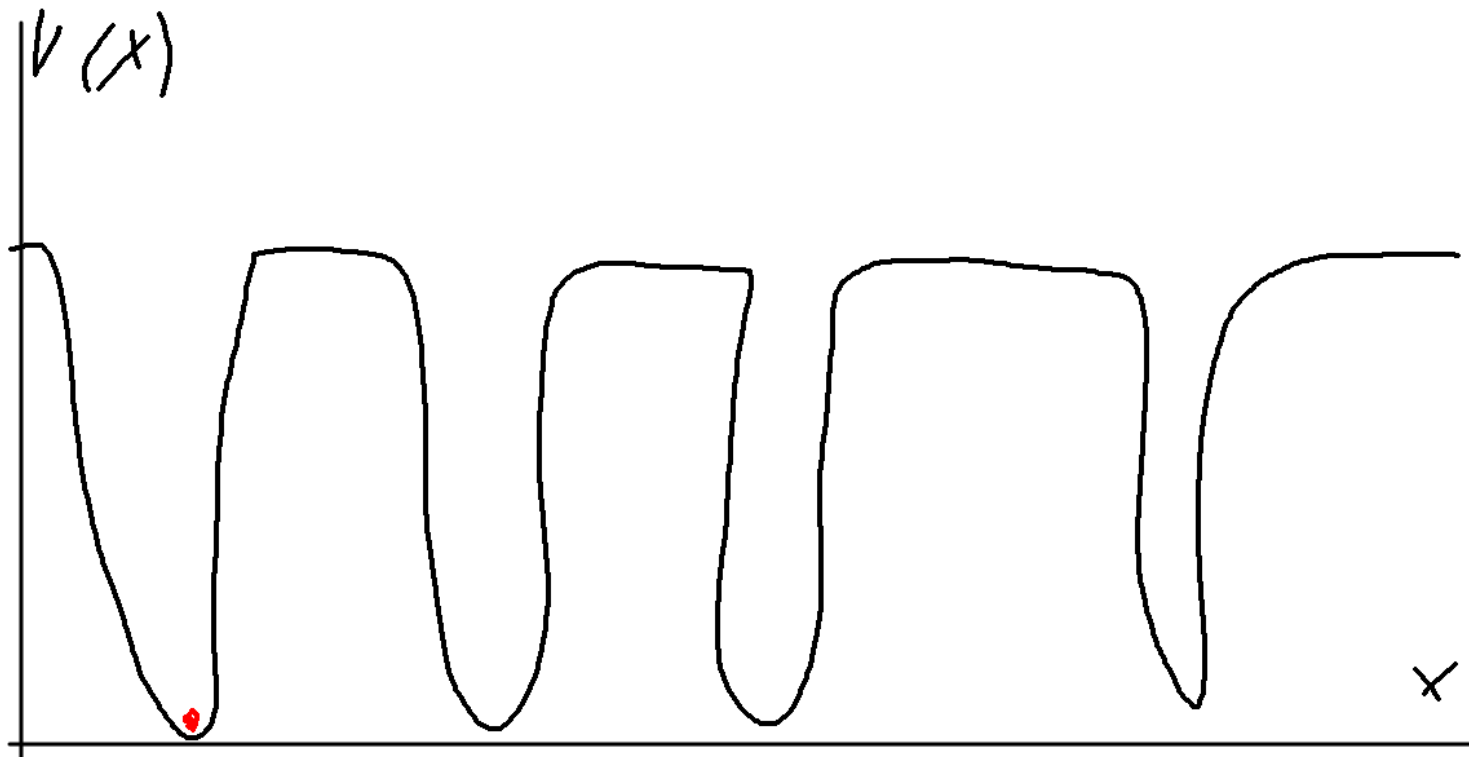
$$\frac{\langle (2S)^2 \rangle}{N} = \frac{1}{\sqrt{N}}$$

For that lets define new variable  $X = \frac{2S}{N}$ , then

$$\rho(X) = \left( \frac{N}{2\pi} \right)^{\frac{1}{2}} e^{-\frac{NX^2}{2}}$$

**Ergodic hypothesis** For closed system ( $B, E, N, V$  are constant) there is equal probability to acquire any of possible states. Such states are called **microcanonical ensemble**.

Example of exceptions:



Particle can't get out of potential well though there are other well is could possible be into.

**Meaning of ergodic hypothesis** Suppose we have two closed Ising systems (with magnetic moments) and we connect them: one with  $N_1 = 5$  and  $2S_1 = 1$  and second with  $N = 10$  and  $2S_2 = -2$ .

Now, suppose we connected two systems to a single one.

If in each side nothing changes,

$$g_f^0 = g_i = \frac{5!}{3! \cdot 2!} \cdot \frac{10!}{6!4!}$$

If one particle changes moment such that  $2S_2 = 0$ :

$$g_f^1 = \frac{5!}{2! \cdot 3!} \cdot \frac{10!}{5!5!}$$

Note that  $\frac{g_f^1}{g_f^0} = \frac{6}{5} > 1$ .

If two particle changes moment such that  $2S_2 = -2$ :

$$g_f^2 = \frac{5!}{1! \cdot 4!} \cdot \frac{10!}{6!3!}$$

Note that  $\frac{g_f^1}{g_f^2} = \frac{6 \cdot 4}{5 \cdot 2} > 1$ .

Thus  $g_f^1$  is most degenerated state, and the system will most of the time be on the most degenerated state. In big system, since variance of  $X$  is  $\frac{1}{\sqrt{N}}$ , this state will be observed almost always. I.e., there is flow from second box to the first one.

**Example** Now let's use Gaussian approximation. Then new degeneracy is  $g(N_1, S_1) \cdot g(N_2, S_2)$  and the condition is  $S_1 + S_2 = S$ . We also denote  $N_1 + N_2 = N$ . We are searching for a maximum of degeneracy under constrain.

$$g(N_1, N_2, S_1, S_2) = g_1(0)g_2(0)e^{-\frac{2S_1^2}{N_1} - \frac{2S_2^2}{N_2}}$$

Where  $g_1(0)$ ,  $g_2(0)$  are normalization constants, which doesn't affect optimization. Since  $S_2 = S - S_1$ :

$$g(N_1, N_2, S_1, S_2) = g_1(0)g_2(0)e^{-\frac{2S_1^2}{N_1} - \frac{2(S-S_1)^2}{N_2}}$$

We can optimize  $\ln g$  instead, since, it's monotonous:

$$\begin{aligned} \ln g &= C - \frac{2S_1^2}{N_1} - \frac{2(S-S_1)^2}{N_2} \\ \frac{d \ln g}{dS} &= -\frac{4S_1}{N_1} + \frac{4(S-S_1)}{N_2} = 0 \\ N_1(S-S_1) - N_2S_1 &= 0 \\ N_1S - NS_1 &= 0 \\ S_1 &= \frac{N_1S}{N} \end{aligned}$$

Thus

$$S_2 = \frac{N_2S}{N}$$

How many states are in maximal degeneracy?

$$g(N_1, N_2, S_1, S_2) = g_1(0)g_2(0)e^{-\frac{2S^2}{N}}$$

Suppose we are looking at different state

$$\left\{ S_1 = S_1^{max} + \delta, S_2 = S_2^{max} - \delta \right.$$

Then

$$g(N_1, N_2, S_1, S_2) = g_{max}(N_1, N_2, S_1, S_2) \cdot \exp\left(-\frac{4S_1^{max}\delta}{N_1} - \frac{2\delta^2}{N_1} + \frac{4S_2^{max}\delta}{N_2} - \frac{2\delta^2}{N_2}\right) = g_{max}(N_1, N_2, S_1, S_2) \cdot \exp\left(-\frac{2\delta^2}{N_1} - \frac{2\delta^2}{N_2}\right)$$

For example, if  $N_1 = N_2 = 10^{22}$  and  $\delta = 10^{12}$ , i.e.,  $\frac{\delta}{N_1} = 10^{-10}$ ,

$$g(N_1, N_2, S_1, S_2) = g_{max}(N_1, N_2, S_1, S_2) \cdot e^{-400}$$

**General case** Given two systems with degeneracy  $g_1(N_1, U_1)$  and  $g_2(N_2, U_2)$ .  $U_1 + U_2 = U = \text{const}$  and  $N_1 = \text{const}$ ,  $N_2 = \text{const}$ . We want to find maximal degeneracy:

$$\frac{d}{dU_1} g_1 \cdot g_2 = \frac{\partial g_1}{\partial U_1} \cdot g_2 + \frac{\partial g_2}{\partial U_2} \cdot \underbrace{\frac{\partial U_2}{\partial U_1}}_{-1} \cdot g_1 = 0$$

$$\frac{\partial g_1}{\partial U_1} \cdot \frac{1}{g_1} = \frac{\partial g_2}{\partial U_2} \cdot \frac{1}{g_2}$$

$$\frac{\partial \ln g_1}{\partial U_1} = \frac{\partial \ln g_2}{\partial U_2}$$

## Temperature

$$\frac{1}{T} = k_B + \frac{\partial}{\partial U} \ln g$$

Define entropy (up to constant factor  $k_B$ )

$$\sigma = \ln g(N, U)$$

We also define

$$\frac{1}{\tau} = \frac{1}{k_B T} = \frac{\partial \sigma}{\partial U}$$

If the system is continuous, we define number of states in some small interval as  $\delta E$ , then entropy is

$$\sigma = \ln (g(N, U) \delta E)$$

and

$$\frac{1}{k_B T} = \frac{\partial \sigma}{\partial U} = \frac{\partial}{\partial U} \ln g + \underbrace{\frac{\partial}{\partial U} \ln \delta E}_{\delta E = \text{const} \Rightarrow 0}$$

Also, define heat

$$dQ = \tau d\sigma$$

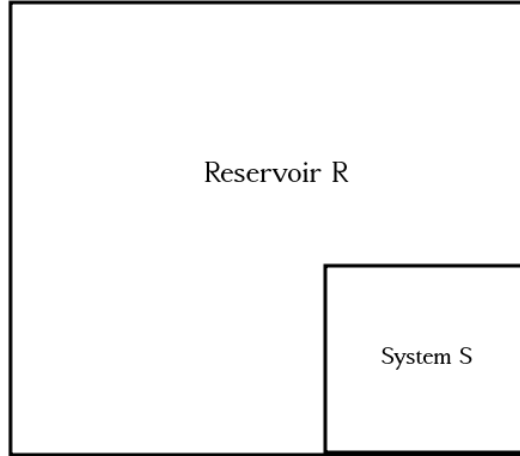
## Assumptions of thermodynamics

1. Heat is form of energy
2. With high probability, the entropy of (non-equilibrium) closed system grows with time.
3. When  $\tau \rightarrow 0$ ,  $\sigma \rightarrow 0$  (there is one state).

## 1.2 Boltzmann distribution

Suppose we divide a closed system into two parts: system and reservoir:





What is probability that system  $S$  will be in state which has energy  $\epsilon$ ?

$$P_S(\epsilon) \propto g_R(N, U_0 + \epsilon)$$

Where  $U_0$  is total energy of reservoir + system. More precisely

$$P_S(\epsilon) = \frac{g_R(N, U_0 + \epsilon)}{g(U_0)}$$

For two states, ratio of probabilities is

$$\frac{P_S(\epsilon_1)}{P_S(\epsilon_2)} = \frac{g_R(N, U_0 - \epsilon_1)}{g_R(N, U_0 - \epsilon_2)} = e^{\sigma_R(U_0 - \epsilon_1) - \sigma_R(U_0 - \epsilon_2)}$$

We assume that reservoir is much larger than system, i.e.,  $U_0 \gg \epsilon_0$ :

$$\sigma_R(U_0 - \epsilon) = \sigma_R(U_0) - \frac{\partial \sigma_R}{\partial U} \epsilon + \mathcal{O}(\epsilon^2) \approx \sigma_R(U_0) - \frac{1}{\tau} \epsilon$$

Thus

$$\frac{P_S(\epsilon_1)}{P_S(\epsilon_2)} = \frac{g_R(N, U_0 - \epsilon_1)}{g_R(N, U_0 - \epsilon_2)} = e^{-\frac{1}{\tau}(\epsilon_1 - \epsilon_2)} = \frac{e^{-\frac{\epsilon_1}{\tau}}}{e^{-\frac{\epsilon_2}{\tau}}}$$

If we want for any  $\epsilon$

$$P_S(\epsilon) \propto e^{-\frac{\epsilon}{\tau}}$$

We want to define the partition function:

$$Z(\tau) = \sum_{\text{states}} e^{-\frac{\epsilon_{\text{state}}}{\tau}}$$

and thus we normalize

$$P_S(\epsilon) = \frac{e^{-\frac{\epsilon}{\tau}}}{Z(\tau)}$$

this is called Boltzmann factor.

Such system is called canonical ensemble.

### 1.3 Pressure

Suppose we have microcanonical ensemble of volume  $V$  and dimensions  $x, y, z$ . If we move one of box walls by  $\Delta z$ , then we have

$$\underbrace{Pxy}_F \cdot (-\Delta z) = -P\Delta V = \Delta W = \Delta E$$

We want energy difference to depend on two independent things - volume change and heat:

$$E = -P\Delta V + \tau\Delta\sigma$$

Thus we define

$$P = -\left(\frac{\partial E}{\partial V}\right)_{N,\sigma}$$

We can rewrite

$$dU = \tau d\sigma - P dV$$

#### Ideal gas in 3D

$$g(U, V, N) = \frac{3N}{2} V^N (2mU)^{\frac{3N}{2}-1} \frac{\pi^{\frac{3N}{2}}}{h^{3N} \Gamma\left(\frac{3N}{2} + 1\right)}$$

$$\sigma = \ln g = \ln \frac{3N}{2} + N \ln V + \left(\frac{3N}{2} - 1\right) \ln(2mU) - \ln \Gamma\left(\frac{3N}{2} + 1\right) - \ln \frac{\pi^{\frac{3N}{2}}}{h^{3N}}$$

Differentiating in implicit way

$$d\sigma = N \frac{1}{V} \ln dV + \left(\frac{3N}{2} - 1\right) \frac{dU}{U} \approx N \frac{dV}{V} + \frac{3N}{2} \frac{dU}{U}$$

Since  $\sigma$  is unchanged,

$$P = -\left(\frac{\partial U}{\partial V}\right)_{\sigma} = -\frac{2}{3} \frac{U}{V}$$

Alternatively,

$$0 = d\sigma = \frac{\partial \sigma}{\partial U} dU + \frac{\partial \sigma}{\partial V} dV$$

$$\frac{\partial \sigma}{\partial U} \frac{\partial U}{\partial V} + \frac{\partial \sigma}{\partial V} = 0$$

$$\frac{1}{\tau}(-P) + \frac{\partial \sigma}{\partial V} = 0$$

$$\frac{P}{\tau} - \frac{N}{V} = 0$$

$$PV = k_B T N$$

Define  $h = \frac{N}{N_A}$ , for  $N_A$  - Avogadro number, and also  $R = k_B N_A$ , acquiring

$$PV = R h T$$

## 2 Thermodynamical identities

There are two kinds of variables:

- $\sigma, U, V, N$  - extensive variables. If we divide system, they change proportionally.

Entropy representation:

$$\begin{cases} \left(\frac{\partial \sigma}{\partial U}\right)_{V,N} = \frac{1}{\tau} \\ \left(\frac{\partial \sigma}{\partial V}\right)_{U,N} = \frac{P}{\tau} \end{cases}$$

- $T, P$  are intensive variables. If we divide system, they don't change.

Energy representation

$$\begin{cases} \left(\frac{\partial U}{\partial \sigma}\right)_{V,N} = \tau \\ -\left(\frac{\partial U}{\partial V}\right)_{\sigma,N} = P \end{cases}$$

Define chemical potential  $\mu = \left(\frac{\partial U}{\partial N}\right)_{\sigma, V}$  such that

$$dU = \tau d\sigma - P dV + \mu dN$$

Also

$$\sigma(\lambda U, \lambda V, \lambda N) = \lambda \sigma(U, V, N)$$

$$U(\lambda \sigma, \lambda V, \lambda N) = \lambda U(\sigma, V, N)$$

$$\left(\frac{\partial U}{\partial \lambda \sigma}\right)_{V, N} \sigma + \left(\frac{\partial U}{\partial \lambda V}\right)_{\sigma, N} V + \left(\frac{\partial U}{\partial \lambda N}\right)_{\sigma, V} N = U$$

Substituting  $\lambda = 1$  we get Euler equation:

$$U = \tau \sigma - PV + \mu N$$

Differentiating

$$dU = \sigma d\tau + \tau d\sigma - P dV - V dP + \mu dN + N d\mu$$

Remember the energy conservation

$$dU = \tau d\sigma - P dV + \mu dN$$

We get

$$0 = \sigma d\tau - V dP + N d\mu$$

This is called Gibbs–Duhem equation.

Note that we can't just add constant to energy, since it will not fulfill  $U'(\lambda \sigma, \lambda V, \lambda N) = \lambda U'(\sigma, V, N)$ . However, we can add a constant energy per particle.

**Example** Suppose we have microcanonical ensemble. The energy conserved  $dU = 0$ , and in optimal state entropy is maximal, thus  $d\sigma = 0$ . Suppose we have some parameter  $\frac{\partial^2 \sigma}{\partial x^2} < 0$ , for example moving wall of box.

Note that we can use entropy representation: start from maximal entropy  $d\sigma = 0$  and search for minimal energy  $dU = 0$ .

In entropy representation we get

$$\begin{cases} \left(\frac{\partial \sigma}{\partial x}\right)_U = 0 \\ \left(\frac{\partial^2 \sigma}{\partial x^2}\right)_U < 0 \end{cases}$$

In energy representation:

$$\left(\frac{\partial U}{\partial x}\right)_\sigma = \frac{\left(\frac{\partial \sigma}{\partial x}\right)_U}{\left(\frac{\partial \sigma}{\partial U}\right)_x} = -\tau \left(\frac{\partial \sigma}{\partial x}\right)_U$$

Exists point  $x_0$  such that  $\left(\frac{\partial \sigma}{\partial x}\right)_U = 0$ . Since  $\left(\frac{\partial U}{\partial x}\right)_\sigma$  is increasing function, thus  $\frac{\partial^2 U}{\partial x^2} > 0$ , i.e. the point is minimum.

**Canonical ensemble** In canonical ensemble, we get

$$\begin{cases} d(U + U^r) = 0 \\ d(\sigma + \sigma^r) = 0 \end{cases}$$

If the system divided in two, we know that the reservoir can pass only heat to the system, thus:

$$\tau^r d\sigma^r + \tau^1 d\sigma^1 + \tau^2 d\sigma^1 = 0$$

Since the whole microcanonical system (system+reservoir) is isolated:

$$d\sigma^r + d\sigma^1 + d\sigma^2 = 0$$

Subtracting:

$$(\tau^1 - \tau^r) d\sigma^1 + (\tau^2 - \tau^r) d\sigma^2 = 0$$

This equality is always right, thus  $\tau^1 = \tau^2 = \tau^r$ . Substituting  $dU^r$ :

$$dU + \tau^r d\sigma^r = 0$$

Substituting  $d\sigma^r = -d\sigma$  and  $\tau = \tau^r$ :

$$dU - \tau d\sigma = 0$$

$$d(U - \tau\sigma) = 0$$

Define new quantity, free energy:

$$F = U - \tau\sigma = U - TS$$

Note, that if we compress gas, its temperature increases, and this energy goes to the atmosphere (reservoir), and thus part of energy is lost.  $F$  is extensive quantity.

Since  $U^r$  depends only on  $\tau$  and  $\sigma$  we can rewrite

$$F = U(\tau, V, N) - \tau\sigma(\tau, V, N)$$

such that  $F$  doesn't depend on properties of reservoir except temperature.

**Constant pressure** we can replace reservoir with ballon of gas such that the pressure will be kept constant. In this case we minimize a quantity called enthalpy:

$$H = U + PV$$

## 2.1 Average energy in canonical case

$$\langle \epsilon \rangle = \frac{\sum_{states} \epsilon_{st} e^{-\frac{\epsilon_{st}}{\tau}}}{Z(\tau)} = \tau^2 \frac{\partial \ln Z}{\partial \tau}$$

Why is it true?

$$\frac{\partial \ln Z}{\partial \tau} = \frac{1}{Z} \frac{\partial Z}{\partial \tau}$$

Define  $\beta = \frac{1}{\tau}$ , then

$$\frac{\partial}{\partial \tau} = -\frac{1}{\tau^2} \frac{\partial}{\partial \beta}$$

$$\frac{\partial Z}{\partial \tau} = -\frac{1}{\tau^2} \frac{\partial}{\partial \beta} \sum e^{-\beta \epsilon_{st}} = \frac{1}{\tau^2} \sum_{states} \epsilon_{st} e^{-\beta \epsilon_{st}}$$

Thus

$$\frac{\partial \ln Z}{\partial \tau} = \frac{1}{Z \tau^2} \sum_{states} \epsilon_{st} e^{-\frac{\epsilon_{st}}{\tau}}$$

i.e.,

$$\langle \epsilon \rangle = \tau^2 \frac{\partial \ln Z}{\partial \tau}$$

**Magnetic moments with reservoir** Suppose we have magnetic field  $B$ , denote

$$\mu B = \frac{1}{2} \epsilon$$

If we have exactly two moments,

$$Z_1 = e^{-\frac{\epsilon}{2\tau}} + e^{\frac{\epsilon}{2\tau}} = 2 \cosh\left(\frac{\epsilon}{2\tau}\right)$$

and

$$Z_2 = (e^{-\frac{\epsilon}{2\tau}} + e^{\frac{\epsilon}{2\tau}})(e^{-\frac{\epsilon}{2\tau}} + e^{\frac{\epsilon}{2\tau}})$$

And in general,

$$Z_N = Z_1^N$$

For one particle:

$$\langle \epsilon_1 \rangle = \frac{-\frac{1}{2} \epsilon e^{\frac{\epsilon}{2\tau}} + \frac{1}{2} \epsilon e^{-\frac{\epsilon}{2\tau}}}{e^{-\frac{\epsilon}{2\tau}} + e^{\frac{\epsilon}{2\tau}}} = -\frac{\epsilon}{2} \frac{\sinh\left(\frac{\epsilon}{2\tau}\right)}{\cosh\left(\frac{\epsilon}{2\tau}\right)} = -\frac{\epsilon}{2} \tanh\left(\frac{\epsilon}{2\tau}\right)$$

Now for  $N$  particles

$$\langle \epsilon \rangle = \tau^2 \frac{\partial \ln Z}{\partial \tau} \tau^2 \frac{\partial}{\partial \tau} \ln Z_1^N = N \cdot \tau^2 \left(\frac{\epsilon}{2\tau}\right) = N \langle \epsilon_1 \rangle$$

**Thermodynamic perspective** Define  $2S = N^\uparrow - N^\downarrow$ .

$$g(N, S) = \frac{N!}{N^\uparrow! N^\downarrow!}$$

$$\sigma(N, S) = \ln g(N, S) = \frac{1}{2} \ln(2\pi N)^{-1} - \left(\frac{1}{2}N + S\right) \ln\left(\frac{1}{2} + \frac{S}{N}\right) - \left(\frac{1}{2}N - S\right) \ln\left(\frac{1}{2} + \frac{S}{N}\right)$$

Thus

$$F = U - \tau\sigma = -2\mu BS - \frac{\tau}{2} \ln(2\pi N)^{-1} + \left(\frac{1}{2}N + S\right) \tau \ln\left(\frac{1}{2} + \frac{S}{N}\right) + \left(\frac{1}{2}N - S\right) \tau \ln\left(\frac{1}{2} + \frac{S}{N}\right)$$

$$\frac{\partial F}{\partial S} = -2\mu B + \tau \ln\left(\frac{N + 2S}{N - 2S}\right) = 0$$

$$\frac{N + 2S}{N - 2S} = e^{\frac{2\mu B}{\tau}}$$

$$N + 2S = (N - 2S)e^{\frac{2\mu B}{\tau}}$$

$$2S\left(1 + e^{\frac{2\mu B}{\tau}}\right) = N\left(e^{\frac{2\mu B}{\tau}} - 1\right)$$

$$2S = N \frac{e^{\frac{2\mu B}{\tau}} - 1}{1 + e^{\frac{2\mu B}{\tau}}}$$

$$2S = N \frac{e^{\frac{\mu B}{\tau}} - e^{-\frac{\mu B}{\tau}}}{e^{-\frac{\mu B}{\tau}} + e^{\frac{\mu B}{\tau}}} = N \frac{\sinh\left(-\frac{\mu B}{\tau}\right)}{\cosh\left(-\frac{\mu B}{\tau}\right)} = N \tanh\left(-\frac{\mu B}{\tau}\right)$$

Since  $\epsilon = -2\mu BS$

$$\epsilon = -\mu BN \tanh\left(-\frac{\mu B}{\tau}\right)$$

**Connection between  $F$  and  $Z$**

$$F = U - \tau\sigma$$

$$dF = dU - \sigma d\tau - \tau d\sigma$$

$$dU = \tau d\sigma - P dV$$

i.e.,

$$dF = -P dV - \sigma d\tau$$

Thus, if  $\tau$  is constant

$$dF = -P dV$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_\tau$$

If, on contrary, volume is constant

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V$$

If we differentiate first equation, with constant  $\tau$ , we get

$$\left(\frac{\partial F}{\partial V}\right)_\tau + \left(\frac{\partial U}{\partial V}\right)_\tau = \tau \left(\frac{\partial \sigma}{\partial V}\right)_\tau \Rightarrow -P = \left(\frac{\partial U}{\partial V}\right)_\tau - \tau \left(\frac{\partial \sigma}{\partial V}\right)_\tau$$

i.e.,

$$P = -\left(\frac{\partial U}{\partial V}\right)_\tau + \tau \left(\frac{\partial \sigma}{\partial V}\right)_\tau$$

In addition, substituting  $\sigma$ :

$$F = U + \tau \left(\frac{\partial F}{\partial \tau}\right)_V$$

$$U = F - \tau \left(\frac{\partial F}{\partial \tau}\right)_V$$

$$U = -\tau^2 \left[ \frac{\partial}{\partial \tau} \frac{F}{\tau} \right]$$

At the same time

$$U = -\tau^2 \frac{\partial \ln Z}{\partial \tau}$$

$$-\tau^2 \left[ \frac{\partial}{\partial \tau} \frac{F}{\tau} \right] = -\tau^2 \frac{\partial \ln Z}{\partial \tau}$$

$$\frac{F}{\tau} = \ln Z + \alpha$$

for some constant  $\alpha$ .