114036 - Statistical and Thermal Physics

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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 i son 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 filed energy is $U = -\vec{B} \cdot \vec{m} = -\vec{B}\mu$.
Suppose we a 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 μ 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

$$\binom{N}{N_d} = \frac{N!}{\left(\left(\frac{1}{2}N - S\right)!\left(\left(\frac{1}{2}N + S\right)!\right)\right)}$$
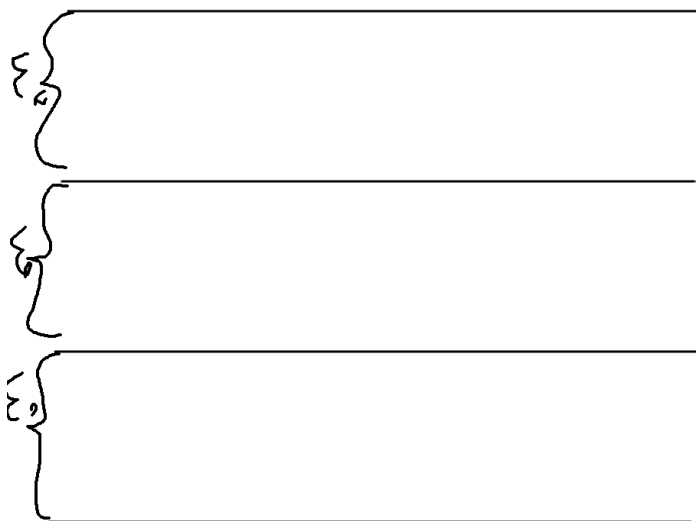
and the energy

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

The degeneracy of the state thus is

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

Particles on shelves (quantum oscillator)   Suppose we have equally-distant shelves, and energy distance between two shelves is ϵ_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 opf shelve (ϵ_0, $4\epsilon_0$, ...). 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), lets 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, its hard to calculate.

Lets 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

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

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 α (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

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

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

$$I_d = \int_{-\infty}^{\infty} \mathrm{d}x_1 \, e^{-x^2} \int_{-\infty}^{\infty} \mathrm{d}x_2 \, e^{-x^2} \ldots \int_{-\infty}^{\infty} \mathrm{d}x_n \, e^{-x^2} = \int_{-\infty}^{\infty} \mathrm{d}x_1 \, \mathrm{d}x_2 \ldots \mathrm{d}x_n \, e^{-\sum_{i=1}^{n} x_i^2}$$

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

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

(Note that when we perform integral over angular dimensions we acquire exactly S_d from Jacobean).
For $y = R^2$, $\mathrm{d}y = 2R \, \mathrm{d}R$:

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

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

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

Back to our particles:

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

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

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

Integral approximation with steepest descent Suppose we want calculate

$$I = \int \mathrm{d}x \, e^{N\phi(x)}$$

for some big N and x_{max} is maximum of ϕ:

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

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

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

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

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

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Example Lets approximate $n!$:
$$\Gamma(n+1) = \int_0^\infty dx\, x^N e^{-x} = \int_0^\infty dx\, e^{N\left(\ln x - \frac{x}{N}\right)}$$

Thus $\phi(x) = \ln x - \frac{x}{N}$, and
$$\phi'(x) = \frac{1}{x} - \frac{1}{N}$$

i.e., $x_{max} = N$. And
$$|\phi''(x)| = \frac{1}{x^2}$$

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

which is Stirling approximation. We usually want to take logarithm:
$$\ln(N!) \approx N\ln N - N + \frac{1}{2}\ln(2\pi N)$$

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

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

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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:

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

Thus variance of $2S$ is N and variance of S is $\frac{N}{4}$. Now, relative standard deviation
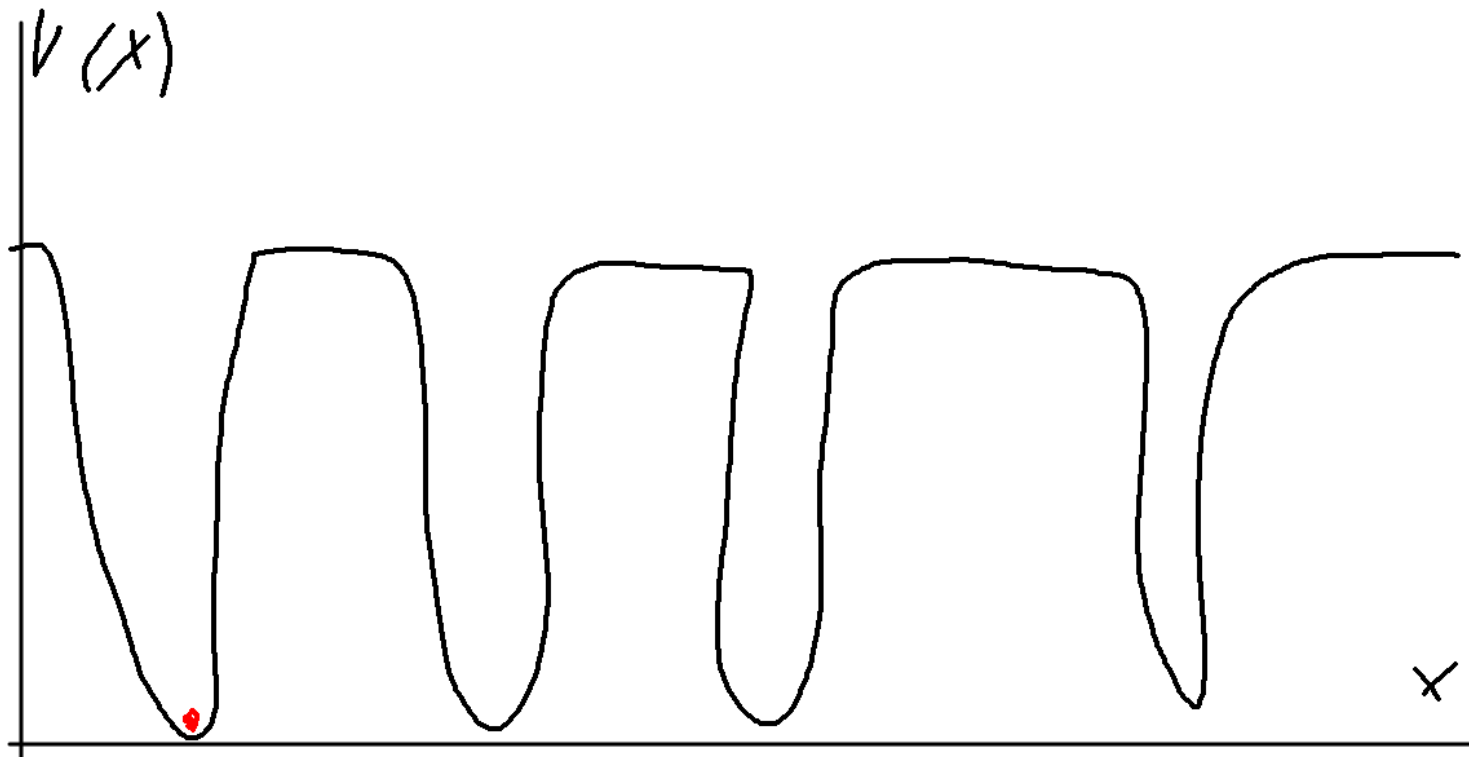$$\frac{\langle (2S)^2 \rangle}{N} = \frac{1}{\sqrt{N}}$$

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

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 observed almost always. I.e., there is flow from second box to the first one.

Example   Now lets 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:

$$\ln g = C - \frac{2S_1^2}{N_1} - \frac{2(S-S_1)^2}{N_2}$$

$$\frac{\mathrm{d}\ln g}{\mathrm{d}S} = -\frac{4S_1}{N_1} + \frac{4(S-S_1)}{N_2} = 0$$

$$N_1(S-S_1) - N_2S_1 = 0$$

$$N_1 S - N S_1 = 0$$

$$S_1 = \frac{N_1 S}{N}$$

Thus

$$S_2 = \frac{N_2 S}{N}$$

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

$$\begin{cases} S_1 = S_1^{max} + \delta \\ S_2 = S_2^{max} - \delta \end{cases}$$

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 δE, then entropy is

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

and

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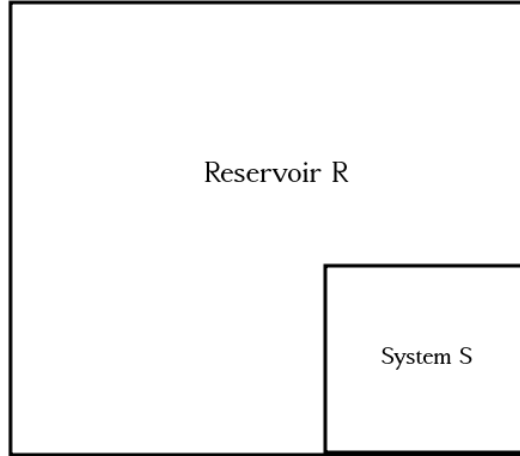
Also, define heat

$$dQ = \tau \, d\sigma$$

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 $\tau \to 0$, $\sigma \to 0$ (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 ϵ?

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

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

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

If we want for any ϵ

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

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 microcanonincal ensemble of volume V and dimensions x,y,z. If we move one of box walls by Δz, 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 σ is unchanged,

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

Alternatively,

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

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

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

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

$$PV = k_B TN$$

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

$$PV = RhT$$

2 Thermodynamical identities

There are two kinds of variables:

- σ, 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

$$\mathrm{d}U = \tau\,\mathrm{d}\sigma - P\,\mathrm{d}V + \mu\,\mathrm{d}N$$

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

$$\mathrm{d}U = \sigma\,\mathrm{d}\tau + \tau\,\mathrm{d}\sigma - P\,\mathrm{d}V - V\,\mathrm{d}P + \mu\,\mathrm{d}N + N\,\mathrm{d}\mu$$

Remember the energy conservation

$$\mathrm{d}U = \tau\,\mathrm{d}\sigma - P\,\mathrm{d}V + \mu\,\mathrm{d}N$$

We get

$$0 = \sigma\,\mathrm{d}\tau - V\,\mathrm{d}P + N\,\mathrm{d}\mu$$

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 $\mathrm{d}U = 0$, and in optimal state entropy is maximal, thus $\mathrm{d}\sigma = 0$. 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 $\mathrm{d}\sigma = 0$ and search for minimal energy $\mathrm{d}U = 0R$.

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

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

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

$$\tau^r\,\mathrm{d}\sigma^r + \tau^1\,\mathrm{d}\sigma^1 + \tau^2\,\mathrm{d}\sigma^1 = 0$$

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

$$\mathrm{d}\sigma^r + \mathrm{d}\sigma^1 + \mathrm{d}\sigma^2 = 0$$

Subtracting:

$$(\tau^1 - \tau^r)\,\mathrm{d}\sigma^1 + (\tau^2 - \tau^r)\,\mathrm{d}\sigma^2 = 0$$

This equality is always right, thus $\tau^1 = \tau^2 = \tau^r$. Substituting $\mathrm{d}U^r$:

$$\mathrm{d}U + \tau^r\,\mathrm{d}\sigma^r = 0$$

Substituting $\mathrm{d}\sigma^r = -\,\mathrm{d}\sigma$ and $\tau = \tau^r$:

$$\mathrm{d}U - \tau\,\mathrm{d}\sigma = 0$$

$$\mathrm{d}(U - \tau\sigma) = 0$$

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 τ and σ 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

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

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

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

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

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

$$\mathrm{d}F = \mathrm{d}U - \sigma\,\mathrm{d}\tau - \tau\,\mathrm{d}\sigma$$

$$\mathrm{d}U = \tau\,\mathrm{d}\sigma - P\,\mathrm{d}V$$

i.e.,

$$\mathrm{d}F = -P\,\mathrm{d}V - \sigma\,\mathrm{d}\tau$$

Thus, if τ is constant

$$\mathrm{d}F = -P\,\mathrm{d}V$$

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

If, on contrary, volume is constant

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

If we differentiate first equation, with constant τ, 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 σ:

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

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

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

At the same time

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

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

$$\frac{F}{\tau} = -\ln Z + \alpha(V)$$

for some constant α depending on volume, and thus we conclude that $\langle \epsilon \rangle = U$.

Quantum particle in box Suppose we have particle in box, it has energy

$$E = \frac{\hbar^2}{2m} \left(\frac{\pi}{2} \right)^2 n^2$$

Note here we have minimal energy which is non-zero, and for this energy we have only one possible state, which confirms third law of thermodynamics (in opposite, in classical mechanics there are many states with minimal energy).

In limit $Z \to 0$ we get

$$Z = g_0 e^{\frac{\epsilon_0}{Z}} + \sum_{\text{high energies}} e^{-\frac{\epsilon}{Z}} \approx g_0 e^{\frac{\epsilon_0}{Z}}$$

From third law $g_0 = 1$.

$$\ln Z = -\frac{\epsilon_0}{Z}$$

$$F = -\tau \ln Z + \alpha \tau = \epsilon_0 + \alpha \tau$$

Since

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

$$\sigma = -\alpha$$

i.e., $\alpha = 0$, meaning

$$F = -\tau \ln Z$$

2.2   Classical ideal gas in statistic approach

In thermodynamics we acquired

$$PV = Nk_B T$$

$$U = \frac{3}{2} Nk_B T$$

$$g(U, V) = V^N U^{\frac{3}{2} N - 1}$$

Partittion function of ideal gas

$$Z_N = \frac{1}{h^{3N}} \int dp_x^1 \int dp_y^1 \int dp_z^1 \ldots \int dp_x^N \int dp_y^N \int dp_z^N \int dx_1 \int dy_1 \int dz_1 \ldots \int dx_N \int dy_N \int dz_N \, e^{-\frac{1}{z} \sum_{i=1}^N \frac{\vec{p}_i^2}{2m\tau}} =$$

$$= \frac{V^n}{h^{3N}} \int dp_x^1 \int dp_y^1 \int dp_z^1 \ldots \int dp_x^N \int dp_y^N \int dp_z^N \, e^{-\frac{1}{z} \sum_{i=1}^N \frac{\vec{p}_i^2}{2m\tau}} =$$

$$= \frac{V^n}{h^{3N}} \int dp_x^1 \int dp_x^1 \, e^{-\frac{1}{z} \frac{p_x^{1\,2}}{2m\tau}} \int dp_y^1 \, e^{-\frac{1}{z} \frac{p_y^{1\,2}}{2m\tau}} \int dp_z^1 \, e^{-\frac{1}{z} \frac{p_z^{1\,2}}{2m\tau}} \ldots \int dp_x^N \, e^{-\frac{1}{z} \frac{p_x^{N\,2}}{2m\tau}} \int dp_y^N \, e^{-\frac{1}{z} \frac{p_y^{N\,2}}{2m\tau}} \int dp_z^N \, e^{-\frac{1}{z} \frac{p_z^{N\,2}}{2m\tau}}$$

Then for each particle

$$Z_1 = \frac{V}{h^3} \int dp_x^1 \int dp_x^1 \, e^{-\frac{1}{z} \frac{p_x^{1\,2}}{2m\tau}} \int dp_y^1 \, e^{-\frac{1}{z} \frac{p_y^{1\,2}}{2m\tau}} \int dp_z^1 \, e^{-\frac{1}{z} \frac{p_z^{1\,2}}{2m\tau}} = \frac{V}{h^3} \left[\int_{-\infty}^{\infty} dp \, e^{-\frac{p^2}{2mz\tau}} \right]^3 \overset{\text{Gaussian}}{=} \frac{V(2\pi m\tau)^{\frac{3}{2}}}{h^3}$$

$$Z_N = Z_1^N$$

$$\langle \epsilon \rangle = \tau^2 \frac{\partial \ln Z_n}{\partial \tau} = \tau^2 N \frac{\partial \ln Z_1}{\partial \tau} = \tau^2 N \cdot \frac{3}{2\tau} = \frac{3}{2} N\tau = \frac{3}{2} Nk_B T$$

Pressure of ideal gas

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

And

$$F = -\tau \ln Z_N = -\tau \ln Z_1^N = -\tau N \ln Z_1 = -\tau N\left(\ln(V) + \ln\left(\tau^{\frac{3}{2}}\right) + \text{const}\right)$$

$$\frac{\partial F}{\partial V} = -\frac{\tau N}{V}$$

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

$$PV = \tau N = k_B N T$$