

Statistical Mechanics

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with L^AT_EX



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Mathematics

Homogeneous Function

Definition

If a function $f(x_1, \dots, x_n)$ of n variables x_1, \dots, x_n is such that, for any constant λ

$$f(\lambda x_1, \dots, \lambda x_n) = \lambda^m f(x_1, \dots, x_n)$$

then $f(\lambda x_1, \dots, \lambda x_n)$ is called homogeneous of degree m , with $m > 1$.

Euler's theorem on homogeneous functions. The partial derivative of homogeneous function obey the relation

$$\sum_{i=1}^n x_i \frac{\partial f}{\partial x_i} = m f$$

Thermodynamic

In context of thermodynamics, extensive properties are homogeneous functions of first order, while intensive properties are homogeneous functions of order zero.

Extensive properties. An extensive property scales linearly with the system's size. Properties such as U , V , m , n , and N are all examples of extensive properties; they will double their values upon doubling the size of the system. Another examples of extensive properties is entropy, stated by second Thermodynamics postulate.

Intensive properties. An intensive property does not depend on the size (or extent) of the system; it is a scale invariant. The ratio between two extensive properties is an intensive property. The molar mass M is therefore an intensive property.

Partial Derivative

Identity Involving Partial Derivative

The Jacobian of $[u(x, y), v(x, y)]$ with respect to (x, y) is defined by

$$\frac{\partial(u, v)}{\partial(x, y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix}$$

Here are some identity relating the Jacobian with partial derivative.

Unity. Unity as in one

$$\frac{\partial(u, v)}{\partial(x, y)} = 1$$

Proof. Trivial

$$\frac{\partial(x, y)}{\partial(x, y)} = \begin{vmatrix} \frac{\partial x}{\partial x} & \frac{\partial x}{\partial y} \\ \frac{\partial y}{\partial x} & \frac{\partial y}{\partial y} \end{vmatrix} = \frac{\partial x}{\partial x} \frac{\partial y}{\partial y} - \frac{\partial x}{\partial y} \frac{\partial y}{\partial x} = 1 \quad \blacksquare$$

Change of order. It can be proved that change of order cost the minus sign

$$\frac{\partial(u, v)}{\partial(x, y)} = -\frac{\partial(v, u)}{\partial(x, y)} = -\frac{\partial(u, v)}{\partial(y, x)}$$

Proof. Those three terms literally have the same value when evaluated

$$\frac{\partial(u, v)}{\partial(x, y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix} = \frac{\partial u}{\partial x} \frac{\partial v}{\partial y} - \frac{\partial u}{\partial y} \frac{\partial v}{\partial x}$$

$$-\frac{\partial(v, u)}{\partial(x, y)} = -\begin{vmatrix} \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \\ \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \end{vmatrix} = \frac{\partial v}{\partial y} \frac{\partial u}{\partial x} - \frac{\partial v}{\partial x} \frac{\partial u}{\partial y}$$

$$\frac{\partial(u, v)}{\partial(y, x)} = -\begin{vmatrix} \frac{\partial u}{\partial y} & \frac{\partial u}{\partial x} \\ \frac{\partial v}{\partial y} & \frac{\partial v}{\partial x} \end{vmatrix} = \frac{\partial u}{\partial x} \frac{\partial v}{\partial y} - \frac{\partial u}{\partial y} \frac{\partial v}{\partial x}$$

See? ■

Jacobian. In terms of Jacobian, partial derivative of u with respect to x can be written as

$$\left. \frac{\partial u}{\partial x} \right|_y = \frac{\partial(u, y)}{\partial(x, y)}$$

Proof. Just evaluate the Jacobian

$$\frac{\partial(u, y)}{\partial(x, y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial y}{\partial x} & \frac{\partial y}{\partial y} \end{vmatrix} = \frac{\partial u}{\partial x} \frac{\partial y}{\partial y} - \frac{\partial u}{\partial y} \frac{\partial y}{\partial x} = \frac{\partial u}{\partial x} \quad \blacksquare$$

Chain rule for partial derivative. The expression is

$$\frac{\partial(u, y)}{\partial(x, y)} = \frac{\partial(u, y)}{\partial(w, z)} \frac{\partial(w, z)}{\partial(x, y)}$$

Proof. The total differential of u and v as function w and z read

$$du = \frac{\partial u}{\partial w} dw + \frac{\partial u}{\partial v} dz \quad \wedge \quad dv = \frac{\partial v}{\partial w} dw + \frac{\partial v}{\partial z} dz$$

We can therefore evaluate the Jacobian

$$\begin{aligned} \frac{\partial(u, y)}{\partial(x, y)} &= \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix} = \begin{vmatrix} \frac{\partial u}{\partial w} \frac{\partial w}{\partial x} + \frac{\partial u}{\partial z} \frac{\partial z}{\partial x} & \frac{\partial u}{\partial w} \frac{\partial w}{\partial y} + \frac{\partial u}{\partial z} \frac{\partial z}{\partial y} \\ \frac{\partial v}{\partial w} \frac{\partial w}{\partial x} + \frac{\partial v}{\partial z} \frac{\partial z}{\partial x} & \frac{\partial v}{\partial w} \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \frac{\partial z}{\partial y} \end{vmatrix} \\ &= \begin{pmatrix} \frac{\partial u}{\partial w} & \frac{\partial u}{\partial z} \\ \frac{\partial v}{\partial w} & \frac{\partial v}{\partial z} \end{pmatrix} \begin{pmatrix} \frac{\partial w}{\partial x} & \frac{\partial w}{\partial y} \\ \frac{\partial z}{\partial x} & \frac{\partial z}{\partial y} \end{pmatrix} = \begin{vmatrix} \frac{\partial u}{\partial w} & \frac{\partial u}{\partial z} \\ \frac{\partial v}{\partial w} & \frac{\partial v}{\partial z} \end{vmatrix} \begin{vmatrix} \frac{\partial w}{\partial x} & \frac{\partial w}{\partial y} \\ \frac{\partial z}{\partial x} & \frac{\partial z}{\partial y} \end{vmatrix} \end{aligned}$$

$$\frac{\partial(u, y)}{\partial(x, y)} = \frac{\partial(u, y)}{\partial(w, z)} \frac{\partial(w, z)}{\partial(x, y)} \quad \blacksquare$$

The real chain rule. We have

$$\left. \frac{\partial x}{\partial z} \right|_y \left. \frac{\partial z}{\partial x} \right|_y = 1$$

Proof. Trivial

$$1 = \frac{\partial(x, y)}{\partial(x, y)} = \frac{\partial(x, y)}{\partial(z, y)} \frac{\partial(z, y)}{\partial(x, y)} = \left. \frac{\partial x}{\partial z} \right|_y \left. \frac{\partial z}{\partial x} \right|_y \quad \blacksquare$$

Yet another chain rule... Even more chain rule...

$$\left. \frac{\partial x}{\partial y} \right|_w = \left. \frac{\partial x}{\partial z} \right|_w \left. \frac{\partial z}{\partial y} \right|_w$$

Proof. Trivial

$$\left. \frac{\partial x}{\partial y} \right|_w = \frac{\partial(x, w)}{\partial(y, w)} = \frac{\partial(x, w)}{\partial(z, w)} \frac{\partial(z, w)}{\partial(y, w)} = \left. \frac{\partial x}{\partial z} \right|_w \left. \frac{\partial z}{\partial y} \right|_w$$

Cyclic rule. This is chain rule all over again...

$$\frac{\partial x}{\partial z} \Big|_y \frac{\partial z}{\partial y} \Big|_x \frac{\partial y}{\partial x} \Big|_z = -1$$

Proof. Trivial

$$\begin{aligned} 1 &= \frac{\partial(x, y)}{\partial(x, y)} = \frac{\partial(x, y)}{\partial(z, y)} \frac{\partial(z, y)}{\partial(z, x)} \frac{\partial(z, x)}{\partial(x, y)} = -\frac{\partial(x, y)}{\partial(z, y)} \frac{\partial(y, z)}{\partial(x, z)} \frac{\partial(z, x)}{\partial(y, x)} \\ &\quad = -\frac{\partial x}{\partial z} \Big|_y \frac{\partial y}{\partial x} \Big|_z \frac{\partial z}{\partial y} \Big|_x \quad \blacksquare \end{aligned}$$

Application in Thermodynamics

Here we will derive some useful intensive parameter used in thermodynamics. We assumed entropy function S has the form of

$$S = S(U, V, N_{i|r})$$

where N is number of chemical potential and $N_{i|r} \equiv N_1, \dots, N_r$. Therefore, its total differential is

$$dS = \frac{\partial S}{\partial U} \Big|_{V, N_{i|r}} dU + \frac{\partial S}{\partial V} \Big|_{U, N_{i|r}} dV + \sum_{j=1}^r \frac{\partial S}{\partial N_j} \Big|_{U, V, N_{i \neq r}} dN_j$$

We also assume the following quantities

$$T = \frac{\partial U}{\partial S} \Big|_{V, N_i}; P = -\frac{\partial U}{\partial V} \Big|_{S, N_i}; \mu_j = \frac{\partial U}{\partial N} \Big|_{S, V, N_{i \neq j}}$$

First identity. As follows

$$\frac{\partial S}{\partial U} \Big|_{V, N_i} = \frac{1}{T}$$

Proof. We use chain rule with $x \rightarrow U, y \rightarrow V, z \rightarrow S$; while keeping all the N_i constant

$$\frac{\partial U}{\partial S} \Big|_{V, N_i} \frac{\partial S}{\partial U} \Big|_{V, N_i} = 1 \implies \frac{\partial S}{\partial U} \Big|_{V, N_i} = \left(\frac{\partial U}{\partial S} \Big|_{V, N_i} \right)^{-1}$$

Then, from the definition of temperature

$$\frac{\partial S}{\partial U} \Big|_{V, N_i} = \frac{1}{T} \quad \blacksquare$$

Second identity. The identity written as

$$\frac{\partial S}{\partial V} \Big|_{U, N_i} = \frac{P}{T}$$

Proof. We invoke cyclic rule with $x \rightarrow U, y \rightarrow V, z \rightarrow S$; while keeping all the N_i constant

$$1 = -\frac{\partial U}{\partial S} \Big|_{V, N_i} \frac{\partial S}{\partial V} \Big|_{U, N_i} \frac{\partial V}{\partial U} \Big|_{U, N_i}$$

Then, from the first identity and the definition of pressure

$$1 = T \frac{\partial S}{\partial V} \Big|_{U, N_i} \frac{1}{P} \implies \frac{\partial S}{\partial V} \Big|_{U, N_i} = \frac{P}{T} \quad \blacksquare$$

Third Identity. Expressed as

$$\left. \frac{\partial S}{\partial N_j} \right|_{U, N_i \neq j} = -\frac{P}{T}$$

Proof. We again invoke cyclic with $x \rightarrow U, y \rightarrow Nj, z \rightarrow S$; while keeping V and all N except N_i constant

$$1 = -\left. \frac{\partial U}{\partial S} \right|_{V, N_i} \left. \frac{\partial S}{\partial N_j} \right|_{U, N_i \neq j} \left. \frac{\partial N_j}{\partial U} \right|_{U, N_i \neq j}$$

Then, from the definition of temperature and chemical potential

$$1 = -T \left. \frac{\partial S}{\partial N_j} \right|_{U, N_i \neq j} \frac{1}{\mu_j} \implies \left. \frac{\partial S}{\partial N_j} \right|_{U, N_i \neq j} = -\frac{\mu_j}{T} \quad \blacksquare$$

Legendre Transform

Definition

Consider monotonic function $f(x)$. The slope of $f(x)$ expressed as

$$s(x) = \frac{d}{dx} f(x)$$

Suppose now we want to transform $f(x)$ into function $G(s)$ as function of its slope. We write

$$G(s) = f[x(s)] - sx(s)$$

where $x(s)$ reads as x in terms of its slope s . The function $G(s)$ referred as Legendre transform of $f(x)$. If we want to transform $G(s)$ back into $f(x)$, called inverse transform, we write

$$f(x) = G[s(x)] + xs(x)$$

Derivation

Consider the same monotonic function $f(x)$. Say that its tangent line intercept the y -axis at Q . Another family of the tangent line of the same slope will also intercept the y -axis; they will, however, did it at different point. We define the intercept of origin O and Q as $G(s)$.

To find the actual intercept, note that line passing through Q has the form $y = mx + Q$. Since we define $G(s)$ as the line OG , we have

$$G(s) = f[x(s)] - sx(s)$$

The differential of G is

$$dG(s) = \frac{\partial G}{\partial s} ds = -x(s) ds$$

Hence

$$x = -\frac{dG(s)}{ds}$$

In a sense the symmetry of $f(x)$ and $G(s)$ can be traced to equation above. $f(x)$ has the slope of s , where $G(s)$ is x . We can therefore write

$$f(x) = G[s(x)] + xs(x)$$

to transform $G(s)$ back to $f(x)$.

Multivariable Function

Single variable transform. Consider some multivariable function, say $f(x, y, z)$. Suppose we want to construct Legendre transform of $f(x, y, z)$ with respect to x . First we have the slope

$$s = \left. \frac{\partial f}{\partial x} \right|_{y,z}$$



Figure: Geometric interpretation of Legendre transformation

We then write the transform of $f(x)$ as

$$\mathcal{L}_x[f(x, y, z)] = f(x(s), y, z) - sx(s)$$

which is the same for single variable function.

Multivariable transform. Suppose that, with the same function, we want to perform Legendre transforms with respect to all variable x, y, z . First we define

$$s = \frac{\partial f}{\partial x} \Big|_{y,x} ; t = \frac{\partial f}{\partial y} \Big|_{x,z} ; u = \frac{\partial f}{\partial z} \Big|_{x,y}$$

We then write

$$\mathcal{L}_{x,y,z}[f(x, y, z)] = f[x(s), y(t), z(u)] - sx(s) - ty(t) - uz(u)$$

State Function And Conservative Field

State function, such as internal energy U and entropy S , can be thought as conservative field. The condition that must be satisfied by conservative field \mathbf{V} is

$$\nabla \times \mathbf{V} = 0$$

Suppose we actually evaluate the curl of vector function $\mathbf{V}(x, y, z)$, we get

$$\nabla \times \mathbf{V} = \begin{pmatrix} \hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ V_x & V_y & V_z \end{pmatrix}$$

$$\nabla \times \mathbf{V} = \hat{\mathbf{i}} \left(\frac{\partial V_z}{\partial y} - \frac{\partial V_y}{\partial z} \right) + \hat{\mathbf{j}} \left(\frac{\partial V_x}{\partial z} - \frac{\partial V_z}{\partial x} \right) + \hat{\mathbf{k}} \left(\frac{\partial V_y}{\partial x} - \frac{\partial V_x}{\partial y} \right)$$

Since \mathbf{V} , as a conservative field, has curl of zero, those term inside parenthesis can be evaluated into

$$\frac{\partial V_z}{\partial y} = \frac{\partial V_y}{\partial z}, \quad \frac{\partial V_x}{\partial z} = \frac{\partial V_z}{\partial x}, \quad \frac{\partial V_y}{\partial x} = \frac{\partial V_x}{\partial y}$$

For state function $U(S, V, N)$, the equation reads

$$\frac{\partial U_N}{\partial V} = \frac{\partial U_V}{\partial N}, \quad \frac{\partial U_S}{\partial N} = \frac{\partial U_N}{\partial S}, \quad \frac{\partial U_V}{\partial S} = \frac{\partial U_S}{\partial V}$$

Of course you can't evaluate the curl of state function, but hear me out. What we consider is not the function U itself, but rather, the differential dU . Its total differential may be written as

$$dU(S, V, N) = \frac{\partial U}{\partial S} \Big|_{V, N} dS + \frac{\partial U}{\partial V} \Big|_{S, N} dV + \frac{\partial U}{\partial N} \Big|_{S, V} dN$$

Here, the differentials (dS, dT, dN) act like unit vector, thus we can pretend that dU is a vector field with components of

$$U_S = \frac{\partial U}{\partial S} \Big|_{V, N}, \quad U_V = \frac{\partial U}{\partial V} \Big|_{S, N}, \quad U_N = \frac{\partial U}{\partial N} \Big|_{S, V}$$

Therefore

$$\frac{\partial}{\partial V} \frac{\partial U}{\partial N} = \frac{\partial}{\partial N} \frac{\partial U}{\partial V}, \quad \frac{\partial}{\partial N} \frac{\partial U}{\partial S} = \frac{\partial}{\partial S} \frac{\partial U}{\partial N}, \quad \frac{\partial}{\partial S} \frac{\partial U}{\partial V} = \frac{\partial}{\partial V} \frac{\partial U}{\partial S}$$

This is what it means to be an exact differential.

Special Function

Gamma Function

Factorial. The factorial is defined by integral

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

Putting $\alpha = 1$ we get

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

Thus we have a definite integral whose value is $n!$ for positive integral n . We can also give a meaning to $0!$; by putting $n = 0$, we get $0! = 1$. By the way, the integral can be evaluated using differentiation under integral sign.

Gamma function definition. Gamma function is used to define the factorial function for noninteger n . We define, for any $p > 0$

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

From this we have

$$\begin{aligned}\Gamma(p) &= \int_0^\infty x^{p-1} e^{-x} dx = (p-1)! \\ \Gamma(p+1) &= \int_0^\infty x^p e^{-x} dx = p!\end{aligned}$$

Recursion relation. The recursion for gamma function is

$$\Gamma(p+1) = p\Gamma(p)$$

Proof. Let us integrate $\Gamma(p+1)$ by parts. Calling $u = x^p$, and $dv = e^{-x} dx$; then we get $du = px^{p-1}$, and $v = -e^{-x}$. Thus

$$\begin{aligned}\Gamma(p+1) &= -x^p e^{-x} \Big|_0^\infty + \int_0^\infty e^{-x} p x^{p-1} dx \\ &= p \int_0^\infty x^{p-1} e^{-x} dx \\ \Gamma(p+1) &= p\Gamma(p) \quad \blacksquare\end{aligned}$$

Negative numbers. We shall now define gamma function for $p \leq 0$ by the recursion relation

$$\Gamma(p) = \frac{\Gamma(p+1)}{p}$$

From this and the successive use of it, it follows that $\Gamma(p)$ becomes infinite not only at zero but also at all the negative integers.



Figure 1: Gaussian integral solved by polar method.

Gaussian integral. We state here important formula

$$\Gamma(p)\Gamma(1-p) = \frac{\pi}{\sin \pi p}$$

We can calculate the value of $\Gamma(1/2)$ using this equation, however we will instead try to derive it using another method. First we consider the definition

$$\Gamma(1/2) = \int_0^\infty \frac{e^{-t}}{\sqrt{t}} dt$$

then we substitute $t = x^2$ and $dt = 2x dx$

$$\Gamma(1/2) = 2 \int_0^\infty e^{-x^2} dx = \int_{-\infty}^\infty e^{-x^2} dx$$

This is the famous Gaussian integral. Refer to figure 1 on how to solve it by polar coordinate.

Since everybody and their grandma already know how to solve Gaussian integral by polar coordinate, I will instead try to solve it by Feynman's trick. First consider the function

$$I(\alpha) = \left(\int_0^\alpha e^{-t^2} dt \right)^2$$

where I is a function of parameter fish α . Then, to evaluate the actual Gaussian integral

$$\int_{-\infty}^\infty e^{-x^2} dx = 2 \lim_{\alpha \rightarrow \infty} \sqrt{I(\alpha)}$$

Before that, I need to evaluate the function $I(\alpha)$ first. To do that, first I differentiate I with respect parameter fish α

$$\begin{aligned}\frac{dI}{d\alpha} &= 2 \int_0^\alpha e^{-t^2} dt \left(\int_0^\alpha \frac{\partial e^{-t^2}}{\partial \alpha} dt + e^{-\alpha^2} \frac{d\alpha}{d\alpha} - e^{-0^2} \frac{d(0)}{d\alpha} \right) \\ \frac{dI}{d\alpha} &= \int_0^\alpha 2e^{-(t^2+\alpha^2)} dt\end{aligned}$$

where I have used Leibniz' rule for differentiating under integral sign. Then, I introduce the variable $u = t/\alpha$ and $du = dt/\alpha$

$$\frac{dI}{d\alpha} = \int_0^1 2e^{-(u^2\alpha^2+\alpha^2)} \alpha du = \int_0^1 2\alpha e^{-\alpha^2(u^2+1)} du$$

Using the fact that

$$\frac{\partial}{\partial \alpha} \frac{e^{-\alpha^2(u^2+1)}}{u^2+1} = -2\alpha e^{-\alpha^2(u^2+1)}$$

I can rewrite the integrand as

$$\frac{dI}{d\alpha} = - \int_0^1 \frac{\partial}{\partial \alpha} \frac{e^{-\alpha^2(u^2+1)}}{u^2+1} du$$

Since the integrand is continuous, I can move the partial differentiation outside the integral and turning it into total differentiation

$$\frac{dI}{d\alpha} = - \frac{d}{d\alpha} \int_0^1 \frac{e^{-\alpha^2(u^2+1)}}{u^2+1} du$$

Hence

$$I(\alpha) = - \int_0^1 \frac{e^{-\alpha^2(u^2+1)}}{u^2+1} du + C$$

All that remains is to find the value of C . Considering the initial definition of $I(\alpha)$ and evaluating at $\alpha = 0$, I get

$$I(0) = \left(\int_0^0 e^{-t^2} dt \right)^2 = 0$$

Therefore

$$\begin{aligned}I(0) &= - \int_0^1 \frac{1}{u^2+1} du + C = 0 \\ C &= \arctan u \Big|_0^1 = \frac{\pi}{4}\end{aligned}$$

And I obtain the complete expression for the fish function

$$I(\alpha) = - \int_0^1 \frac{e^{-\alpha^2(u^2+1)}}{u^2+1} du + \frac{\pi}{4}$$

Now I can evaluate the Gaussian integral

$$\int_{-\infty}^{\infty} e^{-x^2} dx = 2 \lim_{\alpha \rightarrow \infty} \left(- \int_0^1 \frac{e^{-\alpha^2(u^2+1)}}{u^2+1} du + \frac{\pi}{4} \right)^{1/2} = 2 \frac{\sqrt{\pi}}{2}$$

and I find

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$$

Much to my chagrin, it is actually more trouble some than the polar method. Let's try it for comparison

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \left(\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-(x^2+y^2)} dx dy \right)^{1/2}$$

Doing the change of coordinate thing

$$\begin{aligned} \int_{-\infty}^{\infty} e^{-x^2} dx &= \left(\int_0^{2\pi} \int_0^{\infty} e^{-r^2} r dr d\theta \right)^{1/2} \\ \int_{-\infty}^{\infty} e^{-x^2} dx &= \left(2\pi \int_0^{\infty} e^{-r^2} r dr \right)^{1/2} \end{aligned}$$

That integral can be easily evaluated using u substitution; making the substitution $u = -r^2$

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \left(2\pi \int_{-\infty}^0 \frac{e^u}{2} du \right)^{1/2} = \left(2\pi \frac{e^u}{2} \Big|_{-\infty}^0 \right)^{1/2}$$

And I get the same result

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$$

Damn, it is really more shrimp.

Another form of Gaussian integral. Here we state without proof.

$$\begin{aligned} \int_{-\infty}^{\infty} \exp(-\alpha x^2 + \beta x + \gamma) dx &= \sqrt{\frac{\pi}{\alpha}} \exp\left(\frac{\beta^2}{4\alpha} + \gamma\right) \\ \int_{-\infty}^{\infty} \exp\left(\frac{1}{2}ix^2\right) dx &= \sqrt{2\pi} \exp\left(\frac{\pi}{4}i\right) \\ \int_0^{\infty} x^m \exp(-\alpha x^2) dx &= \frac{1}{2\alpha^{(m+1)/2}} \Gamma\left(\frac{m+1}{2}\right) \end{aligned}$$

Here's another one, not really a Gaussian integral, but since it involves natural number it counts

$$\sum_{n=0}^{\infty} n^k e^{-nk} = (-1)^k \frac{d^k}{dk^k} \sum_{n=0}^{\infty} e^{-nx} = (-1)^k \frac{d^k}{dk^k} \frac{1}{1-e^{-x}}$$

Beta Function

Definition. The beta function is also defined by a definite integral

$$B(p, q) \int_0^1 x^{p-1} (1-x)^{q-1} dx$$

for $p > 0$, and $q > 0$.

Change of order. It is easy to show that

$$B(p, q) = B(q, p)$$

Proof. Putting $x = 1 - y$ and $dx = -dy$

$$\begin{aligned} B(p, q) &= - \int_1^0 (1-y)^{p-1} y^{q-1} dy = \int_0^1 y^{q-1} (1-y)^{p-1} dy \\ B(p, q) &= B(q, p) \quad \blacksquare \end{aligned}$$

Integration Range. The range of integration can be changed with

$$B(p, q) = \frac{1}{a^{p+1-1}} \int_0^a y^{p-1} (a-y)^{q-1} dy$$

Another form is

$$B(p, q) = \int_0^\infty \frac{y^{p-1}}{(1+y)^{p+q}} dy$$

Proof. Putting $x = y/a$ and $dx = dy/a$

$$B = \int_0^a \left(\frac{y}{a}\right)^{p-1} \left(1 - \frac{y}{a}\right)^{q-1} \frac{1}{a} dy = \frac{1}{a^{p+1-1}} \int_0^a y^{p-1} (a-y)^{q-1} dy \quad \blacksquare$$

For the second form, we put $x = y/(1+y)$ and $dx = dy/(1+y)^2$

$$\begin{aligned} B(p, q) &= \int_0^\infty \left(\frac{y}{1+y}\right)^{p-1} \left(\frac{(1+y)-y}{1+y}\right)^{q-1} \frac{1}{(1+y)^2} dy \\ B(p, q) &= \int_0^\infty \frac{y^{p-1}}{(1+y)^{p+q}} dy \quad \blacksquare \end{aligned}$$

Trigonometric form. In terms of sine and cosine, the beta function reads

$$B(p, q) = 2 \int_0^{\pi/2} (\sin \theta)^{2p-1} (\cos \theta)^{2q-1} d\theta$$

Proof. Putting $x = \sin^2 \theta$ and $dx = 2 \cos \theta \sin \theta d\theta$

$$\begin{aligned} B(p, q) &= \int_0^{\pi/2} (\sin^2 \theta)^{p-1} (\cos \theta)^{q-1} \cos \theta \sin \theta d\theta \\ B(p, q) &= 2 \int_0^{\pi/2} (\sin \theta)^{2p-1} (\cos \theta)^{2q-1} d\theta \quad \blacksquare \end{aligned}$$

Gamma Function. Beta functions are easily expressed in terms of gamma functions

$$B(p, q) = \frac{\Gamma(p)\Gamma(q)}{\Gamma(p+q)}$$

Proof. First we consider the gamma function of p

$$\Gamma(p) = \int_0^\infty t^{p-1} e^{-t} dt$$

Then we make the substitution $t = y^2$ and $dt = 2y dy$

$$\Gamma(p) = \int_0^\infty y^{2p-2} e^{-y^2} 2y dy = 2 \int_0^\infty y^{2p-1} e^{-y^2} dy$$

Next we calculate the product of two gamma function p and q

$$\Gamma(p)\Gamma(q) = 4 \int_0^\infty \int_0^\infty x^{2p-1} e^{-x^2} y^{2q-1} e^{-y^2} dx dy$$

Like Gaussian integral, this is easier to evaluate in polar coordinate

$$\begin{aligned}\Gamma(p)\Gamma(q) &= 4 \int_0^{\pi/2} \int_0^\infty (r \cos \theta)^{2p-1} (r \sin \theta)^{2q-1} e^{-r^2} r dr d\theta \\ &= 2 \int_0^\infty r^{2(p+q)-1} e^{-r^2} dr \cdot 2 \int_0^{\pi/2} (\cos \theta)^{2p-1} (\sin \theta)^{2q-1} d\theta \\ \Gamma(p)\Gamma(q) &= \Gamma(p+q)B(p,q) \quad \blacksquare\end{aligned}$$

Error Function

We define error function as

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$

There is also closely related integrals which are used and sometimes referred to as the error function called standard normal or Gaussian cumulative distribution function $\Phi(x)$

$$\Phi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^x e^{-t^2/2} dt$$

Here are some of their relations.

$$\begin{aligned}\Phi(x) &= \frac{1}{2} + \frac{1}{2} \operatorname{erf}(x/\sqrt{2}) \\ \Phi(x) - \frac{1}{2} &= \frac{1}{2} \operatorname{erf}(x/\sqrt{2}) \\ \operatorname{erf}(x) &= 2\Phi(x\sqrt{2}) - 1\end{aligned}$$

Proof. Consider the definition of $\Phi(x)$. Making the substitution of $u = t/\sqrt{2}$

$$\begin{aligned}\Phi(x) &= \frac{1}{\sqrt{2\pi}} \int_{u=-\infty}^{u=x/\sqrt{2}} e^{-u^2} \sqrt{2} du \\ &= \frac{1}{\sqrt{\pi}} \left(\int_{-\infty}^0 e^{-u^2} du + \int_0^{\infty} e^{-u^2} du \right) \\ \Phi(x) &= \frac{1}{2} + \frac{1}{2} \operatorname{erf}(x/\sqrt{2}) \quad \blacksquare\end{aligned}$$

To prove the third relation, we first rewrite the equation as

$$\operatorname{erf}(x/\sqrt{2}) = 2\Phi(x) - 1$$

then we make the substitution $u = x/\sqrt{2}$

$$\operatorname{erf}(u) = 2 \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{u\sqrt{2}} e^{-t^2/2} dt - 1 = 2\Phi(x\sqrt{2}) - 1 \quad \blacksquare$$

Complementary error function. Defined as

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} dt$$

Its relations with the actual error function are as follows.

$$\begin{aligned}\operatorname{erfc}(x) &= 1 - \operatorname{erfc}(x) \\ \operatorname{erfc}(x/\sqrt{2}) &= \sqrt{\frac{2}{\pi}} \int_x^\infty e^{-t^2/2} dt\end{aligned}$$

Proof. The first relation is quite easy to prove. Consider

$$\frac{2}{\sqrt{\pi}} \int_{-\infty}^\infty e^{-t^2} dt = 1$$

then

$$\begin{aligned}\frac{2}{\sqrt{\pi}} \left(\int_{-\infty}^x e^{-t^2} + \int_x^\infty e^{-t^2} \right) &= 1 \\ \operatorname{erf}(x) + \operatorname{erfc}(x) &= 1 \quad \blacksquare\end{aligned}$$

To proof the second relation, we substitute the limit of integration from $t = x/\sqrt{2}$ into $x = t\sqrt{2}$

$$\operatorname{erfc}(x/\sqrt{2}) = \frac{2}{\sqrt{\pi}} \int_x^\infty \frac{e^{-t^2/2}}{\sqrt{2}} dt = \sqrt{\frac{2}{\pi}} \int_x^\infty e^{-t^2/2} dt \quad \blacksquare$$

Imaginary error function. We define

$$\operatorname{erfi}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{t^2} dt$$

Here are some relation to the actual error function.

$$\begin{aligned}\operatorname{erf}(ix) &= i \operatorname{erfi}(x) \\ \operatorname{erf}\left(\frac{1-i}{\sqrt{2}}x\right) &= (1-i)\sqrt{\frac{2}{\pi}} \int_0^x (\cos^2 u + i \sin^2 u) du\end{aligned}$$

Riemann zeta function

The Riemann zeta function $\zeta(p)$ is defined by

$$\zeta(p) = \sum_{n=0}^{\infty} \frac{1}{k^p}$$

for real $p > 1$. Here are some value of the Riemann zeta function

$$\zeta(2) = \frac{\pi^2}{6}; \quad \zeta(4) = \frac{\pi^4}{90}; \quad \zeta(6) = \frac{\pi^6}{945}$$

$$\zeta(3) = 1.202; \quad \zeta(5) = 1.036; \quad \zeta(7) = 1.008$$

Integrals. Here are some integral in terms of gamma function and Riemann zeta function.

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

$$\int_0^\infty \frac{x^p e^x}{(e^x - 1)^2} dx = \Gamma(p+1)\zeta(p)$$

$$\int_0^\infty \frac{x^{p-1}}{e^x + 1} dx = (1 - 2^{1-p}) \Gamma(p) \zeta(p)$$

Statistics

Permutation and Combination

Permutation. Consider finite set A with n elements. An r -permutation is an ordered selection of r elements from A , with $1 \leq r \leq n$. In permutation, order does matter, unlike combination, and that all arrangements are distinct. r -permutation of an n elements set is defined as

$$P(n, r) = n(n - 1) \dots (n - r + 1)$$

or simply

$$P(n, r) = \frac{n!}{(n - r)!}$$

Combination. Combination counts the number of ways to chose r object form finite set A with n elements where order of selection does not matter. For all integer n and $1 \leq r \leq n$, the number of combination when r elements are chosen out of finite set with n elements $C(n, r)$ is

$$C(n, r) = \frac{P(n, r)}{r!} = \binom{n}{r}$$

or

$$C(n, r) = \frac{n!}{r!(n - r)!}$$

Difference. Suppose we are choosing 2 people out of 4 to be president and vice-president. Here order matter, thus we say that there are

$$P(4, 2) = \frac{4!}{(4 - 2)!} = 12$$

ways to choose 2 people out of 4 to be president and vice-president. Now, we change the situation into choosing 2 out of 4 people to be given a gift. Here, order does not matter, hence we say that there are

$$C(4, 2) = \frac{4!}{2!(4 - 2)!} = 6$$

ways to choose 2 people out of 4 to be given gift.

Restricted Partition Generating Functions

Definition. To find the number of ways distributing L identical object—called configuration—in N distinct boxes subject to condition that not more than P object are in one box, we use

$$D(N, P, L) = \frac{1}{L!} \left. \frac{d^L}{dx^L} f(x) \right|_{x=0}$$

where

$$f(x) = (1 + x + x^2 + \dots + x^P)^N = \left(\sum_{i=0}^P x^i \right)^N$$

In other hands, the number of configuration of certain set $n_{k|P}$ is given by

$$D(N, P, n_{k|P}) = \frac{N!}{\prod_{i=0}^P n_i!}$$

while the total number of configuration form all possible set is

$$D_T(N, P) = (P + 1)^N$$

For a special case when $L \leq N$, the expression for $D(N, P, L)$ simplify into

$$D(N, P, L) = \frac{1}{L!} \frac{(N + L - 1)!}{(N - 1)!}$$

Derivation. Let the boxes be numbered $1, \dots, N$ and p_i as number of objects in i -th box, then

$$\sum_{i=1}^N p_i = L$$

with $0 \leq p_i \leq P$. Set obtained form interchanging p_i and p_k , with $p_i \neq p_k$ is counted as different set, however the exchange same exchange with $p_i = p_k$ does not count as different set. Let also n_k as the number of boxed having k number object, hence we have these two restricted for our combination

$$\sum_{k=0}^P n_k = N, \quad \sum_{k=0}^P k n_k = L$$

which we will denote as restriction R_I and R_{II} respectively.

Now consider the number of configuration $D(N, P, n_{k|P})$ obtained by counting different ways to choose the set of $n_{k|P} \equiv (n_1, \dots, n_P)$, which is evaluated by choosing n_0 from N boxes, followed by choosing n_1 from $N - n_0$ boxes, and so on. Hence,

$$\begin{aligned} D(N, P, n_{k|P}) &= \binom{N}{n_0} \cdots \binom{N - \cdots - n_{p-1}}{n_p} \\ &= \frac{N!}{n_0!(N - n_0)!} \cdots \frac{(N - \cdots - n_{p-1})!}{n_p!(N - \cdots - n_p)!} \\ D(N, P, n_{k|P}) &= \frac{N!}{\prod_{i=0}^P n_i!} \end{aligned}$$

The number of configuration satisfies the first condition, however it does not satisfy the second condition since the number of objects in the set $n_{k|P}$ is

$$\sum_{k=0}^P k n_k \equiv M(n_{k|P})$$

is not necessarily L . Our task is then to find the configuration D which satisfies our restriction, formally

$$D(N, P, L) = \sum_{R_I \text{ and } R_{II}} D(N, P, n_{k|P})$$

To find the number of configuration that satisfy those two restriction, we first consider the value of summing $D(N, P, n_{k|P})$ over all possible value of n_k ; this makes it so that D satisfies the first condition, but not the second. Formally

$$D_T(N, P) \equiv \sum_{R_I} D(N, P, n_{k|P})$$

Using the result that we derived previously

$$D_T(N, P) = \frac{N!}{\prod_{i=0}^P n_i!}$$

Recall the multinomial theorem

$$\left(\sum_{i=0}^P x_i \right)^N = \sum_{R_I} \frac{N}{\prod_{i=0}^P n_i!} \prod_{i=0}^P x_i^{n_i}$$

Let $x_i = 1$ for all i , and we get

$$(P+1)^N = \sum_{R_I} \frac{N}{\prod_{i=0}^P n_i!}$$

Therefore

$$D_T(N, P) = (P+1)^N$$

This is the number of ways to distribute $M = 0, \dots, NP$ objects in N boxes, with each box only having maximum P objects. What we want however is $M = L$. To do that, we put $x_i = x^i$ in to multinomial theorem

$$\begin{aligned} \left(\sum_{i=0}^P x^i \right)^N &= \sum_{R_I} \frac{N}{\prod_{i=0}^P n_i!} \prod_{i=0}^P x^{i \cdot n_i} = \sum_{R_I} \frac{N}{\prod_{i=0}^P n_i!} x^{\sum_{i=0}^P i \cdot n_i} \\ \left(\sum_{i=0}^P x^i \right)^N &= \sum_{R_I} \frac{N}{\prod_{i=0}^P n_i!} x^{M(n_{i|P})} \end{aligned}$$

Clearly,

$$D_T(N, P, L) = \text{Coefficient of } x^L \text{ in } \left(\sum_{i=0}^P x^i \right)^N$$

which is obtained by

$$D(N, P, L) = \frac{1}{L!} \frac{d^L}{dx^L} \left(\sum_{i=0}^P x^i \right)^N \Big|_{x=0} \blacksquare$$

Now we consider special case when $L \leq P$. Note that the L -th derivative of $f(x)$, especially x^{L+k} with $k \equiv 1, 2, \dots$ at $x = 0$ is also zero. We can expand the definition of $f(x)$ as polynomial degree P into degree infinity and write

$$f(x) = \left(\sum_{i=0}^{\infty} x^i \right)^N$$

Evaluating it

$$f(x) = (1-x)^{-N}$$

Substituting it into the expression for $D(N, P, L)$, we see that

$$\begin{aligned} D(N, P, L) &= \frac{1}{L!} \frac{d^L}{dx^L} (1-x)^N = \frac{1}{L!} N \frac{d^{L-1}}{dx^{L-1}} (1-x)^{N-1} \\ &= \frac{1}{L!} N(N+1) \frac{d^{L-2}}{dx^{L-2}} (1-x)^{N-2} \end{aligned}$$

Hence, in general

$$D(N, P, L) = \frac{1}{L!} \frac{(N+L-1)!}{(N-1)!} \blacksquare$$

Thermodynamics

Key Concepts

Few Terminologies

1. **Heat and energy.** Heat is considered a form of energy. It can be converted to work, and in turn can be produced by consuming work. Work and heat together obey law of conservation of energy.
2. **Thermodynamic equilibrium.** The state of a thermodynamic system which does not change with time is called the state of thermodynamic equilibrium.
3. **State variable.** The state variables—such as pressure P , volume V , and temperature T —in the state of equilibrium are not independent. The relationship between them is known as the equation of state.
4. **Thermodynamic transformation.** The state of a system changes when the external conditions are changed. When its state changes, the system is said to undergo thermodynamic transformation.
5. **Quasi-static.** If the state variables change so slowly that the system can be assumed to be in thermodynamic equilibrium at any instant then the transformation of the system is said to be quasi-static.
6. **Reversible and irreversible.** If the transformation is carried such that it is possible to retrace the steps from its final to the initial state by reversing the external conditions then it is called reversible. Else the transformation is called irreversible.
7. **Isolated system.** A system enclosed by partition such that no exchange of volume, mole number, heat or work is possible.
8. **Simple system.** A system which is microscopically homogeneous, isotropic, electrically neutral, and not under external force.
9. **Composite system** A system consisting two or more subsystems.
10. **Adiabatic system.** If the transformation is such that the system does not exchange heat with its surroundings then the transformation is said to be adiabatic.
11. **Isothermal.** A transformation in which temperature of the system remains unchanged is called isothermal.
12. **Isobaric.** A transformation in which pressure of the system remains unchanged is called isobaric.
13. **Heat reservoir.** A thermal or heat reservoir is a system so large that addition or removal of a finite amount of heat from it does not change its temperature.
14. **Cyclic transformation.** If a transformation is such that it restores the system to its initial state then it is called cyclic.

The Ideal Gas

The ideal gas model represents the gas particles as point particles (i.e. a material body having mass but no spatial extent), and assumes that there are no (attractive or repulsive) physical interactions between them. For an ideal gas composed of N particles or n moles in equilibrium, the pressure P is related with the volume V occupied by the gas and its temperature T , through the ideal gas equation:

$$PV = nRT = Nk_B T$$

where $R = 8.315$ joule/mole K $k_B = 1.38 \times 10^{-16}$ erg/K. The ideal gas equation was stated in 1834 by Benoit Emile Clapeyron (1799-1864) and results from combining the old gas laws:

1. **Boyle's law.** If temperature is kept constant, the pressure is proportional to the density, $P \propto \rho$.
2. **Amonton's law.** If volume is kept constant, the pressure is proportional to the temperature, $V \propto T$.
3. **Gay-Lussac' law.** If pressure is kept constant, the volume is proportional to the temperature, $V \propto T$
4. **Avogadro's hypothesis.** If pressure, volume and temperature of two gases are the same, then both gases have the same number of particles

Since, in addition to the equation of state relating pressure, volume, and temperature, complete description of thermodynamic properties requires also the knowledge of its internal energy as a function of the state variables

$$U = \frac{3}{2} N k_B T$$

Van der Waals Equation of State. The equation of state for a real gas derived by van der Waals was also based on the kinetic theory and the Virial theorem. Here we give standard phenomenological derivation of the equation, obtained by introducing following modifications in the ideal gas law:

1. **Specific volume.** It is assumed that the molecules are not point particles but are hard spheres. This results in each molecule excluding some volume, say b , from the total volume V . It was argued that the ideal gas law should therefore be modified to replace V by $V - Nb$.
2. **Force of attraction.** The molecules attract each other when separated by distances greater than the molecular radius r_0 . Assuming that the molecules are distributed uniformly, each molecule in the interior is acted upon by forces on all sides resulting in net-zero force; however near the boundary surfaces therefore experience a net inward force resulting in reduction of pressure. This causes net reduction of pressure proportional to $(N/V)^2$ which must be subtracted from the pressure appearing in the ideal gas law.

Under the suggested modifications, the ideal gas law assumes the form

$$P = \frac{Nk_B T}{V - Nb} - \frac{a}{(V/N)^2} = \frac{k_B T}{v - b} - \frac{a}{v^2}$$

where $v = V/N$ is the specific volume. And for the internal energy of single particle

$$u = ck_B T - \frac{a}{v}$$

Entropy of ideal gas. Consider a reversible process which takes N molecules of an ideal gas be in equilibrium in the state A to the equilibrium state B . The process being reversible is described by the form of the first law which, on reversible process takes the form of

$$dU = T dS - P dV \quad (1)$$

Solving for the entropy

$$dS = \frac{dT}{T} + \frac{P}{T} dV \quad (2)$$

Considering T can be written as

$$T = \frac{PV}{Nk_B} = \frac{U}{cNk_B}$$

then

$$dS = Nk_B \left(c \frac{dU}{U} + \frac{dV}{V} \right)$$

On integrating the equation above, we get

$$S = nK_B [c \ln U + \ln V] + K$$

where K is the integration constant. Determination of absolute value of entropy in a state would, of course, require knowledge of K . However, it plays no role in computing entropy change in going from state A to state B as in that case

$$S(B) - S(A) = Nk_B \left[c \ln \frac{U_B}{U_A} + \ln \frac{V_B}{V_A} \right]$$

Carnot Engine

The Carnot engine (or machine) is a theoretical heat engine envisioned by Sadi Carnot that operates a reversible cyclic process termed Carnot cycle.

If it is assumed that heat cannot be transported from a cold to a hot reservoir without doing any work then

1. No engine is more efficient than reversible Carnot engine.
2. All reversible Carnot engines operating between same reservoirs have same efficiency.

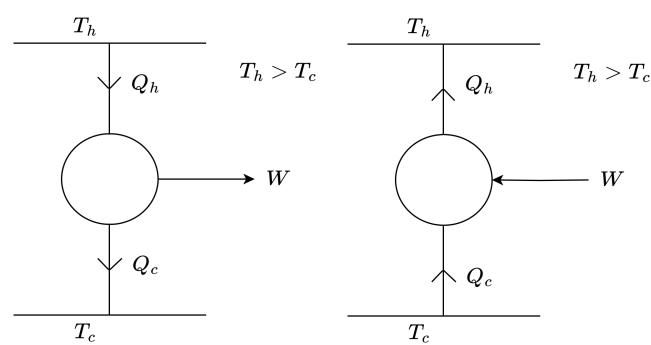


Figure: Carnot engine and reverse Carnot engine.

The work produced in one cycle of the process is the difference in the amount of heat absorbed and the heat $-W = Q_h - Q_c$. Hence, efficiency μ defined as the ratio of work W produced by the engine to the amount of heat Q_h received by it,

$$\mu = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h}$$

where the last line is obtained from clever derivation. I won't go into the derivation itself, but one important part of the derivation also prove, for a reversible Carnot engine operating with any fluid and process,

$$\frac{Q_h}{T_h} = \frac{Q_c}{T_c}$$

Also note that the T in question is measure in kelvin, not Celsius.

Cyclic Process. Consider the cyclic process comprises a sequence of four reversible processes of a thermodynamic system, namely, an isothermal expansion, an adiabatic expansion, an isothermal compression, and an adiabatic compression. Suppose also that the working fluid is an ideal gas. Those processes are as follows.

- Point A.** The gas is initially in equilibrium at temperature T_h and its pressure and volume P_A, V_A . The temperature is kept constant by keeping the gas in contact with a heat reservoir at the desired temperature. The gas is then let to expand isothermally to volume V_B with its pressure.
- Point B.** At B the gas is isolated from the heat reservoir. The amount of heat absorbed along $A \rightarrow B$ may be evaluated using the first law $dU = dQ - P dV$, along with the two equation of state $PV = Nk_B T$ and $U = cNk_B T$. Since the temperature has the constant value, $dU = 0$. Therefore,

$$dQ = Nk_B T_h \frac{dV}{V}$$

Integrating between initial and final volumes

$$Q_h = Nk_B T_h \ln \frac{V_B}{V_A}$$

The gas is then expands further but without exchanging heat with the environment, an adiabatic expansion. It continues till it volume and pressure become V_C and P_C .

3. **Point C.** At C it is brought in contact with the reservoir at temperature T_C . First we consider the transformation of $B \rightarrow C$. Since it is adiabatic, it does not involve exchange of heat. The first law reads as

$$dU + P dV = 0$$

Now we use the equations of state

$$\begin{aligned} C_V dT + P dV &\implies dT + \frac{P dV}{C_V} \implies \frac{dT}{T} + \frac{P dT}{cNk_B T} \\ &\implies \frac{dT}{T} + \frac{dV}{cV} \implies \frac{dT}{T} + (\gamma - 1) \frac{dV}{V} \end{aligned}$$

And we obtain

$$\frac{dT}{T} + (\gamma - 1) \frac{dV}{V} = 0$$

On integrating the equation above between the state, we get

$$\ln \frac{T_C}{T_B} + (\gamma - 1) \ln \frac{V_C}{V_B} = 0$$

We can write

$$\ln \frac{T_C}{T_B} + (\gamma - 1) \ln \frac{V_C}{V_B} = \ln \frac{T_C}{T_B} \frac{V_C^{\gamma-1}}{V_B^{\gamma-1}}$$

which implies

$$\frac{V_C^{\gamma-1}}{V_B^{\gamma-1}} = 1$$

In other words

$$TV^{\gamma-1} = \text{constant.}$$

Expressing T in terms of P and V

$$PV^{\gamma-1} = \text{constant.}$$

And expressing V in terms of P and T

$$TP^{-v} = \text{constant.}$$

where $v = (\gamma - 1)/\gamma$. These equations are called **adiabatic equations of state**.

Due to the reservoir T_c , the gas compresses isothermally till its volume and pressure become V_D , P_D .

4. **Point D.** At D it is again isolated. As before, we consider the transformation of $C \rightarrow D$ first. Along CD , the temperature has the constant value T_c and volume varies from V_C to V_D leads to the following expression for the heat **received** by the gas:

$$Q'_C = Nk_B T_c \ln \frac{V_D}{V_C}$$

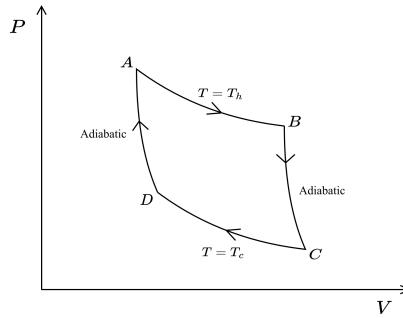


Figure: PV diagram of a cyclic Carnot process.

Since $V_D < V_D$, the heat absorbed by the gas is negative, which means that a positive amount of heat is delivered to the reservoir. Hence, the amount of heat delivered to the reservoir is

$$Q_C = -Q'_C = Nk_B T_c \ln \frac{V_C}{V_D}$$

The gas is then compressed adiabatically till its pressure, volume, and temperature attain their initial values P_A , V_A , and T_h . Also, since the process from D to A is adiabatic, no heat is exchanged with the surroundings.

Carnot's equation in cyclic processes. The Carnot's equation still holds true even in cyclic process. To prove this, first we're applying adiabatic equation to path BC

$$T_B V_B^{\frac{1}{\gamma}-1} = T_C V_C^{\frac{1}{\gamma}-1} \implies \left(\frac{V_B}{V_C}\right)^{\frac{1}{\gamma}-1} = \frac{T_C}{T_B} \implies \left(\frac{V_B}{V_C}\right)^{\frac{1}{\gamma}-1} = \frac{T_c}{T_h}$$

In similar manner, the adiabatic transformation along DA gives

$$\left(\frac{V_D}{V_A}\right)^{\frac{1}{\gamma}-1} = \frac{T_A}{T_D} \implies \left(\frac{V_D}{V_A}\right)^{\frac{1}{\gamma}-1} = \frac{T_h}{T_c}$$

On comparing these, it is seen that

$$\frac{V_B}{V_C} = \frac{V_A}{V_D} \implies \frac{V_C}{V_D} = \frac{V_B}{V_A}$$

This leads to

$$\frac{Q_h}{Q_c} = \frac{Nk_B T_h \ln V_B/V_A}{Nk_B T_c \ln V_C/V_D} \implies \frac{Q_h}{Q_c} = \frac{T_h}{T_c}$$

which is the Carnot's equation.

Efficiency of cyclic Carnot engine. To find efficiency of the process under consideration from first principles note that total work done by the gas in the cycle, due to first law, is

$$W = \oint (dQ - dU) = \oint dQ$$

Since no heat is exchanged on adiabatic paths BC and DA , the closed integral becomes

$$\oint dQ \int_A^B dQ + \int_C^D dQ = Q_h - Q_c$$

In other words

$$W = Q_h - Q_c$$

The relation derived above is independent of the equation of state obeyed by the working fluid. Using this equation, the efficiency reads

$$\mu = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h}$$

Specific Heat

Invoking the first law we have

$$dU = dQ - P dV \begin{cases} \left. \frac{\partial U}{\partial T} \right|_V = \left. \frac{\partial Q}{\partial T} \right|_V \\ \left. \frac{\partial U}{\partial T} \right|_P = \left. \frac{\partial Q}{\partial T} \right|_P - P \left. \frac{\partial V}{\partial T} \right|_P \end{cases}$$

The first quantity is defined as heat capacity at constant volume

$$C_V \equiv \left. \frac{\partial Q}{\partial T} \right|_V = \left. \frac{\partial U}{\partial T} \right|_V$$

While, from the second cases, heat capacity at constant pressure can be defined as

$$C_P \equiv \left. \frac{\partial Q}{\partial T} \right|_P$$

Both equation can be combined into

$$\begin{aligned} C_P - C_V &= \left. \frac{\partial U}{\partial T} \right|_P + P \left. \frac{\partial V}{\partial T} \right|_P - \left. \frac{\partial U}{\partial T} \right|_V \\ &= \frac{\partial}{\partial T} C_V T \Big|_P + P \frac{\partial}{\partial T} \frac{Nk_B T}{P} \Big|_P - \frac{\partial}{\partial T} C_V T \Big|_V \\ C_P - C_V &= Nk_B \end{aligned}$$

In terms of the parameter gamma γ , called adiabatic constant, defined by

$$\gamma = \frac{C_P}{C_V}$$

Using these, the equation yields

$$\begin{aligned} C_V \left(\frac{C_P}{C_V} - 1 \right) &= Nk_B \\ C_V &= \frac{Nk_B}{\gamma - 1} = cNk_B \end{aligned}$$

Internal Energy

The independence of internal energy to volume was proved by Thomson and Joule (in 1845) which involved direct measurement of temperature of the gas. It is also known experimentally that the heat capacity of ideal gas is independent of temperature. Consequently, C_V is a constant so that

$$U(V, T) = C_V T = c N k_B T$$

For an ideal monoatomic gas, $c = 3/2$ thus $\lambda = 5/3$

Entropy

The relation for the reversible cyclic process may then be rewritten as $Q_h/T_h + (-Q_c/T_c) = 0$. The quantity

$$S \equiv \frac{Q}{T}$$

is called entropy of the system. The name entropy was coined by Clausius to describes some transformation taking place inside the system.

Total change in entropy of the system in a reversible Carnot cycle is zero, $\Delta S_{\text{sys}} \equiv 0$, while change in entropy of the environment during the process in question is also zero, $\Delta S_{\text{env}} \equiv 0$. Increase in entropy of the environment may be considered as the measure of the lost work, $W' = W - T \Delta S_{\text{env}}$.

For any reversible path with O as any reference point

$$S(A) = \int_O^A \frac{dQ}{T}$$

Thus, the change in entropy in going from A to B is given by

$$S(B) - S(A) = \int_A^B \frac{dQ}{T}$$

Thermodynamics' Law

Zeroth Law

The zeroth law states that if a system A is in thermal equilibrium with B and also separately with C then B and C are in thermal equilibrium with each other.

The consequences of this law is the equation

$$g(P_B, V_B) = g(P_C, V_C)$$

This shows that there exists a function $g(P, V)$ which has the same value for systems B and C in thermal equilibrium. However, neither this law nor the other laws of thermodynamics determine the form of the function $g(P, V)$.

First Law

The first law is the statement of conservation of energy. It states that the internal energy dU of a thermodynamic system is a state function such that if dQ is the amount of heat absorbed and dW the amount of work done by the system in an arbitrary transformation then change dU in its internal energy is given by

$$dU = dQ - dW$$

Some texts refer the work as positive dW , instead of negative. This is due to difference of definition. As stated, dW here defined as the amount of work **done by** the system; on another, it may be defined as the amount **done on** system.

The work may consist of several components each caused by change in some macroscopic control parameter, so that

$$dW = - \sum_{i=1}^m F_i d\xi_i$$

The F_i is the “force” associated with the change in ξ_i . The negative sign is due to dW as work performed by the system. If the volume V is the only macroscopic control parameter then the internal energy reads

$$dU = dQ - P dV$$

or gas gains energy when its volume decreases and loses energy when its volume increases. By applying the second law, we can also say

$$dU = T dS - P dV$$

Second Law

There are two equivalent ways of stating the second law:

- Kelvin statement:** There does not exist any thermodynamic transformation whose sole effect is to extract heat from a heat reservoir and convert it entirely into work.
- Clausius' statement:** There does not exist any thermodynamic transformation whose sole effect is to extract heat from a body at lower temperature and deliver it to the one at higher temperature.

By yet another derivation that I do not show, the statement can be written as

$$\oint \frac{dQ}{T} = 0$$

Note that the equation only holds true for reversible Carnot process. It is straightforward to prove that the equation above implies that the integral is independent of path between A and B if the process is reversible. For irreversible process

$$\int_{\text{irr}} \frac{dQ}{T} < \int_{\text{rev}} \frac{dQ}{T}$$

In other words, the change in entropy over an irreversible path between two states is less than that on any reversible path between same states.

Here we also state some consequences of the second law.

Entropy of the universe. Consider a system interacting with a reservoir, drawing the amount dQ of heat from it at temperature T by reversible or irreversible process. The quantity dQ/T for the system therefore may or may not stand for change in its entropy. However, $-dQ/T$ stands for the reservoir's, since all processes inside a reservoir are reversible. As the system changes from A to B ,

$$\begin{aligned}\Delta S_{\text{sys}} &= \Delta S_{\text{sys}} + \Delta S_{\text{env}} \\ &= [S(B) - S(A)] - \int_A^B \frac{dQ}{T} \\ \Delta S_{\text{sys}} &\geq 0\end{aligned}$$

The equation above shows that entropy of the universe never decreases.

Entropy of thermally isolated system. Assume that the system is thermally isolated, then $dQ = 0$. Hence, $\Delta S_{\text{env}} = 0$. As a consequence of, as the system transforms from state A to state B , its entropy cannot decrease:

$$S(B) - S(A) \geq 0$$

Maximum entropy principle. In approaching thermodynamic equilibrium, the entropy of an isolated system must tend to a maximum, and the final equilibrium state is the one for which the entropy is greatest.

Work lost. Consider a reversible process which takes a system from state A to state B . By the first law,

$$U_B - U_A = \int_{\text{rev}} T dS_{\text{sys}} - dW_{\text{rev}}$$

since for reversible process, $dQ = T dS_{\text{sys}}$. Now, consider another process which connects the same two states as in the said reversible process but now by an irreversible path, then

$$U_B - U_A = \int_{\text{irr}} dQ - dW_{\text{irr}}$$

due to $dQ \neq T dS_{\text{sys}}$ for irreversible process. Since internal energy is a state variable, the value of $U_B - U_A$ is same whether the process is reversible or not. Hence, on equating them

$$W_{\text{rev}} - W_{\text{irr}} = W_{\text{lost}} = \int_{\text{rev}} T dS_{\text{sys}} - \int_{\text{irr}} dQ$$

For an isothermal irreversible process

$$\begin{aligned} W_{\text{lost}} &= T \left[\int_{\text{rev}} dS_{\text{sys}} - \int_{\text{irr}} \frac{dQ}{T} \right] \\ &= T(\Delta S_{\text{sys} + \Delta S_{\text{env}}}) \\ W_{\text{lost}} &= T\Delta S_{\text{uni}} \end{aligned}$$

where the second line is obtained from the definition of change of entropy in environment.

Isentropic process. Adiabatic process is defined as the one which does not involve exchange of heat with the environment. We also know that $dQ = T dS$ if the process is irreversible. Hence, entropy is unchanged in a reversible adiabatic process. Such a process is called isentropic.

Third Law

The second law determines change in entropy but not its absolute value. Third law achieves that end. An interesting consequence of it, not elaborated here, is the question of unattainability of $T = 0$.

Planck's formulation. The entropy of any system at $T = 0$ is zero

$$S_{T=0} = 0$$

Nernst's heat theorem. The change in entropy is zero as $T \rightarrow 0$:

$$\lim_{T \rightarrow 0} \Delta S = 0$$

Thermodynamics Postulate

In this approach, thermodynamics is built using entropy as its basis, instead of the traditional thermodynamics laws. We treat entropy as fundamental function characterizing thermodynamics state. We henceforth will discuss four postulates of thermodynamics and its connection with thermodynamics laws.

First Postulate

Simple system in equilibrium can be characterized by its internal energy U , volume V and number molecule N_1, \dots, N_r of its chemical components.

In essence, this postulate simply confirm the existence of equilibrium state.

Second Postulate

The entropy function S is a first order homogeneous function with the properties of assuming maximum value when external constrains are removed.

Also called the maximum entropy principle.

Third Postulate

Entropy has the following properties.

1. The total entropy system is the sum entropy of each subsystem.
2. The entropy function is single-valued, continuous, differentiable, and monotonically increasing with respect to internal energy U over its entire domain.

We will also consider the implication next.

Fourth Law

If the system for which

$$\left. \frac{\partial U}{\partial S} \right|_{V, N_i|r} = 0$$

applies, the entropy of the system vanishes.

The equivalent of Third thermodynamics law.

Implication

Entropy's arguments. Since the entropy function, implied by the second postulate, is an extensive parameter. Therefore, by the first postulate, entropy is a function of

$$S = S(U, V, N_{i|r}) \quad \text{where} \quad N_{i|r} = N_1, \dots, N_r$$

Extensive properties. Due to implication from the second postulate, the entropy function the relation

$$S(\lambda U, \lambda V, \lambda N_{i|r}) = \lambda S(U, V, N_{i|r})$$

Since entropy is also homogeneous function of the first order, it also obeys

$$S = U \frac{\partial S}{\partial V} \Big|_{U, N_{i|r}} + V \frac{\partial S}{\partial V} \Big|_{V, N_{i|r}} + \sum_{j=1}^r N_j \frac{\partial S}{\partial N_j} \Big|_{V, N_{i \neq r}}$$

Invoking the relation between intensive parameters and partial derivative of entropy, we have

$$S = \frac{U}{T} + \frac{PV}{T} - \sum_{j=1}^r \frac{N_j \mu_j}{T}$$

This is also called Euler's equation, entropy version.

Monotonic function. The property of increasing monotonically implies

$$\frac{\partial S}{\partial U} \Big|_{V, N_{i|r}} > 0$$

Invoking the relation of temperature with partial derivative of entropy

$$\frac{1}{T} > 0 \implies T > 0$$

Another statement of the third law

Third thermodynamics law. Using the relation of temperature and the partial derivative of entropy, we can write the fourth postulate as

$$\frac{\partial U}{\partial S} \Big|_{V, N_{i|r}} = T = 0$$

Which is the temperature when entropy of any system reaches zero.

Internal energy function. All that properties with respect to internal energy imply that entropy might be converted into internal energy. We can therefore say that internal energy is a function of the same extensive parameter

$$U = U(S, V, N_{i|r}) = ST - PV + \sum_{j=1}^r N_j \mu_j$$

where the last term is due to euler equation.

Connection With the Old Laws

We know that internal energy U is a function of entropy S , volume V , and number of particle $N_i|_r$. We can therefore write the total derivative of U as

$$dU = \frac{\partial U}{\partial S} \Big|_{V, N_i} dS + \frac{\partial U}{\partial V} \Big|_{S, N_i} dV + \sum_{j=1}^r \frac{\partial U}{\partial N_j} \Big|_{S, V, N_i \neq j} dN_j$$

We then define

$$T = \frac{\partial U}{\partial S} \Big|_{V, N_i}, P = -\frac{\partial U}{\partial V} \Big|_{S, N_i}, \mu_j = \frac{\partial U}{\partial N} \Big|_{S, V, N_i \neq j}$$

to write the total derivative as

$$dU = T dS - P dV + \sum_{j=1}^r \mu_j dN_j$$

We shall now consider the justification of these definitions.

Temperature. Consider Isolated system containing gas. The system is the partitioned in such way so that there is no exchange of heat work, and particle. The system is said to be under these constrain

$$dU_T = dU_1 + dU_2 = 0, \quad dV_1 = dV_2, \quad , dN_1 = dN_2$$

By the extensive properties of entropy, we can say

$$dS_T = dS_1 + dS_2$$

and for the total differential of itself

$$dS_T = \frac{\partial S_T}{\partial U_T} \Big|_{V_T, N_T} dU_T + \frac{\partial S_T}{\partial V_T} \Big|_{U_T, N_T} dV_T + \frac{\partial S_T}{\partial N_T} \Big|_{S_T, V_T} dN_T$$

It follows that

$$dS_T = \frac{\partial S_1}{\partial U_1} \Big|_{V_1, N_1} dU_1 + \frac{\partial S_2}{\partial U_2} \Big|_{V_2, N_2} dU_2 = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dU_1$$

At equilibrium, $dS_T = 0$, by the second postulate. Since $dU_1 = -dU_2$ is not implied to be zero, the expression inside parenthesis must be zero. This implies

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

at equilibrium, which is consistent to our definition of thermodynamics equilibrium.

Pressure. Suppose now that the system's partition does allow the flow of heat and work. The constraints change into

$$dU_T = dU_1 + dU_2 = 0, \quad dV_T = dV_1 + dV_2 = 0, \quad , dN_1 = dN_2$$

Thus

$$dS_T = \frac{\partial S_1}{\partial U_1} \Big|_{V_1, N_1} dU_1 + \frac{\partial S_2}{\partial U_2} \Big|_{V_2, N_2} dU_2 + \frac{\partial S_1}{\partial V_1} \Big|_{U_1, N_1} dV_1 + \frac{\partial S_2}{\partial V_2} \Big|_{U_2, N_2} dV_2$$

Applying the relation between temperature and pressure with partial derivative of entropy, we obtain

$$dS_T = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_1$$

At equilibrium, this equation yields

$$\frac{1}{T_1} = \frac{1}{T_2} \quad \wedge \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Combining both of the equation, we get the result that

$$T_1 = T_2 \quad \wedge \quad P_1 = P_2$$

at equilibrium, according to our understanding of thermodynamics equilibrium.

Chemical potential. This time, we allow the exchange of particle inside the isolated system. However, we also design it in such a way so that the exchange of heat and work is not allowed. The constraints turn into

$$dU_T = dU_1 + dU_2 = 0, \quad dV_1 = dV_2 = 0, \quad dN_T = dN_1 + dN_2 = 0$$

Hence

$$dS_T = \frac{\partial S_1}{\partial U_1} \Big|_{V_1, N_1} dU_1 + \frac{\partial S_2}{\partial U_2} \Big|_{V_2, N_2} dU_2 + \frac{\partial S_1}{\partial N_1} \Big|_{U_1, V_1} dN_1 + \frac{\partial S_2}{\partial N_2} \Big|_{U_2, V_2} dN_2$$

We then use the relation between temperature and chemical potential with partial derivative of entropy

$$dS_T = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 + \left(\frac{\mu_2}{T_2} - \frac{\mu_1}{T_1} \right) dN_1$$

Using the maximum entropy principle, we have

$$\frac{1}{T_1} = \frac{1}{T_2} \quad \wedge \quad \frac{\mu_2}{T_2} = \frac{\mu_1}{T_1}$$

Which implies

$$T_1 = T_2 \quad \wedge \quad \mu_2 = \mu_1$$

As before, this is according to the definition of thermodynamics equilibrium.

Thermodynamics' Potentials

Both entropy and internal energy are a function of volume and number of particle, which are extensive parameters. In experiment, however, we only controls intensive parameters, such as temperature and pressure. Thermodynamics potentials provide a way to describe system using intensive parameters.

Helmholtz Potential

By performing Legendre transform of $U(S, V, N)$ with respect to S , we get

$$\begin{aligned}\mathcal{L}_S[U(S, V, N)] &= U \left[S \left(\frac{\partial U}{\partial S} \right), V, N \right] - \frac{\partial U}{\partial S} S \left(\frac{\partial U}{\partial S} \right) \\ \mathcal{L}_S[U(S, V, N)] &= U[S(T), V, N] - TS(T)\end{aligned}$$

We define the resulting function as Helmholtz potential or Free energy

$$F(T, V, N) = U[S, V, N] - TS$$

Partial derivative relation. The differential of F read as

$$\begin{aligned}dF &= dU - T dS - S dT = T dS - P dV + \mu dN - T dS - S dT \\ dF &= -S dT - P dV + \mu dN\end{aligned}$$

Therefore

$$S = -\left. \frac{\partial F}{\partial T} \right|_{V,N}, \quad P = -\left. \frac{\partial F}{\partial V} \right|_{T,N}, \quad \mu = \left. \frac{\partial F}{\partial N} \right|_{T,V}$$

Physical meaning. Consider system undergoing thermodynamics transform from state A to B . Suppose that the temperature T , volume V , and number of particle N is held constant during the transformation; according to the second law,

$$\int_{\text{irr}} \frac{dQ}{T} \leq \int_{\text{rev}} \frac{dQ}{T} \implies \frac{dQ}{T} \leq dS \implies dQ \leq T dS$$

Partial derivative relation. The differential of F is then

$$dF = dU - T dS \implies dF \leq dU - dQ$$

Using the first law and the result from the second law, we have

$$dF \leq 0 \quad \text{for } dT = dV = dN = 0$$

Therefore, Helmholtz potential never increases in thermodynamics transformation which is performed under isothermal, isovolume, and iso-number-of-particle conditions.

Gibbs Potential

Gibbs potential is obtained by performed Legendre transformation to $U(S, V, N)$ with respect S and V . Consider

$$\begin{aligned}\mathcal{L}_{S,V}[U(S, V, N)] &= U\left[S\left(\frac{\partial U}{\partial S}\right), V\left(\frac{\partial U}{\partial V}\right), N\right] \\ &\quad - \frac{\partial U}{\partial S}S\left(\frac{\partial U}{\partial S}\right) - \frac{\partial U}{\partial V}V\left(\frac{\partial U}{\partial V}\right) \\ \mathcal{L}_S[U(S, V, N)] &= U[S(T), V(P), N] - TS(T) + PV(P)\end{aligned}$$

Hence

$$G(T, P, N) = U(S, V, N) - TS + PV$$

By invoking the Euler equation in terms of internal energy, we can also write Gibbs potential in terms of chemical potential

$$G(T, P, N) = TS - PV + \mu N - TS + PV = \mu N$$

Partial derivative relation. Now, consider the total differential of G

$$\begin{aligned}dG &= dU - T dS - S dT + P dV + V dP \\ &= T dS - P dV + \mu dN - T dS - S dT + P dV + V dP \\ dG &= -S dT + V dT + \mu dN\end{aligned}$$

It follows that

$$S = -\frac{\partial G}{\partial T}\Big|_{P,N}, \quad V = \frac{\partial G}{\partial P}\Big|_{T,N}, \quad \mu = \frac{\partial G}{\partial N}\Big|_{T,P}$$

Physical meaning. We again consider the same system under transformation. The transformation, however, performed under the same temperature T , pressure P , and number of particle N . We write the differential of G as

$$dG = dU - T dS + P dV = dQ - T dS$$

Using the result we obtained earlier from the second law

$$dG \leq 0, \quad \text{for } dT = dP = dN = 0$$

We have proofed that in isothermal, isobaric, and iso-number-of-particle, Gibbs potential never increases.

Enthalpy

Suppose we perform Legendre transformation of $U(x, y, z)$ with respect to V , we write

$$\begin{aligned}\mathcal{L}_V[U(S, V, N)] &= U\left[S, V\left(\frac{\partial U}{\partial V}\right), N\right] - \frac{\partial U}{\partial V}V\left(\frac{\partial U}{\partial V}\right) \\ \mathcal{L}_V[U(S, V, N)] &= U[S, V(P), N] + PV(P)\end{aligned}$$

This function is defined as enthalpy

$$H(S, P, N) = U(S, V, N) + PV$$

Partial derivative relation. We write the differential of H as

$$dH = dU + P \, dV + V \, dP = T \, dS - P \, dV + \mu \, dN + P \, dV + V \, dP$$

$$dH = T \, dS + V \, dP + \mu \, dN$$

Hence

$$T = \frac{\partial H}{\partial S} \Big|_{P,N}, \quad V = \frac{\partial H}{\partial P} \Big|_{S,N}, \quad \mu = \frac{\partial H}{\partial N} \Big|_{S,P}$$

Physical meaning. We can also write the differential of H as

$$dH = dU + P \, dV + V \, dP = dQ - P \, dV + \mu \, dN + P \, dV + V \, dP$$

$$dH = dQ + V \, dP + \mu \, dN$$

This equation show that in an isobaric and iso-number-of-particle process, change in enthalpy is the amount of heat absorbed. Enthalpy is often called the heat function.

Now we consider again the same thermodynamics transformation as before with the following modification of constrains: entropy S , pressure P , and number of particle N are made to be constant. By the last result, we write the differential of H as

$$dH = dQ + V \, dP + \mu \, dN \implies dH \leq T \, dS + V \, dP + \mu \, dN$$

Applying the transformation constrains, we get

$$dH \leq 0 \quad \text{for} \quad dS = dP = dN = 0$$

In other words, enthalpy can never increase in isentropic, isobaric, and iso-number-particle.

Grand Potential

Grand potential is obtained by performing Legendre transform of $U(S, V, N)$ with respect to S and N

$$\begin{aligned} \mathcal{L}_{S,N} [U(S, V, N)] &= U \left[S \left(\frac{\partial U}{\partial S} \right), V, N \left(\frac{\partial U}{\partial N} \right) \right] - \frac{\partial U}{\partial S} S \left(\frac{\partial U}{\partial S} \right) \\ &\quad - \frac{\partial U}{\partial N} N \left(\frac{\partial U}{\partial N} \right) \end{aligned}$$

$$\mathcal{L}_{S,N} [U(S, V, N)] = U [S(T), V, N(\mu)] - TS(T) - \mu N(\mu)$$

Hence

$$\Omega(T, V, \mu) = U(S, V, N) - TS - \mu N$$

Due to Euler's equation, we can rewrite the grand potential it terms of pressure and volume

$$\Omega(T, V, \mu) = TS - PV + \mu N - TS - \mu N = -PV$$

Partial differential relation. We can write the total differential of Ω as

$$\begin{aligned} d\Omega &= dU - T \, dS - S \, dT - \mu \, dN - N \, d\mu \\ &= T \, dS - P \, dV + \mu \, dN - T \, dS - S \, dT - \mu \, dN - N \, d\mu \\ d\Omega &= -P \, dV - S \, dT - N \, d\mu \end{aligned}$$

And Hence

$$S = -\frac{\partial \Omega}{\partial T} \Big|_{V,\mu}, \quad P = -\frac{\partial \Omega}{\partial V} \Big|_{T,\mu}, \quad N = -\frac{\partial \Omega}{\partial \mu} \Big|_{T,V}$$

Maxwell Relations

Maxwell Relations

Since internal energy U is a state function, its Legendre transform, the thermodynamics potentials, is also a state function. One of the characteristic of state function is that their differential is an exact differential.

For constant particle $dN = 0$, we write those the state functions differential as

$$\begin{aligned} dU(S, V) &= \frac{\partial U}{\partial S} \Big|_V dS + \frac{\partial U}{\partial V} \Big|_S dV = T dS - P dV \\ dF(T, V) &= \frac{\partial F}{\partial T} \Big|_V dT + \frac{\partial F}{\partial V} \Big|_T dV = -S dT - P dV \\ dG(T, P) &= \frac{\partial G}{\partial T} \Big|_P dT + \frac{\partial G}{\partial P} \Big|_T dP = -S dT + V dP \\ dH(S, P) &= \frac{\partial H}{\partial S} \Big|_P dS + \frac{\partial H}{\partial P} \Big|_S dP = T dS + V dP \end{aligned}$$

Them being exact would imply

$$\begin{array}{ll} \frac{\partial T}{\partial V} \Big|_S = -\frac{\partial P}{\partial S} \Big|_V & \frac{\partial S}{\partial V} \Big|_T = \frac{\partial P}{\partial T} \Big|_V \\ \frac{\partial S}{\partial P} \Big|_T = -\frac{\partial V}{\partial T} \Big|_P & \frac{\partial T}{\partial P} \Big|_S = \frac{\partial V}{\partial S} \Big|_P \end{array}$$

Fundamental Set

Definition. Three fundamental set are: heat capacity at constant volume C_V , adiabatic compressibility κ_S , and adiabatic thermal expansion α_S ; which are defined as follows.

$$C_V = \frac{\partial Q}{\partial T} \Big|_V = \frac{\partial U}{\partial T} \Big|_V, \quad \kappa_S = -\frac{1}{V} \frac{\partial V}{\partial P} \Big|_S, \quad \alpha_s = \frac{1}{V} \frac{\partial V}{\partial T} \Big|_S$$

Primary Set

Definition. Primary set also contain three parametes: heat capacity at constant pressure C_P , isothermal compressibility κ_T , and isobaric thermal expansion α_S ; which are defined as follows.

$$C_P = \frac{\partial Q}{\partial T} \Big|_P = \frac{\partial H}{\partial T} \Big|_P, \quad \kappa_T = -\frac{1}{V} \frac{\partial V}{\partial P} \Big|_P, \quad \alpha_s = \frac{1}{V} \frac{\partial V}{\partial T} \Big|_P$$

Statistical Mechanics

Kinetic Theory

Maxwell Distribution

Maxwell assumes that the random velocity of particles can be described by some probability distribution. He then derived the formula for average number of particles whose velocity lies between $(\mathbf{v}, \mathbf{v} + d\mathbf{v})$. The single-particle distribution function $F(\mathbf{v})$ is given by Maxwell distribution:

$$F(\mathbf{v}) = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{mv^2}{2k_B T} \right)$$

To find the probability of N particles within interval (v_1, v_2) , we then integrate that probability function

$$\int_{v_1}^{v_2} N \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{mv^2}{2k_B T} \right) d^3\mathbf{v}$$

where $d^3\mathbf{v} = dv_x dv_y dv_z$. This can be simplified into

$$4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{v_1}^{v_2} v^2 \exp \left(-\frac{mv^2}{2k_B T} \right) dv$$

Maxwell Distribution Derivation

Maxwell first noted that the distribution function $F(\mathbf{v})$ with respect to x -axis does not affect $F(\mathbf{v})$ with respect to y -axis and z -axis, since they are at right angle, orthogonal, and independent. Hence, He wrote that a particle velocity lies at $(\mathbf{v}, \mathbf{v} + d\mathbf{v})$ as

$$F(\mathbf{v}) d^3\mathbf{v} = f(v_x) f(x_y) f(v_z) dx dy dz$$

Then also argued that the probability only depend on the magnitude of \mathbf{v} , thus

$$f(v_x) f(x_y) f(v_z) = g(v_x^2 + v_y^2 + v_z^2)$$

should apply. This functional equation is solved by

$$f(\alpha) = Be^{-A\alpha^2} d\alpha$$

Substituting this solution back, we obtain

$$F(\mathbf{v}) = B \exp [-A (v_x^2 + v_y^2 + v_z^2)]$$

All that left is normalization

$$\int_{\mathbb{R}^3} B \exp [-A (v_x^2 + v_y^2 + v_z^2)] d^3\mathbf{v} = 1$$

The integral may be evaluated as three product of the same integral

$$\int_{\mathbb{R}^3} \exp [-A (v_x^2 + v_y^2 + v_z^2)] d^3\mathbf{v} = \left(\int_{-\infty}^{\infty} e^{-A\alpha^2} d\alpha \right)^3$$

This is Gaussian integral if $A = 1$, since it is not however, we substitute $\omega = A\alpha^2$ and $d\omega = \sqrt{A}d\alpha$

$$\int_{\mathbb{R}^3} \exp[-A(v_x^2 + v_y^2 + v_z^2)] d^3\mathbf{v} = \left(\frac{1}{\sqrt{A}} \int_{-\infty}^{\infty} e^{-A\omega^2} d\omega \right)^3 = \left(\frac{\pi}{2} \right)^{3/2}$$

It follows that the normalization constant is $B = (A/\pi)^{3/2}$. Putting it all together

$$F(\mathbf{v}) = \left(\frac{A}{\pi} \right)^{3/2} e^{-Av^2}$$

with $v^2 = v_x^2 + v_y^2 + v_z^2$. All that left then is to find the value of A , which is determined by some physical quantity—for no mathematics technique can determine the value of A .

To do so, let us do some physics. Consider an area orthogonal to x -axis dA of a container V with N particles of gases. The number of particles moving at positive x -axis is

$$dN = \frac{1}{V} N dV = \frac{Nv_{x+}}{V} dt dA$$

where dV is the volume occupied by dN particle

$$dV = v_{x+} dt dA$$

Each particle hits the wall with momentum p and reflected—perfectly—back, thus changing its momentum

$$p = mv_{x+} \implies dp = 2mv_{v+}$$

Hence the total change of momentum of particles dN

$$dp_x = dp dN = \frac{2mv_{x+}^2 N}{V} dt dA$$

Since force is the change of momentum, we can say

$$F_x = \frac{dp_x}{dt}$$

Finally we can determine the one of macroscopic observable, which is pressure

$$P = \frac{F_x}{dA} = \frac{2mN}{V} \langle v_{x+}^2 \rangle$$

The expression for pressure P is not yet complete. We need to evaluate the term $\langle v_{x+}^2 \rangle$. To do so, consider an observable $G(\mathbf{v})$, which is a function of v alone. The observed value $\langle G(\mathbf{v}) \rangle$ is

$$\langle G(\mathbf{v}) \rangle = \int_{\mathbb{R}^3} G(\mathbf{v}) F(\mathbf{v}) d^3\mathbf{v}$$

Since both G and F are a function of v alone, the integral can be easily evaluated in spherical coordinate

$$\langle G(\mathbf{v}) \rangle = \int_0^{2\pi} \int_0^\pi \int_0^\infty G(v) F(v) v^2 \sin \theta dv d\theta d\phi = 4\pi \int_0^\infty v^2 G(v) F(v) dv$$

Next we will determine the expectation value of $\langle v \rangle$ and $\langle v^2 \rangle$. For $\langle v \rangle$, we have

$$\langle v \rangle = \frac{4A^{3/2}}{\sqrt{\pi}} \int_0^\infty v^3 e^{-Av^2} dv = \frac{2A^{3/2}}{\sqrt{\pi A^4}} \Gamma(2) = \frac{2}{\sqrt{A\pi}}$$

As for $\langle v^2 \rangle$, we find

$$\langle v^2 \rangle = \frac{4A^{3/2}}{\sqrt{\pi}} \int_0^\infty v^4 e^{-Av^2} dv = \frac{2A^{3/2}}{\sqrt{\pi A^5}} \Gamma\left(\frac{5}{2}\right) = \frac{3}{2A}$$

Eliminating A

$$\begin{cases} \frac{1}{A} = \frac{\pi}{4} \langle v \rangle^2 \\ \frac{1}{A} = \frac{2}{3} \langle v^2 \rangle \end{cases} \quad \langle v^2 \rangle = \frac{3\pi}{8} \langle v \rangle^2$$

As we stated before, our choice of axis is the one such that they are orthogonal, and independent. Thus,

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{\langle v_x^2 + v_y^2 + v_z^2 \rangle}{3}$$

Since $\langle v_{x+}^2 \rangle = \langle v_x^2 \rangle / 2$

$$\langle v_{x+}^2 \rangle = \frac{\langle v^2 \rangle}{6}$$

Substituting this into our expression for P

$$P = \frac{mN}{3V} \langle v^2 \rangle = \frac{2N}{3V} u$$

where u is the average kinetic energy per particles

$$u = \frac{1}{2} m \langle v^2 \rangle$$

The equation above implies that for two gases with the same pressure, the equation

$$\frac{m_1 N_1}{3V_1} \langle v_1^2 \rangle = \frac{m_2 N_2}{3V_2} \langle v_2^2 \rangle$$

should apply. Since we are considering an ideal gas, we can therefore invoke Avogadro's hypothesis and obtain

$$m_1 \langle v_1^2 \rangle = m_2 \langle v_2^2 \rangle$$

In other words, ideal gas with the same mass, number of particles, pressure, and volume, have the same amount of kinetic energy and obey both our equation of pressure P and kinetic energy u . Now, using the equation of ideal gas, we have the relation

$$\frac{Nk_b T}{V} = \frac{mN}{3V} \langle v^2 \rangle = \frac{2N}{3V} u$$

Solving for u and $\langle v^2 \rangle$

$$u = \frac{3}{2} k_b T \quad \text{and} \quad \langle v^2 \rangle = 3 \frac{k_b T}{m}$$

Result for u also prove the same conclusion obtained from thermodynamics. Finally, we can solve for A by using both results we obtained form $\langle v^2 \rangle$

$$\langle v^2 \rangle = 3 \frac{k_b T}{m} = \frac{3}{2A} \implies A = \frac{m}{2k_B T}$$

To put a nice little bow over everything, we write the complete form of Maxwell distribution

$$F(\mathbf{v}) = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{mv^2}{2k_B T} \right) \blacksquare$$

where, as before, $v^2 = v_x^2 + v_y^2 + v_z^2$

Maxwell Distribution for Relative Velocities

Maxwell distribution also works on composite system. This is due to it also works on relative velocities. We shall prove this.

Consider two system with N_1 and N_2 Particles. We then want to find the probability of pairs of particles whose relative velocity is \mathbf{V} . We define such probability density function as

$$\int_{\mathbb{R}^3} G(\mathbf{V}) d^3\mathbf{V} = \iint_{\mathbb{R}^3} N_1 N_2 F_1(\mathbf{v}) F_2(\mathbf{v} + \mathbf{V}) d^3\mathbf{v} d^3\mathbf{V}$$

To avoid ambiguity, we shall write it more explicitly as

$$G(\mathbf{V}) = N_1 N_2 \left(\frac{m_1 m_2}{4\pi^2 k_B^2 T_1 T_2} \right)^{3/2} \exp \left[-\frac{m_1}{2k_B T_1} (v_x^2 + v_y^2 + v_z^2) \right] \\ \exp \left[-\frac{m_2}{2k_B T_2} (\{v_x + V_x\}^2 + \{v_y + V_y\}^2 + \{v_z + V_z\}^2) \right]$$

Then, as is the case from before, the integral can be evaluated as product of three identical integrals

$$\int_{\mathbb{R}^3} G(\mathbf{V}) d^3\mathbf{V} = N_1 N_2 \left(\frac{m_1 m_2}{4\pi^2 k_B^2 T_1 T_2} \right)^{3/2} \\ \int_{\mathbb{R}^3} \left[\int_{-\infty}^{\infty} \exp \left(-\frac{m_1}{2k_B T_1} \omega^2 - \frac{m_2}{2k_B T_2} \{\omega + \Omega\}^2 \right) d\omega \right]^3 d^3\mathbf{V}$$

... Scary integrals. Let's first try to evaluate the term inside square parenthesis

$$\int_{-\infty}^{\infty} \exp \left[- \left(\frac{m_1}{2k_B T_1} + \frac{m_2}{2k_B T_2} \right) \omega^2 - 2 \frac{m_2}{2k_B T_2} \Omega \omega - \frac{m_2}{2k_B T_2} \Omega^2 \right] d\omega$$

Since the last term is a constant, we can take it outside the integral

$$\exp \left[-\frac{m_2}{2k_B T_2} \Omega^2 \right] \int_{-\infty}^{\infty} \exp \left[- \left(\frac{m_1 T_2 + m_2 T_1}{2k_B T_1 T_2} \right) \omega^2 - \frac{m_2 \Omega}{k_B T_2} \omega \right] d\omega$$

The integral itself can be evaluated using the general form of Gaussian integral

$$\int_{-\infty}^{\infty} \exp(-\alpha x^2 + \beta x + \gamma) dx = \sqrt{\frac{\pi}{\alpha}} \exp\left(\frac{\beta^2}{4\alpha} + \gamma\right)$$

Using the equation above

$$\exp\left[-\frac{m_2}{2k_B T_2} \Omega^2\right] \exp\left[\Omega^2 \frac{m_2^2}{k_B^2 T_2^2} \frac{1}{4} \frac{2k_B T_1 T_2}{m_1 T_2 + m_2 T_1}\right] \left[\pi \frac{2k_B T_1 T_2}{m_1 T_2 + m_2 T_1}\right]^{1/2}$$

Combining the exponent, we get

$$\exp\left[\Omega^2 \left(\frac{m_2^2 k_B T_1 T_2}{2k_B T_2^2 (m_1 T_2 + m_2 T_1)} - \frac{m_2}{2k_B T_2}\right)\right] \left[\pi \frac{2k_B T_1 T_2}{m_1 T_2 + m_2 T_1}\right]^{1/2}$$

Next simply evaluate the terms inside parenthesis

$$\exp\left[\Omega^2 \left(\frac{m_2 \{m_2 k_B T_1 T_2 - m_1 k_B T_2 - m_2 k_B T_1 T_2\}}{2k_B T_2^2 (m_1 T_2 + m_2 T_1)}\right)\right] [\dots]^{1/2}$$

where I have taken some liberties to not write the last term constant due to \hbox overfull problem. Anyway, we obtain

$$\exp\left[-\frac{m_2 m_1 k_B T_2 T_2}{2k_B T_2^2 (m_1 T_2 + m_2 T_1)} \Omega^2\right] \left[\pi \frac{2k_B T_1 T_2}{m_1 T_2 + m_2 T_1}\right]^{1/2}$$

Before substituting back into our original integral, note that Ω is the dummy variable we used for the term \mathbf{V} ; or rather V_i , where i is i -th component of Cartesian coordinate. Hence,

$$\begin{aligned} \int_{\mathbb{R}^3} G(\mathbf{V}) d^3\mathbf{V} &= N_1 N_2 \left(\frac{m_1 m_2}{4\pi^2 k_B^2 T_1 T_2}\right)^{3/2} \\ \int_{\mathbb{R}^3} \left[\exp\left[-\frac{m_2 m_1 k_B T_2 T_2}{2k_B T_2^2 (m_1 T_2 + m_2 T_1)} V_i^2\right] \left[\frac{2\pi k_B T_1 T_2}{m_1 T_2 + m_2 T_1}\right]^{1/2} \right]^3 d^3\mathbf{V} \end{aligned}$$

Recall that $V^2 = V_x^2 + V_y^2 + V_z^2$, then we can simply our equation

$$\begin{aligned} \int_{\mathbb{R}^3} G(\mathbf{V}) d^3\mathbf{V} &= \int_{\mathbb{R}^3} N_1 N_2 \left(\frac{1}{2\pi k_B} \frac{m_1 m_2}{m_1 T_2 + m_2 T_1}\right)^{3/2} \\ &\quad \exp\left[-\frac{m_2 m_1}{2(m_1 T_2 + m_2 T_1)} V^2\right] d^3\mathbf{V} \end{aligned}$$

Since we are integrating over the same limit, we can conclude that

$$G(\mathbf{V}) = N_1 N_2 \left(\frac{1}{2\pi k_B} \frac{m_1 m_2}{m_1 T_2 + m_2 T_1}\right)^{3/2} \exp\left[-\frac{m_2 m_1}{2(m_1 T_2 + m_2 T_1)} V^2\right]$$

The equation above shows that the probability distribution function for composite system has the same form as Maxwell distribution, hence Maxwell distribution function also works on composite system. \square

Boltzmann Entropy

Ludwig Boltzmann



Figure: Ludwig Boltzmann, by P. L. Dutton

Discrete Energy Levels

In this model, Boltzmann postulates in a gas of N particle, that each particle has discretely spaced value of energy kinetic ϵP . The permutation of configuration $E_k|N \equiv E_1, \dots, E_N$ denote distinct configuration. State of system is then defined as set $n_k \equiv n_0, \dots, n_P$ where n_k is the number of molecule having $k\epsilon$ energy level.

Each configuration must also obey the following restriction.

$$\sum_{k=0}^P n_k = N, \quad U = \epsilon \sum_{k=0}^P k n_k$$

or simply

$$\sum_{k=0}^P n_k = N, \quad \sum_{k=0}^P k n_k = L$$

Table: system with two possible energy level $(0, \epsilon)$

State $n_{k P} = (n_0, n_1)$	Configuration $E_k N = (E_1, E_2, E_3)$
$(3, 0)$	$(0, 0, 0)$
$(2, 1)$	$(\epsilon, 0, 0), (0, \epsilon, 0), (0, 0, \epsilon)$
$(1, 2)$	$(\epsilon, \epsilon, 0), (\epsilon, 0, \epsilon), (0, \epsilon, \epsilon)$
$(0, 3)$	$(\epsilon, \epsilon, \epsilon)$

The first restriction says that each configuration is in such way that the sum of each element n_k is the total number of particle N , while the second restriction rule the total energy U of the system.

To determine the total configuration of a specific configuration $n_{k|P}$, we use

$$D(N, P, n_{k|P}) = N! \left(\prod_{i=0}^P n_i! \right)^{-1}$$

To find the total configuration of a system, we're then summing all possible state that can be achieved by the system in question. After that, we obtain

$$D_T(N, P) = (P + 1)^N$$

For a special case when $L \leq P$, the equation above turns into

$$\mathcal{P}(N, L) = \frac{1}{L!} \frac{(N + L - 1)!}{(N - 1)!}$$

Table: State and configuration a system with $N = P = 7$, and $L \leq P$

State $n_{k P} = (n_0, n_1, n_2, n_3, n_4, n_5, n_6, n_7)$	Number of configuration $D(N, P, n_{k P})$
$(6, 0, 0, 0, 0, 0, 0, 1)$	$\frac{7!}{6!0!0!0!0!0!1!} = 7$
$(5, 1, 0, 0, 0, 0, 1, 0)$	$\frac{7!}{5!1!0!0!0!0!1!0!} = 42$
$(5, 0, 1, 0, 0, 1, 0, 0)$	$\frac{7!}{5!0!1!0!0!1!0!0!} = 42$
$(5, 0, 0, 1, 1, 0, 0, 0)$	$\frac{7!}{5!0!0!1!1!0!0!0!} = 42$
$(4, 2, 0, 0, 0, 1, 0, 0)$	$\frac{7!}{4!2!0!0!0!1!0!0!} = 105$
$(4, 1, 1, 0, 1, 0, 0, 0)$	$\frac{7!}{4!1!1!0!1!0!0!0!} = 210$
$(4, 0, 2, 1, 0, 0, 0, 0)$	$\frac{7!}{4!0!2!1!0!0!0!0!} = 105$

(4, 1, 0, 2, 0, 0, 0, 0)	$\frac{7!}{4!1!0!2!0!0!0!} = 105$
(3, 3, 0, 0, 1, 0, 0, 0)	$\frac{7!}{3!3!0!0!1!0!0!0!} = 140$
(3, 2, 1, 1, 0, 0, 0, 0)	$\frac{7!}{3!2!1!1!0!0!0!0!} = 420$
(3, 1, 3, 0, 0, 0, 0, 0)	$\frac{7!}{3!1!3!0!0!0!0!0!} = 140$
(2, 4, 0, 1, 0, 0, 0, 0)	$\frac{7!}{2!4!0!1!0!0!0!0!} = 105$
(2, 3, 2, 0, 0, 0, 0, 0)	$\frac{7!}{2!3!2!0!0!0!0!0!} = 210$
(1, 5, 1, 0, 0, 0, 0, 0)	$\frac{7!}{1!5!1!0!0!0!0!0!} = 42$
(0, 7, 0, 0, 0, 0, 0, 0)	$\frac{7!}{0!7!0!0!0!0!0!0!} = 1$

Real™ System. Boltzmann postulates that thermal equilibrium correspond to state with the largest number of configuration. The previous example with $N = 7$ we know that the state in question is $n_{k|P} = (3, 2, 1, 1, 0, 0, 0, 0)$. In real system with large N , it is impossible to determine the equilibrium state using method above.

By Stirling's formula, the logarithm of $D(N, P, n_{k|P})$ is expressed as

$$\ln [D(N, P, n_{k|P})] = N \ln N - N - \sum_{k=0}^P (n_k \ln n_k - n_k)$$

Using equation above, Boltzmann then derive the logarithm of the largest number of configuration, which of course correspond to equilibrium state. The logarithm in question expressed as

$$\ln(\mathcal{P}_{\max}) = (N + L) \ln(N + L) - L \ln(L) - N \ln(N)$$

The number of particle n_k inside configuration above is

$$n_k = N(1 - x)x^k$$

where $x = L/(L + N)$. The expression n_k above maximize the D . If the average kinetic energy $u = U/N = L\epsilon/N$ is much bigger separation ϵ , n_k can be approximated as

$$n_k = \frac{N\epsilon}{u + \epsilon} \left(1 + \frac{\epsilon}{u}\right)^{-k} \approx \frac{N\epsilon}{u} e^{-k\epsilon/u}$$

Proof. To find the desired maximum function, we use Lagrange's multiplier method. We will maximize $D(N, P, n_{k|P})$ for $P \rightarrow \infty$

$$F(n_k) = \ln [D(N, P, n_{k|P})] - \sum_{k=0}^P (\alpha + k\gamma)n_k$$

with respect to n_k . Invoking Stirling's formula for $\ln[D(N, P, n_{k|P})]$, we have

$$F(n_k) = N \ln N - N - \sum_{k=0}^P (\ln n_k - 1 + \alpha + k\gamma)n_k$$

We will now begin the maximization by

$$\begin{aligned} \frac{\partial F}{\partial n_k} = 0 &\implies \frac{\partial}{\partial n_k} (n_k \ln n_k) - 1 + \alpha + k\gamma &= 0 \\ &\ln n_k + \alpha + k\gamma &= 0 \end{aligned}$$

Solving for n_k

$$n = e^{-\alpha-k\gamma} = (e^{-\alpha})(e^{-\gamma})^k$$

for convenience's sake, we use

$$n_k = Ax^k \quad \text{with } A = e^{-\alpha} \wedge x = e^{-\gamma}$$

Using this result for n_k , the first restriction can be written as

$$\sum_{k=0}^P n_k = N \implies A \sum_{k=0}^P x^k = N$$

the series in the equation above is a simple geometric series

$$\sum_{k=0}^P x^k = 1 + x + x^2 + \dots + x^P = \sum_{k=1}^{P+1} x^{k-1}$$

which can be evaluated as

$$A \frac{1 - x^{P+1}}{1 - x} = N$$

Hence

$$A = N \frac{1 - x}{1 - x^{P+1}}$$

Whereas the second restriction reads

$$\sum_{k=0}^P k n_k = L \implies A \sum_{k=0}^P k x^k = L$$

This series is more complicated than before, however it still might be evaluated into

$$L = Ax \frac{\{[P(x-1) - 1]x^P + 1\}}{(x-1)^2}$$

where we have invoked WolframAlpha to evaluate the said series. For a realTM system, we have $P \rightarrow \infty$, therefore those two expression turn into

$$A = \lim_{P \rightarrow \infty} N \frac{1 - x}{1 - \exp(-\gamma P - \gamma)} = N(1 - x)$$

and

$$L = \frac{Ax}{(x-1)^2} \lim_{P \rightarrow \infty} [(P(x-1)e^{-\gamma P} + 1) + 1] = -\frac{Nx(x-1)}{(x-1)^2} = \frac{Nx}{1-x}$$

Rearranging the equation above

$$x = \frac{L}{L + N}$$

Since have found the expression for A , L , and x , we can then write the complete expression for n_k

$$n_k = \frac{N(1-x)}{1-x^{P+1}} x^k$$

applying the condition for real system, we have n_k which maximize the configuration

$$n_k = N(1-x)x^k \lim_{P \rightarrow \infty} \frac{1}{1 - \exp[-\gamma(P+1)]} = N(1-x)x^k$$

Substituting n_k we just obtained inside the expression of $\ln D$, we get

$$\ln(\mathcal{P}_{\max}) = -N \left(\ln(1-x) + \frac{x}{1-x} \ln(x) \right)$$

expressing the equation above in terms of L and N to get

$$\ln(\mathcal{P}_{\max}) = (N+L) \ln(N+L) - L \ln(L) - N \ln(N)$$

Result. We shall now discuss the result of Boltzmann derivation. The case in this discussion will be the same as previously, which is $N = P = 7, L \leq P$. Here we will compare those three result:

1. **Small system.** By this consideration, we know the equilibrium state represented by the following state

$$n_{k|P} = (3, 2, 1, 1, 0, 0, 0, 0)$$

which has 420 number of configuration.

2. **Large system.** Tools we used in this consideration are Stirling's approximation and Lagrange multiplier. We obtain the formula for number of particle n_k with $k\epsilon$ energy

$$n_k = \frac{N(1-x)}{1-x^{P+1}} x^k$$

where x is obtained by solving the following equation

$$(NP - L)x^{P+2} - (NP + N - L)x^{P+1} + (L + N) = 0.$$

Boltzmann solved the equation numerically and obtained $x = 0.5078125$.

3. **Large system with large P approximation.** The equation for n_k in this consideration is written as

$$n_k = N(1-x)x^k$$

Table: The result of those three considerations. Quite accurate except few numbers.

k	n_k for small system	n_k for large system	Same but with large P approximation
0	3	3.4535	3.5
1	2	1.7574	1.75
2	1	0.8943	0.875
3	1	0.4551	0.4375
4	0	0.2316	0.2187
5	0	0.1178	0.10937
6	0	0.0599	0.05468
7	0	0.0304	0.02734

Continuous Energy Distribution

Assume continuous energy E within interval $(0, \infty)$, with a space of ϵ . The function $f(E)$ denote the number of atoms per unit energy. The density function $f(E)$ for continuous energy levels at equilibrium is given by

$$f(E) = \frac{N}{u} e^{-E/u}$$

Permutability measure is defined as

$$\Omega = - \int_0^\infty f(E) \ln [f(E)] dE$$

which, on using the given expression for density function evaluates into

$$\Omega = N(1 + \ln u - \ln N)$$

Derivation. Let n_k be the number of atoms whose energy lies between $(k\epsilon, k\epsilon + \epsilon)$. For any positive integer k ,

$$n_k = \epsilon f(k\epsilon)$$

By taking the limit of $\epsilon \rightarrow 0$, n_k now denote the number of atoms whose energy lies between $(E, E + dE)$

$$n = f(E) \lim_{\epsilon \rightarrow 0} \epsilon$$

As it the case with discrete model, we have the following restriction

$$\sum_{k=0}^P n_k = N, \quad \epsilon \sum_{k=0}^P k n_k = Nu$$

By using the expression for n_k when $\epsilon \rightarrow 0$ these restrictions now read as

$$\int_0^\infty f(E) dE = N, \quad \int_0^\infty E f(E) dE = Nu$$

Now we consider the expression for number of configuration in the limit $D \rightarrow \mathcal{P}$. The expression for the logarithm of D written as

$$\ln D = N \ln N - N - \sum_{k=0}^{\infty} (n_k \ln n_k - n_k)$$

By taking the limit $\epsilon \rightarrow 0$, we have

$$\begin{aligned}\ln \mathcal{P} &= N \ln N - N - \int_0^\infty [f(E) \ln(n_k) - f(E)] dE \\ &= N \ln N - N - \int_0^\infty f(E) \ln[f(E)] dE - \lim_{\epsilon \rightarrow 0} \int_0^\infty f(E) \ln(\epsilon) dE \\ &\quad + \int_0^\infty f(E) dE \\ \ln \mathcal{P} &= N \ln N - \int_0^\infty f(E) \ln[f(E)] dE - N \lim_{\epsilon \rightarrow 0} \ln(\epsilon)\end{aligned}$$

Recall that equilibrium state correspond to the largest number of configuration. Although the equation above, due to the last term, diverges; it can be ignored since maximization does not concern constant. In essence, we what to maximize the logarithm of \mathcal{P} by varying the expression for $f(E)$. Therefore, we maximize the quantity of

$$\Omega \equiv - \int_0^\infty f(E) \ln[f(E)] dE$$

which is defined as permutability measure, with N and Nu constraint. By the Lagrange multiplier method, we have the following auxiliary function

$$F(f) = \int_0^\infty [f \ln(f) + \lambda_1 f + \lambda_2 E f] dE$$

Then, we set its derivative to zero

$$\frac{dF}{df} = \int_0^\infty [\ln f + 1 + \lambda_1 + \lambda_2 E] dE = 0$$

One possible way for an integral to be zero is that the integrand is zero, hence we have

$$\ln(f) + 1 + \lambda_1 + \lambda_2 E = 0$$

which implies

$$\begin{aligned}f(E) &= \exp(-1 - \lambda_1 - \lambda_2 E) \\ f(E) &= Ce^{-\lambda_2 E}\end{aligned}$$

On Using this expression, N constraint now may be evaluated as

$$N = \int_0^\infty Ce^{-\lambda_2 E} dE = \frac{Ce^{\lambda_2 E}}{\lambda_2} \Big|_0^\infty = \frac{C}{\lambda_2}$$

As for Nu constraint

$$\begin{aligned}Nu &= \int_0^\infty E Ce^{-\lambda_2 E} dE = Ce^{-\lambda_2 E} \left(\frac{E}{-\lambda_2} - \frac{1}{\lambda_2^2} \right) \Big|_0^\infty \\ &= \frac{CEe^{\lambda_2 E}}{\lambda_2} \Big|_0^\infty + \frac{Ce^{-\lambda_2 E}}{\lambda_2^2} \Big|_0^\infty = \frac{C}{\lambda_2^2} = \frac{N}{\lambda_2}\end{aligned}$$

We have

$$C = \frac{N}{u} \quad \wedge \quad \lambda_2 = \frac{1}{u}$$

Hence

$$f(E) = Ce^{-\lambda_2 E} = \frac{N}{u} e^{-E/u} \quad \blacksquare$$

Now we evaluate the expression permutability measure

$$\begin{aligned} \Omega &= - \int_0^\infty \frac{N}{u} e^{-E/u} \ln \left[\frac{N}{u} e^{-E/u} \right] dE \\ &= - \int_0^\infty \frac{N}{u} e^{-E/u} \left[\ln \left(\frac{N}{u} \right) - \frac{E}{u} \right] dE \\ &= Ne^{E/u} \ln \left(\frac{N}{u} \right) \Big|_0^\infty + \frac{N}{u^2} (-Eu - u^2) e^{E/u} \Big|_0^\infty \\ \Omega &= -N \ln \left(\frac{N}{u} \right) + N = N(1 + \ln U - \ln N) \quad \blacksquare \end{aligned}$$

Velocity Distribution

Consider continuous varying value of velocity \mathbf{v} within $(-\infty, \infty)$. The number of particle per unit interval is given by

$$f(\mathbf{v}) = N \left(\frac{3m}{4\pi u} \right)^{3/2} \exp \left(-\frac{3mv^2}{4u} \right)$$

Using the relation for gas ideal $u = 3k_B T/2$, one can obtain the same distribution function that Maxwell derived

$$f(\mathbf{v}) = N \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{mv^2}{2k_B T} \right)$$

Derivation. Let $n_{\mathbf{k}}$ be the number of particle whose velocity lies within $(\epsilon\mathbf{v}, \epsilon\mathbf{v} + \epsilon)$, so

$$n_{\mathbf{k}} = \epsilon f(\mathbf{kv})$$

and as $\epsilon \rightarrow 0$

$$n = f(\mathbf{v}) \lim_{\epsilon \rightarrow 0} \epsilon = f(\mathbf{v}) d^3 v$$

As before, we want to find the equilibrium distribution function, $f(\mathbf{v})$ in this case, by maximizing the said distribution function, constrained by N and Nu function. The N constraint simply evaluate into

$$N = \int_{\mathbb{R}^3} f(\mathbf{v}) d^3 v$$

Recall that Nu stands for total energy. In the present case, we involve velocity into our consideration, hence the energy in question is the kinetic energy, which is evaluated by

$$Nu = \frac{m}{2} \langle v^2 \rangle = \frac{m}{2} \int_{\mathbb{R}^3} v^2 f(\mathbf{v}) d^3 v$$

Since $f(\mathbf{v})$ is a function of v alone, we can make the change of variable $d^3 v = v^2 \sin \theta dv ; d\theta d\phi$. Thus, our constraint equations read

$$4\pi \int_0^\infty v^2 f(\mathbf{v}) dv = N, \quad 4\pi \int_0^\infty v^4 f(\mathbf{v}) dv = Nu$$

We then consider the number of configuration \mathcal{P} , which is given by

$$\mathcal{P} = N! \left(\prod_{\mathbf{k}=-\infty}^{\infty} n_{\mathbf{k}}! \right)$$

Taking the logarithm and applying Stirling's approximation,

$$\ln \mathcal{P} = N \ln N - N - \sum_{\mathbf{k}=-\infty}^{\infty} (n_{\mathbf{k}} \ln n_{\mathbf{k}} - n_{\mathbf{k}})$$

Taking the limit $\epsilon \rightarrow 0$

$$\begin{aligned} \ln \mathcal{P} &= N \ln N - N - \int_{\mathbb{R}^3} f(\mathbf{v}) \ln[f(\mathbf{v})] d^3v - \lim_{\epsilon \rightarrow 0} \int_{\mathbb{R}^3} f(\mathbf{v}) \ln(\epsilon) d^3v \\ &\quad + \int_{\mathbb{R}^3} f(\mathbf{v}) d^3v \\ \ln \mathcal{P} &= N \ln N - \int_{\mathbb{R}^3} f(\mathbf{v}) \ln[f(\mathbf{v})] d^3v - N \lim_{\epsilon \rightarrow 0} \ln(\epsilon) \end{aligned}$$

To maximize the logarithm of \mathcal{P} , we defined permutability measure by

$$\Omega = - \int_{\mathbb{R}^3} f(\mathbf{v}) \ln[f(\mathbf{v})] d^3v$$

and maximize it with the N and Nu constraint. We use the first form of those constraints, since they look simpler, and use the second form to evaluate the resulting maximized function, since we can't evaluate it using the first form. Anyway, the auxiliary function reads as

$$F(f) = \int_{\mathbb{R}^3} \left[f \ln(f) + \lambda_1 f + \lambda_2 \frac{m}{2} v^2 f \right] d^3v$$

As for its derivative,

$$\frac{dF}{df} = \int_{\mathbb{R}^3} \left[\ln(f) + 1 + \lambda_1 + \lambda_2 \frac{m}{2} v^2 \right] d^3v = 0$$

which implies

$$\ln(f) + 1 + \lambda_1 + \lambda_2 \frac{m}{2} v^2 = 0$$

Thus

$$f(\mathbf{v}) = \exp \left(-1 - \lambda_1 - \lambda_2 \frac{m}{2} v^2 \right) = C \exp \left(-\frac{\lambda_2 m}{2} v^2 \right)$$

We now use this to evaluate both constraints and determine the value for each constant. For the N constraint

$$\begin{aligned} N &= 4\pi \int_0^\infty v^2 C \exp \left(-\frac{\lambda_2 m}{2} v^2 \right) dv = \frac{4\pi C}{2} \left(\frac{2}{m \lambda_2} \right)^{3/2} \frac{\sqrt{\pi}}{2} \\ &= C \left(\frac{2\pi}{m \lambda_2} \right)^{3/2} \end{aligned}$$

Then the Nu constraint

$$\begin{aligned} Nu &= 4\pi \int_0^\infty v^4 C \exp \left(-\frac{\lambda_2 m}{2} v^2 \right) dv = \frac{4\pi C m}{4} \left(\frac{2}{m \lambda_2} \right)^{5/2} \frac{3\sqrt{\pi}}{4} \\ &= \frac{3}{4} C m \left(\frac{2\pi^{3/5}}{m \lambda_2} \right)^{5/2} \end{aligned}$$

Solving both for N and equating them

$$\begin{aligned} C \left(\frac{2\pi}{m\lambda_2} \right)^{3/2} &= \frac{3}{4u} C m \left(\frac{2\pi^{3/5}}{m\lambda_2} \right)^{5/2} \\ \frac{4u}{3} &= \frac{2m}{m\lambda_2} \\ \lambda_2 &= \frac{3}{2u} \end{aligned}$$

On using this to the previously evaluated N constraint

$$N = C \left(\frac{2\pi}{m} \frac{2u}{3} \right)^{3/2} \implies C = N \left(\frac{3m}{4\pi u} \right)^{3/2}$$

Hence

$$f(\mathbf{v}) = C \exp \left(-\frac{\lambda_2 m}{2} v^2 \right) = N \left(\frac{3m}{4\pi u} \right)^{3/2} \exp \left(-\frac{3m}{4u} v^2 \right) \blacksquare$$

6n Phase Space Distribution

Boltzmann then generalize the distribution function as a function of position and velocity $f = f(\mathbf{r}, \mathbf{v})$ such that the number of particle whose position and velocity lies within $(\mathbf{r} + d\mathbf{r}, \mathbf{v} + d\mathbf{v})$ is given by

$$n = f(\mathbf{r}, \mathbf{v}) d^3r d^3v$$

where the distribution function itself is given by

$$f(\mathbf{r}, \mathbf{v}) = \frac{N}{V} \left(\frac{3m}{4\pi u} \right)^{3/2} \exp \left(-\frac{3m}{4u} v^2 \right)$$

Boltzmann also extend the definition of permutability measure using the said distribution function into

$$\Omega = - \int_{V, \mathbb{R}^3} f(\mathbf{r}, \mathbf{v}) \ln[f(\mathbf{r}, \mathbf{v})] d^3r d^3v$$

which then evaluate into

$$\Omega = N \left[\frac{3}{2} \ln(u) + \ln(V) \right] - N \ln(N) + \frac{3}{2} N \left[\ln \left(\frac{4\pi}{3m} \right) + 1 \right]$$

Derivation. To obtain the said distribution function we begin by maximizing the permutability measure

$$\Omega = - \int f(\mathbf{r}, \mathbf{v}) \ln[f(\mathbf{r}, \mathbf{v})] d^3r d^3v$$

constrained with

$$N = \int f(\mathbf{r}, \mathbf{v}) d^3r d^3v, \quad Nu = \frac{m}{2} \int v^2 f(\mathbf{r}, \mathbf{v}) d^3r d^3v$$

By assuming that the distribution function is only a function of r and v , we can evaluate both constraints into

$$N = 16\pi^2 \int r^2 v^2 f(\mathbf{r}, \mathbf{v}) dr dv, \quad Nu = 8m\pi^2 \int r^2 v^4 f(\mathbf{r}, \mathbf{v}) dr dv$$

Some remark, this evaluation method works since we assume that the particle are uniformly distributed. By Lagrange's method, we define the auxiliary function

$$F(f) = \int \left[f \ln(f) + \lambda_1 f + \lambda_2 \frac{m}{2} v^2 f \right] d^3r d^3v$$

Setting its derivative to zero

$$\frac{dF}{df} = \int \left[\ln(f+) + 1 + \lambda_1 + \lambda_2 \frac{m}{2} v^2 \right] = 0$$

which implies

$$\ln(f) + 1 + \lambda_1 + \lambda_2 \frac{m}{2} v^2 = 0$$

Solving for f , we have the expression for our distribution function, albeit with some constant that needed to be determined

$$f = C \exp \left(-\frac{\lambda_2 m}{2} v^2 \right)$$

Now we plug into N constraint

$$\begin{aligned} N &= 16\pi^2 \int r^2 v^2 C \exp \left(-\frac{\lambda_2 m}{2} v^2 \right) dr dv \\ &= 16\pi^2 C \frac{r^3}{3} \frac{1}{2} \left(\frac{2}{\lambda_2 m} \right)^{3/2} \frac{\sqrt{\pi}}{2} = CV \left(\frac{2\pi}{\lambda_2 m} \right)^{3/2} \end{aligned}$$

and the Nu constraint

$$\begin{aligned} Nu &= 8m\pi^2 \int r^2 v^4 C \exp \left(-\frac{\lambda_2 m}{2} v^2 \right) dr dv \\ &= 8m\pi^2 C \frac{r^3}{3} \frac{1}{2} \left(\frac{2}{\lambda_2 m} \right)^{3/2} \frac{3}{4} \sqrt{\pi} = \frac{3}{4} mCV \left(\frac{2\pi^{3/5}}{\lambda_2 m} \right)^{5/2} \end{aligned}$$

Solving both for N and equating them

$$\begin{aligned} CV \left(\frac{2\pi}{\lambda_2 m} \right)^{3/2} &= \frac{3}{4u} mCV \left(\frac{2\pi^{3/5}}{\lambda_2 m} \right)^{5/2} \\ \frac{4u}{3} &= \frac{2m}{\lambda_2 m} \\ \lambda_2 &= \frac{3}{2u} \end{aligned}$$

On using this to the previously evaluated N constraint

$$N = CV \left(\frac{2\pi}{m} \frac{2u}{3} \right)^{3/2} \implies C = \frac{N}{V} \left(\frac{3m}{4\pi u} \right)^{3/2}$$

Hence

$$f(\mathbf{r}, \mathbf{v}) = C \exp\left(-\frac{\lambda_2 m}{2} v^2\right) = \frac{N}{V} \left(\frac{3m}{4\pi u}\right)^{3/2} \exp\left(-\frac{3m}{4u} v^2\right) \blacksquare$$

Now we evaluate the expression permutability measure

$$\Omega = - \int f(\mathbf{r}, \mathbf{v}) \ln[f(\mathbf{r}, \mathbf{v})] d^3 r d^3 v$$

We have Assumed that $f(\mathbf{r}, \mathbf{v})$ is independent of \mathbf{r} , thus $f(\mathbf{r}, \mathbf{v}) \rightarrow f(\mathbf{v})$ and the equation may be written as

$$\Omega = - \int 4\pi r^2 dr \int f(\mathbf{v}) \ln[f(\mathbf{v})] d^3 v = -V \int f(\mathbf{v}) \ln[f(\mathbf{v})] d^3 v$$

We evaluate this in “spherical” coordinate

$$\begin{aligned} \Omega = -4\pi V \int v^2 \frac{N}{V} \left(\frac{3m}{4\pi u}\right)^{3/2} \exp\left(-\frac{3m}{4u} v^2\right) \\ \ln \left[\frac{N}{V} \left(\frac{3m}{4\pi u}\right)^{3/2} \exp\left(-\frac{3m}{4u} v^2\right) \right] dv \end{aligned}$$

This looks hard, but it is actually very easy. Watch this.

$$\begin{aligned} \Omega = -4\pi N \left(\frac{3m}{4\pi u}\right)^{3/2} \int v^2 \exp\left(-\frac{3m}{4u} v^2\right) \\ \left[\ln \left\{ \frac{N}{V} \left(\frac{3m}{4\pi u}\right)^{3/2} \right\} - \frac{3m}{4u} v^2 \right] dv \end{aligned}$$

then

$$\begin{aligned} \Omega = -4\pi N \left(\frac{3m}{4\pi u}\right)^{3/2} \left[\ln \left\{ \frac{N}{V} \left(\frac{3m}{4\pi u}\right)^{3/2} \right\} \frac{1}{2} \left(\frac{4u}{3m}\right)^{3/2} \frac{\sqrt{\pi}}{2} \right. \\ \left. - \frac{3m}{4u} \frac{1}{2} \left(\frac{4u}{3m}\right)^{5/2} \frac{3\sqrt{\pi}}{4} \right] \end{aligned}$$

and then

$$\begin{aligned} \Omega = -4\pi N \left(\frac{3m}{4\pi u}\right)^{3/2} \left[\frac{\sqrt{\pi}}{4} \left(\frac{4u}{3m}\right)^{3/2} \ln \left\{ \frac{N}{V} \left(\frac{3m}{4\pi u}\right)^{3/2} \right\} \right. \\ \left. - \frac{3\sqrt{\pi}}{8} \left(\frac{4u}{3m}\right)^{3/2} \right] \end{aligned}$$

and then

$$\Omega = -4\pi N \left(\frac{3m}{4\pi u}\right)^{3/2} \frac{\sqrt{\pi}}{4} \left(\frac{4u}{3m}\right)^{3/2} \left[\ln \left\{ \frac{N}{V} \left(\frac{3m}{4\pi u}\right)^{3/2} \right\} - \frac{3}{2} \right]$$

and then

$$\Omega = -N \left[\ln \{N\} + \frac{3}{2} \ln \left\{ \frac{3m}{4\pi} \right\} - \ln \{V\} - \frac{3}{2} \ln \{u\} - \frac{3}{2} \right]$$

and finally then

$$\Omega = N \left[\frac{3}{2} \ln \{u\} + \ln \{V\} \right] - N \ln \{N\} + \frac{3}{2} N \left[\ln \left\{ \frac{4\pi}{3m} \right\} + 1 \right] \blacksquare$$

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