

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...

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

Proof. Trivial

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

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

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

We also assume the following quantities

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

First identity. As follows

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

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

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

Then, from the definition of temperature

$$\left. \frac{\partial S}{\partial U} \right|_{V, N_i} = \frac{1}{T} \blacksquare$$

Second identity. The identity written as

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

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

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

Then, from the first identity and the definition of pressure

$$1 = T \left. \frac{\partial S}{\partial V} \right|_{U, N_i} \frac{1}{P} \implies \left. \frac{\partial S}{\partial V} \right|_{U, N_i} = \frac{P}{T} \blacksquare$$

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

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

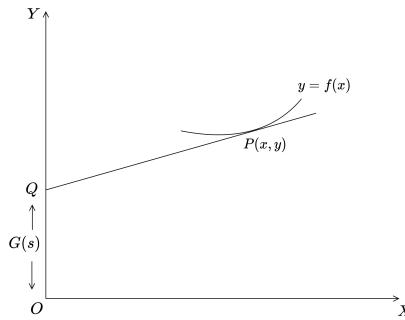


Figure: Geometric interpretation of Legendre transformation

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

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

Incomplete gamma function. Suppose the limit of the integral of gamma function is not $(0, \infty)$. We define the result function as incomplete gamma function. The first kind is the lower gamma function

$$\gamma(p, t) = \int_0^t x^{p-1} e^{-x} dx$$

while the second is the upper gamma function

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



Figure 1: Gaussian integral solved by polar method.

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.

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

$$I(0) = - \int_0^1 \frac{1}{u^2+1} du + C = 0$$

$$C = \arctan u \Big|_0^1 = \frac{\pi}{4}$$

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 have few.

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

And also for incomplete gamma integral

$$\int_0^\infty x^m \exp(-\alpha x) dx = \frac{\Gamma(m+1, s\alpha)}{\alpha^{m+1}}$$

$$\int_s^\infty x^m \exp(-\alpha x^2) dx = \frac{1}{2\alpha^{(m+1)/2}} \Gamma\left(\frac{m+1}{2}, s\alpha\right)$$

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

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

Proof of the first integral. Consider

$$\int_0^\infty x^m \exp(-\alpha x) dx$$

Substitute $\alpha x = t$ and $dx = dt/\alpha$

$$\int_0^\infty \left(\frac{t}{\alpha}\right)^m \frac{\exp(-t)}{\alpha} dt = \frac{1}{\alpha^{m+1}} \int_0^\infty x^m e^{-x} dx = \frac{\Gamma(m+1)}{\alpha^{m+1}} \blacksquare$$

Now suppose the limit is not $(0, \infty)$, say (s, ∞) . Those limits transform

$$x = s \implies t = \alpha s$$

$$x = \infty \implies t = \infty$$

Thus

$$\int_{s\alpha}^\infty \left(\frac{t}{\alpha}\right)^m \frac{\exp(-t)}{\alpha} dt = \frac{1}{\alpha^{m+1}} \int_{\alpha s}^\infty x^m e^{-x} dx = \frac{\Gamma(m+1, s\alpha)}{\alpha^{m+1}} \blacksquare$$

Proof of the second integral. Consider

$$\int_0^\infty x^m \exp(-\alpha x^2) dx$$

By substituting $t = \alpha x^2$, we have the following variable

$$x = \sqrt{\frac{t}{\alpha}} \quad \text{and} \quad dx = \frac{1}{2\sqrt{\alpha t}} dt$$

Thus our integral transforms into

$$\int_0^\infty \left(\frac{t}{\alpha}\right)^{m/2} \frac{\exp(-t)}{2\sqrt{\alpha t}} dt = \frac{1}{2\alpha^{(m+1)/2}} \int_0^\infty t^{(m+1)/2} \exp(-t) dt$$

$$= \frac{1}{2\alpha^{(m+1)/2}} \Gamma\left(\frac{m+1}{2}\right) \blacksquare$$

Now suppose the limit is not $(0, \infty)$, say (s, ∞) . Those limits transform

$$x = s \implies t = \alpha s^2$$

$$x = \infty \implies t = \infty$$

Thus

$$\begin{aligned} \int_{\alpha s^2}^{\infty} \left(\frac{t}{\alpha}\right)^{m/2} \frac{\exp(-t)}{2\sqrt{\alpha t}} dt &= \frac{1}{2\alpha^{(m+1)/2}} \int_{\alpha s^2}^{\infty} t^{(m+1)/2} \exp(-t) dt \\ &= \frac{1}{2\alpha^{(m+1)/2}} \Gamma\left(\frac{m+1}{2}, \alpha s^2\right) \quad \blacksquare \end{aligned}$$

Proof of the third integral. 404.

Proof of the fourth integral. 404.

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

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

Another form is

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

Proof of the first relation. Putting $x = y/a$ and $dx = dy/a$

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

Proof of the second relation. 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

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

Incomplete beta function. Defined as follows.

$$B_t(p, q) = \int_0^t x^{p-1} (1-x)^{q-1} dx$$

This definition is using the first definition of beta function, so for any other definition, say the trigonometric form, we must then change it back into our first definition using whatever substitution. There is also the ratio

$$I_t = \frac{B_t(p, q)}{B(p, q)}$$

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.

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

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

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

Proof of the second relation. 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 of the first relation. The first relation is quite easy to prove. Consider

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

then

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

Proof of the second relation. 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.

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

Striling's Formula

Used to express $n!$ or its logarithm for large n .

$$n! \sim n^n e^{-n} \sqrt{2\pi n}$$

And for its logarithm

$$\ln n! = n \ln n - n$$

Proof. By the definition

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

We then rewrite it as

$$p! = \int_0^\infty \exp(p \ln x - x) dx$$

Substitute $x = p + y\sqrt{p}$ and $dx = \sqrt{p} dy$

$$p! = \int_{-\sqrt{p}}^\infty \exp[p \ln(p + y\sqrt{p}) - p - y\sqrt{p}] \sqrt{p} dy$$

The logarithm above may be expressed as

$$\ln(p + y\sqrt{p}) = \ln p + \ln\left(1 + \frac{y}{\sqrt{p}}\right)$$

Recall the infinite series representation of

$$\ln(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \dots$$

Hence

$$\ln(p + y\sqrt{p}) = \ln p + \frac{y}{\sqrt{p}} - \frac{y^2}{2p} + \frac{y^3}{3p^{3/2}} - \dots$$

Then substituting back

$$p! = \int_{-\sqrt{p}}^\infty \exp\left[p \ln p + \left(\frac{py}{\sqrt{p}} - \frac{py^2}{2p} + \frac{py^3}{3p^{3/2}} - \dots\right) - p - y\sqrt{p}\right] \sqrt{p} dy$$

Pulling the constant out of the integral

$$p! = p^p e^{-p} \sqrt{p} \int_{-\sqrt{p}}^\infty \exp\left[-\frac{y^2}{2} + \frac{y^3}{3p^{1/2}} - \dots\right] dy$$

For larger p , the integral approach the gaussian integral. Therefore,

$$p! \sim p^p e^{-p} \sqrt{2\pi p} \blacksquare$$

If we take its logarithm, the square root term will be negligible and we are able to write

$$\ln p! \sim p \ln p - p \blacksquare$$

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, called configuration, L identical object 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

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

This equation gives the number of ways to distribute L indistinguishable objects in P distinguishable box.

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 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

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

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

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

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.

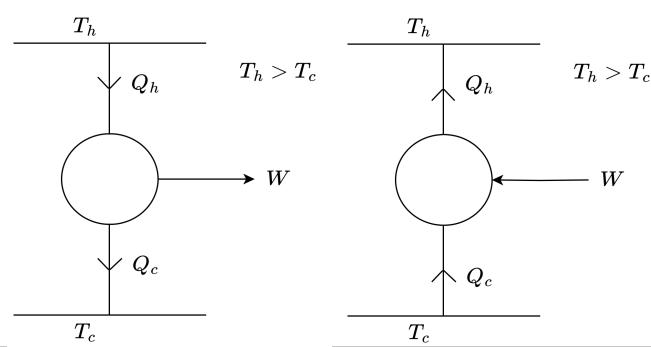


Figure: Carnot engine and reverse Carnot engine.

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:

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

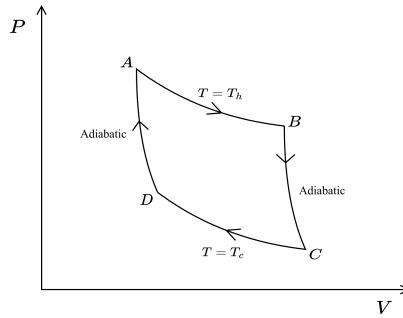


Figure: PV diagram of a cyclic Carnot process.

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

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

In similar manner, the adiabatic transformation along DA gives

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

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 $\gamma = 5/3$

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.

Entropy and internal Energy Relation

I already derived these somewhere, I don't remember

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

and

$$\frac{\partial S}{\partial U} \Big|_{V,N_i} = \frac{1}{T}, \quad \frac{\partial S}{\partial V} \Big|_{U,N_i} = \frac{P}{T}, \quad \frac{\partial S}{\partial N_j} \Big|_{U,N_{i \neq j}} = -\frac{P}{T}$$

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

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

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

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

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

$$\begin{aligned}dH &= dU + P dV + V dP = dQ - P dV + \mu dN + P dV + V dP \\ dH &= dQ + V dP + \mu dN\end{aligned}$$

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 in 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

Introduction

Quantum Statistics

Based on their quantum statistics properties, there are three types of particle, namely

1. **Classics.** This particle obeys Maxwell-Boltzmann (MB) distribution. It assumes particles are distinguishable and can occupy any energy state without restriction.
2. **Boson.** This particle obeys the Bose-Einstein (BE) distribution. It is indistinguishable and can occupy the same quantum state without limit.
3. **Fermion.** This particle obeys Fermi-Dirac (FD) distribution. Fermions are indistinguishable and obey the Pauli exclusion principle, meaning no two fermions can occupy the same quantum state.

Discrete System

Microstate. The number of microstate based on energy level for classical particle is

$$\Omega_{\text{MB}} = N! \prod_k \frac{g_k^{n_k}}{n_k!}$$

for boson

$$\Omega_{\text{BE}} = \prod_k \frac{(n_k + g_k - 1)!}{n_k!(g_k - 1)!}$$

and for fermion

$$\Omega_{\text{FD}} = \prod_k \frac{g_k!}{n_k!(g_k - n_k)!}$$

Example. Consider system with four particles and five unit energy, where each energy level have the following condition.

n	(g_n, ϵ_n)
4	(1, 3)
3	(3, 2)
2	(2, 1)
1	(3, 0)

We have the following macrostate.

$$M_1 = (2, 0, 1, 1)$$

$$M_2 = (1, 2, 0, 1)$$

$$M_3 = (1, 1, 2, 0)$$

$$M_4 = (0, 3, 1, 0)$$

For classical particle, we have also the following number of microstate

$$\Omega_1 = 4! \frac{3^2}{2!} \frac{2^0}{0!} \frac{3^1}{1!} \frac{1^1}{1!} = 324$$

$$\Omega_2 = 144$$

$$\Omega_3 = 648$$

$$\Omega_4 = 96$$

For boson

$$\Omega_1 = \frac{4!1!3!1!}{2!2!1!2!0!} = 18$$

$$\Omega_2 = 9$$

$$\Omega_3 = 36$$

$$\Omega_4 = 12$$

and for fermion

$$\Omega_1 = \frac{3!}{2!} \frac{2!}{2!} \frac{3!}{2!} \frac{1!}{1!} = 9$$

$$\Omega_2 = 3$$

$$\Omega_3 = 18$$

No M_4 for fermion since those three particle cannot have the same energy.

Another example. This time I will do classical particle only. Consider system with $N = E = 7$ unit whose each level of energy obey the following condition.

n	(g_n, ϵ_n)
7	(3, 6)
6	(3, 5)
5	(3, 4)
4	(3, 3)
3	(3, 2)
2	(3, 1)
1	(3, 0)

The corresponding macrostates are as follows.

$$\begin{aligned} M_1 &= (5, 0, 0, 0, 0, 0, 0) & M_7 &= (2, 3, 0, 1, 0, 0, 0) \\ M_2 &= (4, 1, 0, 0, 0, 1, 0) & M_8 &= (3, 0, 3, 0, 0, 0, 0) \\ M_3 &= (4, 0, 1, 0, 1, 0, 0) & M_9 &= (2, 2, 2, 0, 0, 0, 0) \\ M_4 &= (3, 2, 0, 0, 1, 0, 0) & M_{10} &= (1, 4, 1, 0, 0, 0, 0) \\ M_5 &= (4, 0, 2, 0, 0, 0, 0) & M_{11} &= (0, 6, 0, 0, 0, 0, 0) \\ M_6 &= (3, 1, 1, 1, 0, 0, 0) \end{aligned}$$

with the following microstate

$$\begin{array}{ll} \Omega_1 = 6 \cdot 3^6 & \Omega_7 = 60 \cdot 3^6 \\ \Omega_2 = 30 \cdot 3^6 & \Omega_8 = 20 \cdot 3^6 \\ \Omega_3 = 30 \cdot 3^6 & \Omega_9 = 90 \cdot 3^6 \\ \Omega_4 = 60 \cdot 3^6 & \Omega_{10} = 30 \cdot 3^6 \\ \Omega_5 = 15 \cdot 3^6 & \Omega_{11} = 3^6 \\ \Omega_6 = 120 \cdot 3^6 & \end{array}$$

Buku Pak Rouf, soal nomor 1. Consider

Tujuh buah partikel klasik didistribusikan pada lima tingkat energi dengan $\epsilon_s = (s - 1)$ eV dan $g_s = 3$, dengan indeks s adalah nomor tingkat energi. Jika energi total partikel adalah 8 eV, tentukanlah: Jumlah keadaan makro M dan spesifikasinya; Jumlah keadaan mikro untuk tiap M ; Bobot konfigurasi total W_T ; Bilangan penempatan rata-rata $\langle n_s \rangle$; dan Peluang untuk mendapatkan partikel dengan energi 2 eV pada pengambilan pertama

Keadaan sistem dapat digambarkan sebagai berikut.

Tabel: Keadaan sistem

s	g_s	$\epsilon_s = (s - 1)$ eV
5	3	4
4	3	3
3	3	2
2	3	1
1	3	0

Sistem memiliki 12 keadaan makro dengan spesifikasi sebagai berikut.

$$\begin{aligned} M_1 &= (5, 0, 0, 0, 2) & M_7 &= (3, 1, 2, 1, 0) \\ M_2 &= (4, 1, 0, 1, 1) & M_8 &= (2, 3, 1, 1, 0) \\ M_3 &= (4, 0, 2, 0, 1) & M_9 &= (3, 0, 4, 0, 0) \\ M_4 &= (2, 4, 0, 0, 1) & M_{10} &= (2, 2, 3, 0, 0) \\ M_5 &= (4, 0, 1, 2, 0) & M_{11} &= (1, 4, 2, 0, 0) \\ M_6 &= (3, 2, 0, 2, 0) & M_{12} &= (0, 6, 1, 0, 0) \end{aligned}$$

Jumlah keadaan mikro untuk setiap keadaan makro adalah sebagai berikut.

$$\begin{aligned} W_1 &= 7! \frac{3^5}{5!} \frac{3^0}{0!} \frac{3^0}{0!} \frac{3^2}{2!} = 45\,927 \\ W_2 &= 7! \frac{3^4}{4!} \frac{3^1}{1!} \frac{3^0}{0!} \frac{3^1}{1!} \frac{3^1}{1!} = 459\,720 \\ W_3 &= 7! \frac{3^4}{4!} \frac{3^0}{0!} \frac{3^2}{2!} \frac{3^0}{0!} \frac{3^1}{1!} = 229\,635 \\ W_4 &= 7! \frac{3^2}{2!} \frac{3^4}{4!} \frac{3^0}{0!} \frac{3^0}{1!} \frac{3^1}{1!} = 229\,635 \\ W_5 &= 7! \frac{3^4}{4!} \frac{3^0}{0!} \frac{3^1}{1!} \frac{3^2}{2!} \frac{3^0}{0!} = 229\,635 \\ W_6 &= 7! \frac{3^3}{3!} \frac{3^2}{2!} \frac{3^0}{0!} \frac{3^2}{2!} \frac{3^0}{0!} = 102\,160 \\ W_7 &= 7! \frac{3^3}{3!} \frac{3^1}{1!} \frac{3^2}{2!} \frac{3^1}{1!} \frac{3^0}{0!} = 302\,180 \\ W_8 &= 7! \frac{3^2}{2!} \frac{3^3}{3!} \frac{3^1}{1!} \frac{3^1}{1!} \frac{3^0}{0!} = 918\,540 \\ W_9 &= 7! \frac{3^3}{3!} \frac{3^0}{0!} \frac{3^4}{4!} \frac{3^0}{0!} \frac{3^0}{0!} = 76\,545 \end{aligned}$$

$$W_{10} = 7! \frac{3^2}{2!} \frac{3^2}{2!} \frac{3^3}{3!} \frac{3^0}{0!} \frac{3^0}{0!} = 459\ 720$$

$$W_{11} = 7! \frac{3^1}{1!} \frac{3^4}{4!} \frac{3^2}{2!} \frac{3^0}{0!} \frac{3^0}{0!} = 229\ 635$$

$$W_{12} = 7! \frac{3^0}{0!} \frac{3^6}{6!} \frac{3^1}{1!} \frac{3^0}{0!} \frac{3^0}{0!} = 15\ 309$$

Untuk menghitung bilangan penempatan rata, diperlukan jumlah keadaan mikro total:

$$\begin{aligned} W_T &= \sum_{k=1}^{12} W_k = 45\ 927 + 459\ 270 + 229\ 635 \\ &\quad + 229\ 635 + 229\ 635 + 102\ 060 + 306\ 180 + 918\ 540 \\ &\quad + 76\ 545 + 459\ 270 + 229\ 635 + 15\ 309 = 3\ 301\ 641 \end{aligned}$$

Jumlah partikel rata-rata untuk tingkat energi pertama $s = 1$ adalah

$$\begin{aligned} \langle n_1 \rangle &= \frac{\sum_k n_1 W_k}{W_T} = \frac{1}{3\ 301\ 641} (5 \cdot 45927 + 4 \cdot 459270 + 4 \cdot 229635 \cdot \\ &\quad + 2 \cdot 229635 \cdot + 4 \cdot 229635 \cdot + 3 \cdot 102060 + 3 \cdot 306180 + 2 \cdot 918540 \\ &\quad + 3 \cdot 76545 + 2 \cdot 459270 + 1 \cdot 229635 + 0 \cdot 15309) \approx 2.666 \end{aligned}$$

Untuk tingkat energi kedua

$$\begin{aligned} \langle n_2 \rangle &= \frac{\sum_k n_2 W_k}{W_T} = \frac{1}{3\ 301\ 641} (0 \cdot 45927 + 1 \cdot 459270 + 0 \cdot 229635 \\ &\quad + 4 \cdot 229635 + 0 \cdot 229635 + 2 \cdot 102060 + 1 \cdot 306180 + 3 \cdot 918540 \\ &\quad + 0 \cdot 76545 + 2 \cdot 459270 + 4 \cdot 229635 + 6 \cdot 15309) \approx 1.991 \end{aligned}$$

Untuk tingkat energi ketiga

$$\begin{aligned} \langle n_3 \rangle &= \frac{\sum_k n_3 W_k}{W_T} = \frac{1}{3\ 301\ 641} (0 \cdot 45927 + 0 \cdot 459270 + 2 \cdot 229635 \\ &\quad + 0 \cdot 229635 + 1 \cdot 229635 + 0 \cdot 102060 + 2 \cdot 306180 + 1 \cdot 918540 \\ &\quad + 4 \cdot 76545 + 3 \cdot 459270 + 2 \cdot 229635 + 1 \cdot 15309) \approx 1.326 \end{aligned}$$

Untuk tingkat energi keempat

$$\begin{aligned} \langle n_4 \rangle &= \frac{\sum_k n_4 W_k}{W_T} = \frac{1}{3\ 301\ 641} (0 \cdot 45927 + 1 \cdot 459270 + 0 \cdot 229635 \\ &\quad + 0 \cdot 229635 + 2 \cdot 229635 + 2 \cdot 102060 + 1 \cdot 306180 + 1 \cdot 918540 \\ &\quad + 0 \cdot 76545 + 0 \cdot 459270 + 0 \cdot 229635 + 0 \cdot 15309) \approx 0.7109 \end{aligned}$$

Dan untuk tingkat kelima

$$\begin{aligned} \langle n_5 \rangle &= \frac{\sum_k n_5 W_k}{W_T} = \frac{1}{3\ 301\ 641} (2 \cdot 45927 + 1 \cdot 459270 + 1 \cdot 229635 \\ &\quad + 1 \cdot 229635 + 0 \cdot 229635 + 0 \cdot 102060 + 0 \cdot 306180 + 0 \cdot 918540 \\ &\quad + 0 \cdot 76545 + 0 \cdot 459270 + 0 \cdot 229635 + 0 \cdot 15309) \approx 0.3060 \end{aligned}$$

Sebagai pembuktian,

$$N = \sum_s^5 n_s = 2.666 + 1.991 + 1.326 + 0.7109 + 0.3060 = 7$$

sesuai keadaan sistem.

Kemungkinan mendapatkan partikel dengan energi 2 eV, atau dengan tingkat energi ketiga, adalah

$$P(\epsilon_3) = \frac{\langle n_3 \rangle}{N} = \frac{1,326}{7} \approx 19\%$$

Maxwell-Boltzman Distribution

Maxwell-Boltzman 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 3D distribution function $f(\mathbf{v})$ is given by Maxwell distribution:

$$n(\mathbf{v}) d^3\mathbf{v} = N \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left(-\frac{mv^2}{2kT} \right) d^3\mathbf{v}$$

where $v^2 = v_x^2 + v_y^2 + v_z^2$ and $d^3\mathbf{v} = dv_x dv_y dv_z$. The single component distribution is given by

$$n(v_x) dv_x = N \left(\frac{m}{2\pi kT} \right)^{1/2} \exp \left(-\frac{mv_x^2}{2kT} \right) dv_x$$

This can be transformed into speed distribution function as

$$n(v) dv = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 \exp \left(-\frac{mv^2}{2kT} \right) dv$$

By using $\mathbf{v} = \mathbf{p}/m$ and $d^3\mathbf{v} = d^3\mathbf{p}/m^3$, we can also express it in terms of momentum

$$n(\mathbf{p}) d^3\mathbf{p} = N \left(\frac{1}{2\pi m k T} \right)^{3/2} \exp \left(-\frac{p^2}{2mkT} \right) d^3\mathbf{p}$$

and

$$n(p) dp = 4\pi N \left(\frac{1}{2\pi m k T} \right)^{3/2} p^2 \exp \left(-\frac{p^2}{2mkT} \right) dp$$

In terms of energy, the distribution function is given by

$$n(E) dE = \frac{2\pi N}{(\pi k T)^{3/2}} \sqrt{E} \exp \left(-\frac{E}{k_B T} \right) dE$$

In general, the number of particle in $g(E)$ energy state is

$$n(E) dE \approx g(E) \exp \left(-\frac{E}{kT} \right) dE$$

Maxwell's 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

$$F(\mathbf{v}) d^3\mathbf{v} = f(v_x)f(v_y)f(v_z) dv_x dv_y dv_z$$

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

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

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

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

with α as dummy variable. 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

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

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

$$\begin{aligned} \frac{1}{A} &= \frac{\pi}{4} \langle v \rangle^2 \\ \frac{1}{A} &= \frac{2}{3} \langle v^2 \rangle \end{aligned} \left\{ \begin{aligned} \langle v^2 \rangle &= \frac{3\pi}{8} \langle v \rangle^2 \end{aligned} \right.$$

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

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

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

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

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

$$\langle v^2 \rangle = 3 \frac{kT}{m} = \frac{3}{2A} \implies A = \frac{m}{2kT}$$

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

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

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

Boltzmann's Derivation

We will now derive the Maxwell distribution using Boltzmann's method. 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 $\epsilon \rightarrow 0$

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

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

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

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

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

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

$$\mathcal{P} = \prod_{\mathbf{k}=-\infty}^{\infty} \frac{N!}{n_{\mathbf{k}}!}$$

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

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

$$= C \left(\frac{2\pi}{m\lambda_2} \right)^{3/2}$$

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

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

Einstein's Derivation

The number of way to distribute N_E distinct particle into P_E distinct cells is

$$\mathcal{P}_E = P_E^{N_E}$$

where

$$P_E = \frac{2\pi}{h^3} V (2m)^{3/2} \sqrt{E} dE$$

Hence the number of distribution for all energy interval is

$$\mathcal{P}_E = \prod_{E=0}^{\infty} P_E^{N_E}$$

The total number of configuration is obtained by multiplying the number of configuration for distinct case \mathcal{P}_E by the number of ways to distribute N_E particle from N

$$\mathcal{P} = N! \prod_E \frac{P_E^{N_E}}{N_E!}$$

By applying Stirling's approximation, the logarithm reads

$$\ln \mathcal{P} = \sum_E N_E \ln P_E + N \ln N - N - \sum_E N_E \ln N_E + N_E$$

$$\ln \mathcal{P} = \sum_E N_E \ln \left(\frac{P_E}{N_E} \right) + N \ln(N)$$

Then define the following function according to Lagrange's method

$$F = \sum_E N_E \ln \left(\frac{P_E}{N_E} \right) + N \ln(N) + \lambda_1 \sum_E N_E + \lambda_2 \sum_E E N_E$$

where we have used the N and U constraints. Then set its derivative to zero

$$\ln \left(\frac{P_E}{N_E} \right) - 1 + \lambda_1 + \lambda_2 E = 0$$

Solving for N_E

$$\begin{aligned} \frac{P_E}{N_E} &= C_1 \exp(-\lambda_2 E) \\ N_E &= P_E C_2 \exp(-\beta E) \end{aligned}$$

Inserting this into N constraint

$$N = \sum_E P_E C_2 e^{-\beta E} = \frac{2\pi}{h^3} V (2m)^{3/2} C_2 \int_0^\infty \sqrt{E} e^{-\beta E} dE$$

The integral is solved as follows. Consider

$$I = \int_0^\infty \sqrt{x} e^{-ax} dx$$

Make change of variable $u = -ax$. We have then $d\alpha = -a dx$ and $\sqrt{x} = i\sqrt{\alpha/a}$. The integral then reads

$$I = -\frac{i}{a^{3/2}} \int_0^{-\infty} \sqrt{\alpha} e^\alpha d\alpha$$

By choosing $u = \sqrt{\alpha}$ and $dv = e^\alpha$, consequently we have $du = 1/2\sqrt{\alpha}$ and $v = e^\alpha$. Using method of integral by parts,

$$I = -\frac{i}{a^{3/2}} \left[e^\alpha \sqrt{\alpha} \Big|_0^{-\infty} - \int_0^{-\infty} \frac{e^\alpha}{2\sqrt{\alpha}} d\alpha \right] = \frac{i}{2a^{3/2}} \int_0^{-\infty} \frac{e^\alpha}{\sqrt{\alpha}} d\alpha$$

We again make the change of variable $t^2 = \alpha$; which implies $d\alpha = 2t dt$. Although in this case, the lower limit remains the same, namely zero, the upper limit has two possible value due to quadratic nature of our variable

$$t^2 = -\infty \implies t = \pm\infty i$$

The value we pick is the negative one; this is due to the nature of logarithm. Recalling the definition of imaginary error function. The integral above can be recast as

$$I = \frac{i}{a^{3/2}} \int_0^{-\infty i} e^{t^2} dt = \frac{i\pi}{2a^{3/2}} \operatorname{erfi}(-\infty i)$$

Hence, the result is

$$I = \frac{\pi}{2a^{3/2}}$$

a positive value. For positive value $t = -\infty i$, the resulting integral will be negative instead. We want the positive value of the integral since we will be taking the logarithm. Positive argument will ensure the value of our logarithm is real, since it represent the logarithm of number a configuration, which is positive real.

Now plugging the result of previous integral, we have

$$N = \frac{2\pi}{h^3} V (2m)^{3/2} C_2 \frac{\sqrt{\pi}}{2\beta^{3/2}} = C_2 V \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2}$$

or by solving of C_2 ,

$$C_2 = \frac{N}{V} \left(\frac{h^2 \beta}{2\pi m} \right)^{3/2}$$

And by plugging this into N_E , we also have

$$N_E = \frac{N}{V} P_E \exp(-\beta E) \left(\frac{h^2 \beta}{2\pi m} \right)^{3/2}$$

The logarithm of maximum configuration then

$$\begin{aligned} \ln \mathcal{P}_{\max} &= \sum_E N_E \ln \left[\frac{V}{N} \exp(\beta E) \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2} \right] + N \ln(N) \\ \ln \mathcal{P}_{\max} &= N \ln(V) + \frac{3}{2} N \ln \left(\frac{2\pi m}{h^2 \beta} \right) + \beta U \end{aligned}$$

As for the entropy

$$S = N k_B \ln(V) + \frac{3}{2} N k_B \ln \left(\frac{2\pi m}{h^2 \beta} \right) + k_B \beta U$$

Using the thermodynamics relationship of

$$\frac{1}{T} = \frac{\partial S}{\partial U} \Big|_{V,N} = k_B U \implies \beta = \frac{1}{T}$$

Now the number of particle within $(\nu, \nu + d\nu)$ can be evaluated as

$$\begin{aligned} N_E &= \frac{N}{V} \frac{2\pi}{h^3} V (2m)^{3/2} \sqrt{E} \exp \left(-\frac{E}{k_B T} \right) \left(\frac{h^2}{2\pi k_B T m} \right)^{3/2} dE \\ N_E &= \left(\frac{\sqrt[3]{4} N^{2/3}}{\sqrt{\pi} k_B T} \right)^{3/2} \sqrt{E} \exp \left(-\frac{E}{k_B T} \right) dE \end{aligned}$$

and the distribution function as

$$n_E = \left(\frac{\sqrt[3]{4} N^{2/3}}{\sqrt{\pi} k_B T} \right)^{3/2} \sqrt{E} \exp \left(-\frac{E}{k_B T} \right)$$

We can also recover the ideal gas law using the thermodynamics relationship

$$\frac{P}{T} = \frac{\partial S}{\partial V} \Big|_{S,N} = \frac{N k_B}{V} \implies P V = N k_B T$$

Thermodynamics Derivation

We consider the number of configuration of classical particle

$$\mathcal{W} = N! \prod_s \frac{g_s^{n_s}}{n_s!}$$

where

$$g_s = 2\pi V(2m)^{3/2} \sqrt{E} dE$$

Unlike Einstein's derivative, we did not divide it by h^3 . Here s denote the number of energy level; the product then start from the lowest energy level to the highest. Then by applying Stirling's formula

$$\ln \mathcal{W} = \sum_s n_s \ln \left(\frac{g_s}{n_s} \right) + N \ln(N)$$

Since \mathcal{W} , or rather its logarithm, is a function of (N, g_s, n_s) , we write its total differential as

$$d(\ln \mathcal{W}) = \frac{\partial \ln \mathcal{W}}{\partial N} dN + \frac{\partial \ln \mathcal{W}}{\partial g_s} dg_s + \frac{\partial \ln \mathcal{W}}{\partial n_s} dn_s$$

Recall that N stands for the number of particle and g_s is the number of degeneracy within said energy. Both values are constant, hence

$$d(\ln \mathcal{W}) = \frac{\partial \ln \mathcal{W}}{\partial n_s} dn_s = \sum_E \left[\ln \left(\frac{g_s}{n_s} \right) - 1 \right] dn_s$$

Now we consider the constraints, which are number of particle and energy

$$N = \sum_s n_s, \quad \text{and} \quad E = \sum_s n_s \epsilon_s$$

In equilibrium, both are also constant, hence

$$\sum_s dn_s = 0 \quad \text{and} \quad \sum_s (\epsilon_s dn_s + n_s d\epsilon_s) = 0$$

To simplify the energy constraint, recall the first thermodynamics law

$$dE = dQ - P dV$$

The change of energy by $\epsilon_s dn_s$ corresponds to energy transfer through particle exchange, which is related to heat transfer in thermodynamics; while the change by $n_s d\epsilon_s$ represents the energy change due to changes in the energy levels themselves, which is associated with work, such as change of volume. Hence, the relations

$$\sum_s \epsilon_s dn_s = dQ \quad \text{and} \quad \sum_s n_s d\epsilon_s = -P dV$$

In equilibrium, the volume of system is also constant, hence our constraints

$$\sum_s dn_s = 0 \quad \text{and} \quad \sum_s \epsilon_s dn_s = 0$$

By Lagrange's method, we construct the following auxiliary function

$$F(n_s) = \sum_s \left[\ln \left(\frac{g_s}{n_s} \right) - 1 + \lambda_1 + \lambda_2 \epsilon_s \right] dn_s$$

Setting its derivative to zero

$$\ln \left(\frac{g_s}{n_s} \right) - 1 + \lambda_1 + \lambda_2 \epsilon_s = 0$$

Solving for n_s , we have

$$n_s = g_s \alpha \exp(-\beta \epsilon_s)$$

To determine the value of β , we write the auxiliary function as

$$F = d(\ln \mathcal{W}) + \lambda_1 dN + \lambda_2 dQ$$

Consider the case closed reversible process. We have $dN = 0$ and $dQ = T dS$. Using this result and setting the value of the auxiliary function to zero, as it was before, we have

$$d(\ln \mathcal{W}) = -\beta dQ = -\beta T dS = -\beta T k d(\ln \mathcal{W}) \implies \beta = -\frac{1}{kT}$$

The relation between the constant λ_2 and β is simply $\lambda_2 = \beta$. I write it that way thinking there are some changes to the constant, not realizing both are the same. λ_1 and α are different though.

Next we determine the value of α . Consider the number of particle constraint. By substituting the value of n_s and g_s we have

$$\begin{aligned} N &= \int_0^\infty \alpha 2\pi V (2m)^{3/2} \sqrt{E} \exp \left(-\frac{E}{kT} \right) dE \\ &= A 2\pi V (2m)^{3/2} \frac{\sqrt{\pi}}{2} (kT)^{3/2} = \alpha (2\pi m kT)^{3/2} V \end{aligned}$$

Hence,

$$\alpha = \frac{N}{(2\pi m kT)^{3/2} V}$$

The complete form of our distribution function is then

$$\begin{aligned} n(E) dE &= \frac{N}{(2\pi m kT)^{3/2} V} 2\pi V (2m)^{3/2} \sqrt{E} \exp \left(-\frac{E}{kT} \right) dE \\ n(E) dE &= \frac{2\pi N}{(\pi kT)^{3/2}} \sqrt{E} \exp \left(-\frac{E}{k_B T} \right) dE \quad \blacksquare \end{aligned}$$

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

$$G(\mathbf{V}) = N_1 N_2 \left(\frac{m_1 m_2}{4\pi^2 k^2 T_1 T_2} \right)^{3/2} \exp \left[-\frac{m_1}{2kT_1} (v_x^2 + v_y^2 + v_z^2) \right] \\ \exp \left[-\frac{m_2}{2kT_2} (\{v_x + V_x\}^2 + \{v_y + V_y\}^2 + \{v_z + V_z\}^2) \right]$$

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

$$\int_{\mathbb{R}^3} G(\mathbf{V}) d^3\mathbf{V} = N_1 N_2 \left(\frac{m_1 m_2}{4\pi^2 k^2 T_1 T_2} \right)^{3/2} \\ \int_{\mathbb{R}^3} \left[\int_{-\infty}^{\infty} \exp \left(-\frac{m_1}{2kT_1} \omega^2 - \frac{m_2}{2kT_2} (\omega + \Omega)^2 \right) d\omega \right]^3 d^3\mathbf{V}$$

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

$$\int_{-\infty}^{\infty} \exp \left[-\left(\frac{m_1}{2kT_1} + \frac{m_2}{2kT_2} \right) \omega^2 - 2 \frac{m_2}{2kT_2} \Omega \omega - \frac{m_2}{2kT_2} \Omega^2 \right] d\omega$$

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

$$\exp \left[-\frac{m_2}{2kT_2} \Omega^2 \right] \int_{-\infty}^{\infty} \exp \left[-\left(\frac{m_1 T_2 + m_2 T_1}{2kT_1 T_2} \right) \omega^2 - \frac{m_2 \Omega}{kT_2} \omega \right] d\omega$$

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

$$\exp \left[-\frac{m_2}{2kT_2} \Omega^2 \right] \exp \left[\Omega^2 \frac{m_2^2}{k^2 T_2^2} \frac{1}{4} \frac{2kT_1 T_2}{m_1 T_2 + m_2 T_1} \right] \left[\pi \frac{2kT_1 T_2}{m_1 T_2 + m_2 T_1} \right]^{1/2}$$

Combining the exponent, we get

$$\exp \left[\Omega^2 \left(\frac{m_2^2 k T_1 T_2}{2kT_2^2 (m_1 T_2 + m_2 T_1)} - \frac{m_2}{2kT_2} \right) \right] \left[\pi \frac{2kT_1 T_2}{m_1 T_2 + m_2 T_1} \right]^{1/2}$$

Next simply evaluate the terms inside parenthesis

$$\exp \left[\Omega^2 \left(\frac{m_2 \{m_2 k T_1 T_2 - m_1 k T_2 - m_2 k T_1 T_2\}}{2kT_2^2 (m_1 T_2 + m_2 T_1)} \right) \right] [\dots]^{1/2}$$

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

$$\exp \left[-\frac{m_2 m_1 k T_2 T_2}{2kT_2^2 (m_1 T_2 + m_2 T_1)} \Omega^2 \right] \left[\pi \frac{2kT_1 T_2}{m_1 T_2 + m_2 T_1} \right]^{1/2}$$

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,

$$\int_{\mathbb{R}^3} G(\mathbf{V}) d^3\mathbf{V} = N_1 N_2 \left(\frac{m_1 m_2}{4\pi^2 k^2 T_1 T_2} \right)^{3/2} \int_{\mathbb{R}^3} \left[\exp \left[-\frac{m_2 m_1 k T_2 T_2}{2kT_2^2(m_1 T_2 + m_2 T_1)} V_i^2 \right] \left[\frac{2\pi k T_1 T_2}{m_1 T_2 + m_2 T_1} \right]^{1/2} \right]^3 d^3\mathbf{V}$$

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

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

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

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

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

Physical Quantity

Few physical quantities that can be derived from the MB distribution function are as follows. First we have the average velocity

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}}$$

then the most probable velocity

$$v_{mp} = \sqrt{\frac{2kT}{m}}$$

and the root-mean-square

$$v_{rms} = \sqrt{\frac{3kT}{m}}$$

We also have flux, that is a number of particles per unit area per unit time

$$\Gamma = \frac{1}{4} \rho \langle v \rangle$$

To determine the fraction of particle within certain range of value, say energy

$$\text{Fraction} = \int_{x_1}^{x_2} f(x) dx$$

where $f(x) = n(x)/N$ is normalized distribution function. Alternately, for small range, we can use Leibniz formula

$$\text{Fraction} = \left[f \left(\frac{x_1 + x_2}{2} \right) \right] (x_2 - x_1)$$

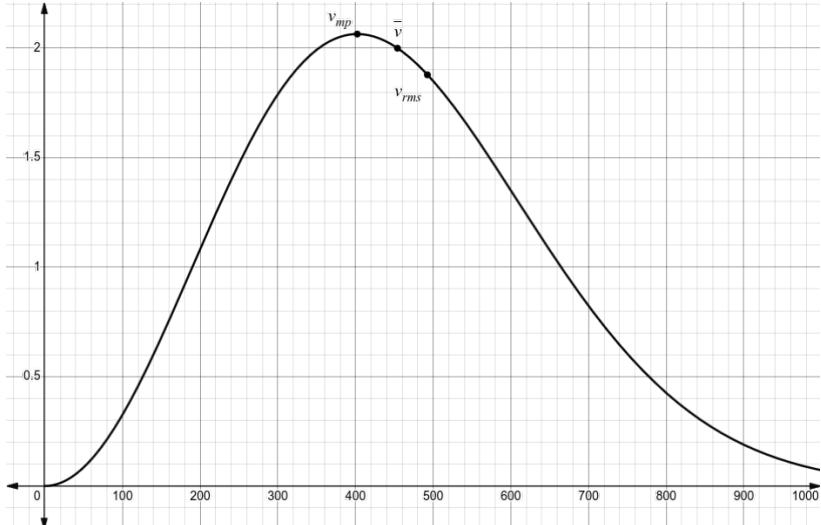


Figure: MB distribution function. In general, $v_{mp} < \langle v \rangle < v_{rms}$

Derivation. The derivation of $\langle v \rangle$ and v_{rms} are quite trivial. For the expectation value of velocity

$$\begin{aligned}\langle v \rangle &= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty v^3 \exp\left(-\frac{mv^2}{2kT}\right) dv \\ &= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{1}{2} \left(\frac{2kT}{m}\right)^{4/2} \Gamma(2) = \sqrt{\frac{8kT}{\pi m}}\end{aligned}$$

And for root-mean-square-velocity

$$\begin{aligned}v_{rms} &= \left[4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty v^4 \exp\left(-\frac{mv^2}{2kT}\right) dv \right]^{1/2} \\ &= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{1}{2} \left(\frac{2kT}{m}\right)^{5/2} \Gamma\left(\frac{5}{2}\right) = \sqrt{\frac{3kT}{m}}\end{aligned}$$

To find the most probable velocity, we maximize the distribution function. Hence, setting the derivative with respect to velocity to zero

$$4N \left(\frac{m}{2\pi kT}\right)^{3/2} \left[2v \exp\left(-\frac{mv^2}{2kT}\right) - v^2 \frac{mv}{kT} \exp\left(-\frac{mv^2}{2kT}\right) \right] = 0$$

Solving for velocity, we have

$$\begin{aligned}2v \exp\left(-\frac{mv^2}{2kT}\right) &= \frac{mv^3}{kT} \exp\left(-\frac{mv^2}{2kT}\right) \\ v &= \sqrt{\frac{2kT}{m}}\end{aligned}$$

To derive flux, we need to recall

$$dN \frac{N}{V} v_{x+} dA dt$$

Using the definition of particle density $\rho = N/V$ and flux $\Gamma = N/At$, we conclude

$$\Gamma = \rho v_{x+}$$

We find the x component of the velocity by

$$\langle v_x \rangle = \int v_x f(v_x) dv_x$$

We find

$$\begin{aligned} \langle v_x \rangle &= \left(\frac{m}{2\pi kT} \right)^{1/2} \int v_x \exp\left(\frac{-mv^2}{2kT}\right) dv_x \\ &= \left(\frac{m}{2\pi kT} \right)^{1/2} \frac{1}{2} \left(\frac{2\pi kT}{m} \right)^{1/2} \Gamma(2) = \sqrt{\frac{kT}{2\pi m}} \end{aligned}$$

We could simply substitute this result into our flux equation, or alternately we write

$$\langle v \rangle = \sqrt{\frac{8kT}{m}} = 4 \langle v_x \rangle$$

and substituting into the flux equation for much cleaner result

$$\Gamma = \frac{1}{4} \rho \langle v \rangle$$

Appendix: Contoh Soal (Buku Pak Rouf)

Misalkan N buah partikel klasik didistribusikan pada 5 tingkat energi dengan energi $s = kT \ln s$ dan $g_s = 6 - s$, dengan indeks s adalah nomor tingkat energi. Dengan memanfaatkan distribusi MB: Hitunglah peluang untuk mendapatkan partikel dengan energi $\epsilon = kT \ln 3$ pada pengambilan pertama; Bila energi total asembel E adalah $1000 \text{ } kT$, hitunglah jumlah partikel N ; jumlah partikel dengan energi $\epsilon = kT \ln 3$

Jumlah total partikel dapat diketahui dengan

$$N = \sum_{s=1}^5 n_s = n_1 + n_2 + n_3 + n_4 + n_5$$

Jumlah partikel yang menempati energi tertentu adalah

$$n(\epsilon_s) \approx g(\epsilon_s) \exp\left(-\frac{\epsilon}{kT}\right)$$

Menggunakan persamaan diatas, rasio masing-masing partikel adalah

$$n_1 : n_2 : n_3 : n_4 : n_5 = 5 : 8 : 9 : 8 : 5 = 1 : \frac{8}{5} : \frac{9}{5} : \frac{8}{5} : 1$$

Dalam n_1 , jumlah total partikel adalah

$$N = n_1 \left(1 + \frac{8}{5} + \frac{9}{5} + \frac{8}{5} + 1\right) = 7n_1$$

Dalam N , jumlah partikel pada tingkat energi ketiga adalah

$$n_3 = \frac{9}{5} n_1 = \frac{9}{35} N$$

Sehingga peluang mendapatkan partikel tersebut adalah

$$P(\epsilon_3) = \frac{9N/35}{N} \approx 26\%$$

Jumlah energi total dapat diketahui dengan

$$\begin{aligned} E &= \sum_{s=1}^5 n_s 2\epsilon_s = n_1 \epsilon_1 + n_2 \epsilon_2 + n_3 \epsilon_3 + n_4 \epsilon_4 + n_5 \epsilon_5 \\ &= n_1 kT \left(1 \cdot 0 + \frac{8}{5} \cdot \ln 2 + \frac{9}{5} \cdot \ln 3 + \frac{8}{5} \cdot \ln 4 + 1 \cdot \ln 5\right) \approx 6.914 \text{ } kT n_1 \end{aligned}$$

Jika diketahui bahwa energi total adalah $1000 \text{ } kT$, maka

$$n_1 = \frac{1000 \text{ } kT}{6.914 \text{ } kT} \approx 145$$

Sehingga jumlah partikel total adalah

$$N = 7n_1 \approx 1015$$

Jumlah partikel pada tingkat energi ke tiga adalah

$$n_3 = \frac{9}{5} n_1 = \frac{9}{5} \cdot 145 \approx 260$$

atau dengan peluang pengambilan

$$n_3 = P(\epsilon_3) \cdot N \approx 260$$

Bose-Einstein Distribution

Distribution for Boson

The distribution for indistinguishable ideal quantum gas—also called boson—the Bose-Einstein distribution. In general, the number of particle per unit energy interval is given by

$$n(E) = \frac{g(E)}{\exp[(E - \mu)/k_B T] - 1}$$

For a free bosonic gas, the density state is

$$g(E) = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}$$

then the distribution function simply evaluate into

$$n(E) = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{E^{1/2}}{\exp[(E - \mu)/k_B T] - 1}$$

Energy and Frequency Cells

Quintessential step in Einstein's method is to distribute state of particle into certain cells. There are two kinds of cells, one for distributing particle in terms of their energy P_E and another in terms of their frequency P_ν . For energy, we write

$$P_E = \frac{2\pi}{h^3} V (2m)^{3/2} \sqrt{E} dE$$

and for frequency

$$P_\nu = \frac{8\pi V \nu^2}{c^3} d\nu$$

Energy Cells derivation. He first considers the energy of non-relativistic particle, which is

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

This implies

$$p = \sqrt{2mE}, \quad dp = \frac{m}{p} dE = \frac{m}{\sqrt{2mE}} dE$$

This will be used to determine the volume of $(\mathbf{r}, \mathbf{p} + d\mathbf{p})$ phase space

$$\begin{aligned} d\omega &= V \frac{4}{3}\pi [(p + dp)^3 - p^3] = \frac{4}{3}\pi V [3p^2 dp + 3p d^2 p + d^3 p] \\ &= 4\pi V p^2 dp = 4\pi V 2mE \frac{m}{\sqrt{2mE}} dE = 2\pi (2m)^{3/2} \sqrt{E} dE \end{aligned}$$

The said volume then divided into cells of h^3 volume. Let this number of distinct cells as

$$P_E = \frac{d\omega}{h^3} = \frac{2\pi}{h^3} V (2m)^{3/2} \sqrt{E} dE$$

Frequency Cells derivation. He considered gas of photon with energy of $E = h\nu$ and momentum $p = h\nu/c$. He assumed that quantum state is described by space and momentum phase space. Next he determined the volume of phase space within interval $(\nu, \nu + d\nu)$, which is

$$d\omega = V d\mathcal{V}$$

where V is the spatial volume and $d\mathcal{V}$ is the momentum volume of the shell within radii $h(\nu + d\nu)/c, h\nu$. The said shell volume is given by

$$\begin{aligned} d\mathcal{V} &= (\mathcal{V} + d\mathcal{V}) - \mathcal{V} = \frac{4\pi h^3}{3c^3} [(\nu + d\nu)^3 - \nu^3] \\ &= \frac{4\pi h^3}{3c^3} [3\nu^2 d\nu + 3\nu d^2\nu + d^3\nu] = \frac{4\pi h^3}{c^3} \nu^2 d\nu \end{aligned}$$

The resulting volume of phase space $d\omega$ is

$$d\omega = \frac{4\pi V h^3}{c^3} \nu^2 d\nu$$

This volume then divided by Bose into cells of volume h^3 . The number P_ν as phase space cells available to the photon within $(\nu, \nu + d\nu)$ expressed by

$$P_\nu = \frac{2}{c^3} d\omega = \frac{8\pi V \nu^2}{c^3} d\nu$$

where the factor of 2 comes after taking account the two direction of polarization.

Bose's Derivation

The number of configuration \mathcal{P}_E for distributing N_E indistinguishable particle in P_E boxes is given by

$$\mathcal{P}_E = \frac{(N_E + P_E - 1)}{N_E!(P_E - 1)!}$$

This gives configuration for particle within $(E, E + dE)$, conversely the total configuration is given by

$$\mathcal{P} = \prod_{E=0}^{\infty} \mathcal{P}_E$$

We then move to determining the entropy $S = k_B \ln \mathcal{P}_{\max}$ by maximizing the logarithm of \mathcal{P} with respect to N_E subjected to the following constraints.

$$N = \sum_{E=0}^{\infty} N_E, \quad U = \sum_{E=0}^{\infty} EN_E$$

Using Stirling's approximation on said logarithm, we have

$$\ln \mathcal{P} = \sum_E \ln \frac{(N_E + P_E - 1)}{N_E!(P_E - 1)!}$$

$$\ln \mathcal{P} = \sum_E (N_E + P_E) \ln(N_E + P_E) - N_E \ln(N_E) - P_E \ln(P_E)$$

By Lagrange's method

$$F = \ln \mathcal{P} + \lambda_1 \sum_E N_E + \lambda_2 \sum_E E N_E$$

Setting its derivative to zero

$$\ln(N_E + P_E) + 1 - \ln(N_E) - 1 + \lambda_1 + \lambda_2 E = 0$$

Taking the exponential and solving for N_E

$$\frac{N_E + P_E}{N_E} = \exp(-\lambda_1 - \lambda_2 E)$$

$$N_E = \frac{P_E}{\exp(-\lambda_1 - \lambda_2 E) - 1}$$

Substituting this value into the logarithm of \mathcal{P}

$$\ln \mathcal{P}_{\max} = \sum_E \left[(N_E + P_E) \left[\ln(P_E) + \ln \left(\frac{\exp(-\lambda_1 - \lambda_2 E)}{\exp(-\lambda_1 - \lambda_2 E) - 1} \right) \right] \right.$$

$$\left. - P_E \ln(P_E) - N_E [\ln(P_E) - \ln(\exp\{-\lambda_1 - \lambda_2 E\} - 1)] \right]$$

then

$$\ln \mathcal{P}_{\max} = \sum_E \left[(N_E + P_E) \ln \left(\frac{\exp(-\lambda_1 - \lambda_2 E)}{\exp(-\lambda_1 - \lambda_2 E) - 1} \right) \right.$$

$$\left. + N_E \ln(\exp\{-\lambda_1 - \lambda_2 E\} - 1) \right]$$

moreover

$$\ln \mathcal{P}_{\max} = \sum_E \left[N_E (-\lambda_1 - \lambda_2 E) + P_E \ln \left(\frac{\exp(-\lambda_1 - \lambda_2 E)}{\exp(-\lambda_1 - \lambda_2 E) - 1} \right) \right]$$

Hence

$$S = \sum_E k_B P_E \ln \left(\frac{\exp(-\lambda_1 - \lambda_2 E)}{\exp(-\lambda_1 - \lambda_2 E) - 1} \right) - k_B(N\lambda_1 + U\lambda_2)$$

On using the following relations

$$\frac{1}{T} = \frac{\partial S}{\partial U} \Big|_{V,N}, \quad -\frac{\mu}{T} = \frac{\partial S}{\partial N} \Big|_{U,V}$$

we have

$$\frac{1}{T} = -\lambda_2 k_B \implies \lambda_2 = -\frac{1}{k_B T}$$

and

$$-\frac{\mu}{T} = \lambda_1 k_B \implies \lambda_1 = \frac{\mu}{k_B T}$$

Thus

$$N_E = \frac{2\pi}{h^3} \frac{V(2m)^{3/2} \sqrt{E}}{\exp[(E - \mu)/k_B T] - 1} dE$$

The quantity n_E is defined as the number of molecules per unit energy interval

$$n_E = \frac{N_E}{dE} = \frac{2\pi}{h^3} \frac{V(2m)^{3/2} \sqrt{E}}{\exp[(E - \mu)/k_B T] - 1} \blacksquare$$

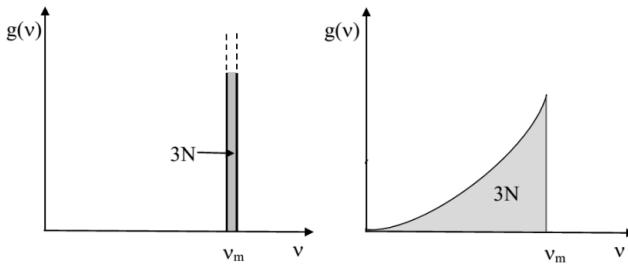


Figure: Density of state based on Einstein's and Debye's model.

Phonon

A phonon is a quantum mechanical quantization of the modes of vibrations for elastic structures of interacting particles. Phonons behave as a quasi particle that carries energy and momentum.

As quantized lattice vibrations, phonons can have three polarization directions: one direction of longitudinal and two for transversal, all with respect to the direction of propagation. Thus, for N phonons, the total state of frequency is $3N$. Two of the popular model for the frequency density of state is Einstein's and Debye.

Experimental result shows that

$$C_V = \begin{cases} 3NK = 3R & \text{at high temperature} \\ AT^3 & \text{at low temperature} \end{cases}$$

Both Einstein and Debye were able to predict the result for high temperature, however only Debye were able to predict the result for low temperature.

Einstein's model. Here, he assumed that all the $3N$ oscillator oscillate with the same frequency. Thus, all the $3N$ state is equal to ν_m

$$g(\nu) = 3N\delta(\nu - \nu_m)$$

Debye's model. Unlike Einstein, he assumed that the density of state is quadratic up to maximum frequency ν_m . The said density of state is given by

$$g(\nu) = \begin{cases} \frac{9N}{\nu_m^3}\nu^2, & \nu \leq \nu_m \\ 0, & \nu_m < \nu \end{cases}$$

To derive said DoS, recall that it is proportional to the square of frequency. Hence, the DoS assumes the form of

$$g(\nu) = A\nu^2$$

On integrating this within all allowed frequency $(0, \nu_m)$, we have

$$3N = \int_0^{\nu_m} A\nu^2 d\nu = A \frac{1}{3} \nu_m^3$$

Then simply solve for the constant

$$A = \frac{9N}{\nu_m^3}$$

Einstein' Solid

Einstein's theory on solid is only accurate for large T , experimental data disagree with his theory for small T . On using the DoS given by Einstein's model, the phonon density reads

$$n(\nu) = \frac{3N\delta(\nu - \nu_m)}{\exp(h\nu/kT) - 1}$$

We determine the total energy of given phonon as

$$E = \int_0^\infty E(\nu)n(\nu) d\nu$$

Using said distribution

$$\begin{aligned} E &= \int_0^\infty h\nu \frac{3N\delta(\nu - \nu_m)}{\exp(h\nu/kT) - 1} d\nu \\ E &= \frac{3Nh\nu_m}{\exp(h\nu_m/kT) - 1} \end{aligned}$$

The experimental data that was mentioned prior takes the form of heat capacitance, hence Einstein's theory should give the heat capacitance by using the definition

$$C_V = \left. \frac{\partial E}{\partial T} \right|_{V,N=N_A}$$

Large temperature. For this case, the exponential term is small, hence it can be approximated with

$$\exp\left(\frac{h\nu}{kT}\right) = 1 + \frac{h\nu}{kT}$$

and the expression for energy may be written

$$E = \frac{3Nh\nu_m}{h\nu_m/kT} = 3NkT$$

We can then write the heat capacitance as

$$C_V = 3N_A k = 3R$$

Small temperature. In this case, the exponential term can be expanded and the expression for energy may be written

$$E = 3Nh\nu_m \exp\left(-\frac{h\nu_m}{kT}\right)$$

We can then write the heat capacitance as

$$\begin{aligned} C_V &= 3N_A h\nu_m \left(\frac{h\nu_m}{kT^2} \right) \exp\left(-\frac{h\nu_m}{kT}\right) \\ C_V &= 3N_A k \left(\frac{\theta_D}{T} \right)^2 \exp\left(-\frac{\theta_D}{T}\right) \end{aligned}$$

where $\theta_D = h\nu_m/k$ is the Debye temperature

Debye's Solid

Unlike Einstein's theory, Debye's theory agree with experimental data for both low and high T . Let us consider the phonon density

$$n(\nu) = \frac{9N}{\nu_m^3} \frac{\nu^2}{\exp(h\nu/kT) - 1} \quad \nu \leq \nu_m$$

Then the total energy

$$E = \int_0^{\nu_m} \frac{9Nh}{\nu_m^3} \frac{\nu^3}{\exp(h\nu/kT) - 1} d\nu$$

Since the integral is expressed as incomplete Riemann-Zeta function, we need some simplification. In other word, we make assumption.

Large temperature. For this case, the exponential term is small, thus the integral simplifies into

$$E = \frac{9Nh}{\nu_m^3} \int_0^{\nu_m} \frac{\nu^3}{h\nu/kT} d\nu = \frac{9N}{\nu_m^3} kT \frac{1}{3} \nu_m^3 = 3NkT = 3RT$$

And we then have the heat capacitance

$$C_V = 3R$$

Small temperature. First we define $x = h\nu/kT$, then we have

$$\nu = \frac{xkT}{h}, \quad dv = \frac{kT}{h} dx$$

By making the substitution, our integral reads

$$E = \int_0^{h\nu_m/kT} \frac{9Nh}{\nu_m^3} \left(\frac{xkT}{h} \right)^3 \frac{1}{\exp(h\nu/kT) - 1} \frac{kT}{h} dx$$

We also define Debye temperature $\theta_D = h\nu/k$

$$\begin{aligned} E &= \frac{9Nk}{\delta_D^3} T^4 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} dx \\ E &= \frac{9Nk}{\delta_D^3} 6 \frac{\pi^4}{90} T^4 = \frac{3\pi^4 Nk}{5\theta_D} T^4 \end{aligned}$$

Which mean that the heat capacitance

$$C_V = \frac{12\pi^4 R}{5\theta_D} T^3$$

Planck Distribution

Blackbody radiation

In his theory of blackbody radiation, energy density at frequency ν inside cavity with temperature T is given by

$$\mathcal{U}(\nu, T) = \rho u$$

where ρ is the number of radiation modes per unit volume and u is the average energy at said frequency. Both quantity respectively are given by

$$\rho = \frac{8\pi\nu^2}{c^3}, \quad u = \frac{h\nu}{\exp(h\nu/kT) - 1}$$

Hence

$$\mathcal{U}(\nu, T) = \frac{8\pi h}{c^3} \frac{\nu^3}{\exp(h\nu/kT) - 1}$$

or, we can write it in terms of λ

$$\mathcal{U}(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{\exp(hc/\lambda kT) - 1}$$

The particle density as function of wavelength

$$n(\lambda, T) = \frac{8\pi}{\lambda^4} \frac{1}{\exp(hc/\lambda kT) - 1}$$

And the relation with energy density

$$\mathcal{U}(\lambda) = n(\lambda)E(\lambda)$$

with $E = hc/\lambda$.

Planck's Derivation

In his work, Planck assumes that the walls of the cavity act as oscillator with energy of integer multiple ϵ . This has some similarity with Boltzmann discrete model. We denote n_k as the number particle with $k\epsilon$ energy, with maximum energy of $P\epsilon$. Therefore, we have the following constraints.

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

Planck he defined entropy as

$$S_P = k \ln(W) + C$$

where

$$W = \frac{\mathcal{R}}{\mathcal{J}}$$

is the probability of the N atoms have $p\epsilon$ energy. In other hand, \mathcal{R} denotes the number of said configuration and \mathcal{J} denotes the total configuration. It then may be written as

$$S_P = k \ln \mathcal{R}$$

where \mathcal{R} is given by

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

The logarithm of \mathcal{R} can be evaluated as

$$\begin{aligned} \ln \mathcal{R} &= (N+L-1)[\ln(N+L-1) - 1] - L[\ln(L) - 1] \\ &\quad - (N-1)[\ln(N-1) - 1] \end{aligned}$$

and then

$$\ln \mathcal{R} = (N+L-1)\ln(N+L-1) - L\ln L - (N-1)\ln(N-1)$$

and then

$$\begin{aligned} \ln \mathcal{R} &= (N+L)\ln(N+L-1) - \ln(N+L-1) - L\ln L \\ &\quad - N\ln(N-L) + \ln(N-1) \end{aligned}$$

and then

$$\begin{aligned} \ln \mathcal{R} &= (N+L) \left[\ln \left(\frac{N+L-1}{N+L} \right) + \ln(N+L) \right] - L\ln L \\ &\quad - N \left[\ln \left(\frac{N-1}{N} \right) + \ln(N) \right] - \ln \left(\frac{N+L-1}{N+L} \right) \end{aligned}$$

then finally we rewrite it as

$$\begin{aligned} \ln \mathcal{R} &= (N+L)\ln(N+L) - L\ln L - N\ln N \\ &\quad - N\ln \left(\frac{N-1}{N} \right) + (N+L-1)\ln \left(\frac{N+L-1}{N+L} \right) \end{aligned}$$

For large N, L ; those last two terms will approach zero. Hence,

$$\ln \mathcal{R} = (N+L)\ln(N+L) - L\ln L - N\ln N$$

This equation give the same result for $\ln(\mathcal{P}_{\max})$ in the case of Boltzmann discrete model. Therefore, we write

$$S_P = Nk \left[\left(1 + \frac{u}{\epsilon} \right) \ln \left(1 + \frac{u}{\epsilon} \right) - \frac{u}{\epsilon} \ln \left(\frac{u}{\epsilon} \right) \right]$$

Based on empirical data, Planck concludes that entropy is a function of energy and frequency

$$S_P = f \left(\frac{u}{\nu} \right)$$

On comparing those two equation, it can be seen that energy ϵ is proportional to frequency ν . To show this relationship, we then write $\epsilon = h\nu$. By solving the equation of entropy S_P for average energy u we will have the desired result.

To do so, we use the thermodynamics relationship

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

Change the variable we are differentiating against to average energy

$$\frac{\partial S_P}{\partial U} = \frac{1}{N} \frac{\partial S_P}{\partial u}$$

Then

$$\frac{1}{T} = k \left[\frac{1}{\epsilon} \ln \left(1 + \frac{u}{\epsilon} \right) + \left(1 + \frac{u}{\epsilon} \right) \left(1 + \frac{u}{\epsilon} \right)^{-1} \frac{1}{\epsilon} - \frac{1}{\epsilon} \ln \left(\frac{u}{\epsilon} \right) - \frac{u}{\epsilon} \frac{1}{u \epsilon} \right]$$

Moreover

$$\frac{1}{T} = \frac{k}{\epsilon} \left[\ln \left(1 + \frac{u}{\epsilon} \right) - \ln \left(\frac{u}{\epsilon} \right) \right] = \frac{k}{\epsilon} \ln \left(\frac{\epsilon}{u} + 1 \right)$$

Furthermore

$$\frac{\epsilon}{u} + 1 = \exp \left(\frac{\epsilon}{kT} \right)$$

Hence

$$u = \frac{\epsilon}{\exp(\epsilon/kT) - 1}$$

Substituting $\epsilon = h\nu$ from our empirical observation, we obtain

$$u = \frac{hv}{\exp(hv/kT) - 1} \quad \blacksquare$$

Bose's Derivation

Bose derived Planck's law independent of classical electrodynamics to obtain coefficient $8\pi\nu^2/c^3$. He defined the cell \mathcal{P}_ν as a box which photon are distributed. Let $n_{k\nu}$ defined as the number of boxes that contain k photon of frequency ν . We have then the following constraints.

$$P_\nu = \sum_{k=0}^{\infty} n_{k\nu}, \quad U_\nu = hv \sum_{k=0}^{\infty} kn_{k\nu}$$

or simply

$$P_\nu = \sum_{k=0}^{\infty} n_{k\nu}, \quad N_\nu = \sum_{k=0}^{\infty} kn_{k\nu}$$

where N_ν is the number of photon with frequency ν . The number of configuration is given by

$$\mathcal{P}_\nu = P_\nu! \left(\prod_{k=0}^{\infty} n_{k\nu} \right)^{-1}$$

All of those equations applies for distinct frequency ν , what we what however distribution over all frequency $(0, \infty)$. The expression for constraints is

$$P_\nu = \sum_{k=0}^{\infty} n_{k\nu}, \quad U = h \sum_{k=0}^{\infty} v \sum_{k=0}^{\infty} kn_{k\nu}$$

and the expression for the number of configuration is

$$\mathcal{P} = \sum_{\nu=0}^{\infty} \mathcal{P}_{\nu}$$

As usual, the equation that we want to maximize not the configuration \mathcal{P} itself, but rather its logarithm; which may be written as

$$\ln \mathcal{P} = \sum_{\nu=0}^{\infty} \ln \left[\mathcal{P}_{\nu}! \left(\prod_{k=0}^{\infty} n_{k\nu} \right)^{-1} \right]$$

On using Stirling's approximation

$$\begin{aligned} \ln \mathcal{P} &= \sum_{\nu}^{\infty} \left[\mathcal{P}_{\nu} \ln (\mathcal{P}_{\nu}) - \mathcal{P}_{\nu} - \sum_k^{\infty} \{n_{k\nu} \ln (n_{k\nu}) - n_{k\nu}\} \right] \\ \ln \mathcal{P} &= \sum_{\nu}^{\infty} \left[\mathcal{P}_{\nu} \ln (\mathcal{P}_{\nu}) - \sum_k^{\infty} n_{k\nu} \ln (n_{k\nu}) \right] \end{aligned}$$

Since we want to maximize said logarithm with respect to $n_{k\nu}$, we construct the following function using Lagrange's method.

$$F(n_{k\nu}) = \sum_{\nu} \left[\mathcal{P} \ln \mathcal{P}_{\nu} - \sum_k n_{k\nu} \ln n_{k\nu} \right] + \lambda_1 \sum_k n_{k\nu} + \lambda_2 h \sum_{v,k} v k n_{k\nu}$$

Setting its derivative to zero

$$\frac{dF}{dn_{k\nu}} = -\ln(n_{k\nu}) - 1 + \lambda_1 + \lambda_2 h k \nu = 0$$

which implies

$$n_{k\nu} = \exp (1 - \lambda_1 - \lambda_2 h k \nu) = C \exp (-\lambda_2 h k \nu)$$

Substituting the result into \mathcal{P}_{ν} constraints

$$\mathcal{P}_{\nu} = C \sum_k \exp (-\lambda_2 h k \nu) \implies C = \mathcal{P}_{\nu} \left[\sum_k \exp (-\lambda_2 h k \nu) \right]^{-1}$$

The term inside parenthesis is a geometric series with ratio of $\exp(-\lambda_2 h \nu)$. The constant then can be simply evaluated into

$$C = \mathcal{P}_{\nu} \left[\frac{1}{1 - \exp(-\lambda_2 h \nu)} \right]^{-1} = \mathcal{P}_{\nu} [1 - \exp(-\lambda_2 h \nu)]$$

Hence the $n_{k\nu}$ assumes the form

$$n_{k\nu} = \mathcal{P}_{\nu} [1 - \exp(-\lambda_2 h \nu)] \exp (-\lambda_2 h k \nu)$$

On using this to the expression for logarithm of \mathcal{P} , we obtain

$$\begin{aligned} \ln \mathcal{P}_{\max} &= \sum_{\nu} \left[\mathcal{P}_{\nu} \ln (\mathcal{P}_{\nu}) \right. \\ &\quad \left. - \sum_k n_{k\nu} \ln \{ \mathcal{P}_{\nu} [1 - \exp(-\lambda_2 h \nu)] \exp (-\lambda_2 h k \nu) \} \right] \end{aligned}$$

Then by definition of Boltzmann entropy, we have

$$S_B = k \ln \mathcal{P}_{\max} = \sum_{\nu} k \left[\mathcal{P}_{\nu} \ln (\mathcal{P}_{\nu}) - \sum_k n_{k\nu} \ln \{ \mathcal{P}_{\nu} [1 - \exp(-\lambda_2 h\nu)] \exp(-\lambda_2 h k \nu) \} \right]$$

We then write it as such

$$S_B = \sum_{\nu} k \left[\mathcal{P}_{\nu} \ln (\mathcal{P}_{\nu}) - \sum_k n_{k\nu} \{ \ln(\mathcal{P}_{\nu}) + \ln(1 - \exp\{-\lambda_2 h\nu\}) - \lambda_2 v k h \} \right]$$

additionally

$$S_B = \sum_{\nu} k \left[\lambda_2 h v \sum_k k n_{k\nu} - \sum_k n_{k\nu} \ln(1 - \exp\{-\lambda_2 h\nu\}) \right]$$

Recall the \mathcal{P}_{ν} and U_{ν} constraints

$$S_B = k \left[\lambda_2 U - \sum_{\nu} \mathcal{P}_{\nu} \ln(1 - \exp\{-\lambda_2 h\nu\}) \right]$$

Using the following relationship

$$\frac{1}{T} = \frac{\partial S}{\partial U}$$

we have

$$\frac{1}{T} = k \lambda_2 \implies \lambda_2 = \frac{1}{kT}$$

At last, we have

$$n_{k\nu} = \mathcal{P}_{\nu} \left[1 - \exp \left(-\frac{h\nu}{kT} \right) \right] \exp \left(-\frac{h k \nu}{kT} \right)$$

and

$$S_B = \frac{U}{T} - \sum_{\nu} k \mathcal{P}_{\nu} \ln \left[1 - \exp \left(-\frac{h\nu}{kT} \right) \right]$$

Henceforward, we use these result to evaluate the following quantity. First we evaluate the number of quanta of frequency ν denoted as N_{ν}

$$N_{\nu} = \sum_k k n_{k\nu}$$

Substituting the known value of $n_{k\nu}$, we get

$$\begin{aligned} N_{\nu} &= \sum_k k \mathcal{P}_{\nu} \left[1 - \exp \left(-\frac{h\nu}{kT} \right) \right] \exp \left(-\frac{h k \nu}{kT} \right) \\ &= \mathcal{P}_{\nu} \left[1 - \exp \left(-\frac{h\nu}{kT} \right) \right] \sum_k k \exp \left(-\frac{h k \nu}{kT} \right) \end{aligned}$$

To evaluate such sum we consider the geometric series

$$\sum_{k=0}^{\infty} r^k = \frac{1}{1-r}$$

for $r < 1$. Taking a derivative of both sides to get

$$\sum_{k=0}^{\infty} kr^{k-1} = \frac{1}{(1-r)^2}$$

Then shift the index down by one

$$\sum_{k=-1}^{\infty} (k+1)r^k = \sum_{k=0}^{\infty} (k+1)r^k$$

where the left side is allowed since the series is zero at $k = -1$. Then subtract this series with the first series

$$\sum_{k=0}^{\infty} (k+1)r^k - r^k = \sum_{k=0}^{\infty} kr^k = \frac{1 - (1-r)}{(1-r)^2} = \frac{r}{(1-r)^2}$$

Using the formula above, with

$$r = \exp\left(-\frac{h\nu}{kT}\right)$$

we can now evaluate the number of quanta

$$\begin{aligned} N_{\nu} &= \mathcal{P}_{\nu} \left[1 - \exp\left(-\frac{h\nu}{kT}\right) \right] \exp\left(-\frac{h\nu}{kT}\right) \left[1 - \exp\left(-\frac{h\nu}{kT}\right) \right]^{-2} \\ &= \mathcal{P}_{\nu} \exp\left(-\frac{h\nu}{kT}\right) \left[1 - \exp\left(-\frac{h\nu}{kT}\right) \right]^{-1} \\ &= \mathcal{P}_{\nu} \left[\exp\left(\frac{h\nu}{kT}\right) - 1 \right]^{-1} \\ N_{\nu} &= \sum_k kn_{k\nu} = \frac{\nu^2}{c^3} \frac{8\pi V}{\exp(h\nu/kT) - 1} d\nu \end{aligned}$$

The second is energy within the same frequency

$$U_{\nu} = h\nu N_{\nu} = \frac{\nu^3}{c^3} \frac{8\pi hV}{\exp(h\nu/kT) - 1} d\nu$$

To obtain the average energy per unit frequency, we divide U_{ν} by spatial volume (since we derived it from phase space volume) V and by unit frequency $d\nu$

$$\mathcal{U}(\nu, T) = \frac{U_{\nu}}{V d\nu} = \frac{\nu^3}{c^3} \frac{8\pi h}{\exp(h\nu/kT) - 1}$$

Einstein's Method

Suppose we use Einstein method to rederive Planck's law, just like Bose did. In his method, he distributed the number of identical quanta

N_ν within distinct P_ν cells. The number of configuration in this case is given by

$$\mathcal{P}_\nu = \frac{(N_\nu + P_\nu - 1)}{N_\nu!(P_\nu - 1)!}$$

The logarithm for total frequency reads

$$\ln \mathcal{P} = \sum_\nu (N_\nu + P_\nu) \ln(N_\nu + P_\nu) - N_\nu \ln(N_\nu) - P_\nu \ln(P_\nu)$$

We want to maximize this logarithm constrained by

$$U = h \sum_{\nu=0}^{\infty} \nu N_\nu$$

The constraints on number of quanta simply does not exist since the quanta continuously created and destroyed by the cavity walls. To maximize the said logarithm, we then construct

$$F = \ln \mathcal{P} + \lambda_1 h \sum_\nu \nu N_\nu$$

We then set its derivative to zero

$$\ln(N_\nu + P_\nu) + 1 - \ln(N_\nu) - 1 + \lambda h \nu = 0$$

Hence

$$\begin{aligned} \frac{N_\nu + P_\nu}{N_\nu} \exp(-\lambda_1 h \nu) \\ N_\nu = \frac{P_\nu}{\exp(-\lambda_1 h \nu) - 1} \end{aligned}$$

Substituting this into the logarithm of \mathcal{P} to obtain

$$\ln \mathcal{P}_{\max} = \sum_\nu \left[N_\nu (-\lambda_1 - \lambda_1 E) + P_\nu \ln \left(\frac{\exp(-\lambda_1 E)}{\exp(-\lambda_1 E) - 1} \right) \right]$$

The entropy reads

$$S = \sum_\nu k_B P_E \ln \left(\frac{\exp(-\lambda_1 E)}{\exp(-\lambda_1 E) - 1} \right) - k_B \lambda_1 U$$

Hence

$$\frac{1}{T} = \frac{\partial S}{\partial U} = -k_B \lambda \implies \lambda_1 = \frac{1}{T}$$

Substituting this constant back, we have

$$N_\nu = \frac{\nu^3}{c^3} \frac{8\pi h V}{\exp(h\nu/k_B T) - 1} d\nu, \quad U_\nu = \frac{\nu^3}{c^3} \frac{8\pi h V}{\exp(h\nu/k_B T) - 1} d\nu$$

and

$$\mathcal{U}(\nu, T) = \frac{\nu^3}{c^3} \frac{8\pi h}{\exp(h\nu/k_B T) - 1}$$

which is the same as Bose's result.

Rayleigh-Jeans Model

This model is only accurate for large λ or small ν . The energy density described by this model is

$$\mathcal{U}(\lambda, T) = \frac{8\pi}{\lambda^4} kT \quad \text{or} \quad \mathcal{U}(\nu, T) = \frac{8\pi\nu^2}{c^3} kT$$

Derivation. For large λ , the exponential term approaches zero, so it can be approximated with

$$\exp\left(\frac{hc}{\lambda kT}\right) \approx \frac{hc}{\lambda kT} - 1$$

Hence, the energy density as function of wavelength is

$$\mathcal{U}(\lambda, T) \approx \frac{8\pi hc}{\lambda^5} \frac{1}{(hc/\lambda kT)} = \frac{8\pi}{\lambda^4} kT \quad \blacksquare$$

Wien's Law

In other hand, this model only accurate for small λ or large ν . The energy density based this model is

$$\mathcal{U}(\lambda, T) = \frac{8\pi hc}{\lambda^5} \exp\left(-\frac{hc}{\lambda kT}\right)$$

Wien's model is able to obtain the fact that the product maximum wavelength and temperature is constant, in particular

$$\lambda_m T = 2.897 \text{ mmK}$$

Derivation. For small λ , the exponential term approach infinity, so the denominator term of the Plack distribution can be approximated with

$$\left[\exp\left(\frac{hc}{\lambda kT}\right) - 1\right]^{-1} \approx \exp\left(-\frac{hc}{\lambda kT}\right)$$

Hence

$$\mathcal{U}(\lambda, T) = \frac{8\pi hc}{\lambda^5} \exp\left(-\frac{hc}{\lambda kT}\right)$$

To find the maximum wavelength given by Wien's distribution, we set

$$\frac{du}{d\lambda} = 8\pi hc \left[-\frac{5}{\lambda^6} \exp\left(-\frac{hc}{\lambda kT}\right) \frac{1}{\lambda^5} \frac{hc}{\lambda^2 kT} \exp\left(-\frac{hc}{\lambda kT}\right) \right]$$

into zero to obtain

$$\begin{aligned} \frac{5}{\lambda_m^6} &= \frac{hc}{\lambda_m^7 kT} \\ \lambda_m T &= \frac{hc}{5k} = 2.897 \text{ mmK} \end{aligned}$$

Stefan's Law

$$u = \alpha T^4$$

where $\alpha = 1.65 \cdot 10^{-16} \text{ J/K}^4\text{m}^3$.

Derivation. Integrating $\mathcal{U}(\lambda)$ over all possible wavelength to obtain

$$u = \int_0^\infty \frac{8\pi hc}{\lambda^5} \frac{1}{\exp(hc/\lambda kT) - 1} d\lambda$$

Substituting $x = hc/\lambda kT$, we have $1/\lambda = xkT/hc$ and $d\lambda = -hc/x^2 kT dx$. Thus,

$$\begin{aligned} u &= \int_0^\infty 8\pi hc \left(\frac{xkT}{hc} \right)^5 \frac{1}{e^x - 1} \left(-\frac{hc}{x^2 kT} \right) dx \\ &= \frac{8\pi (kT)^4}{(hc)^3} \int_0^\infty \frac{x^3}{e^x - 1} dx \\ u &= \frac{8\pi (kT)^4}{(hc)^3} 6 \frac{\pi^2}{90} \end{aligned}$$

Evaluating the constant, we finally have

$$u = 7.65 \cdot 10^{-16} T^4 \quad \blacksquare$$

Stefan-Boltzmann's Law

$$I = \sigma T^4$$

where $\sigma = 5.57 \cdot 10^{-8} \text{ J/K}^4\text{m}^2$.

Derivation. Based on MB distribution, the flux of a gas is

$$\Gamma = \frac{1}{4} \rho \langle v \rangle$$

On using this to gas of photon we have

$$\Gamma = \frac{1}{4} nc$$

By using the relation

$$\mathcal{U}(\lambda) = n(\lambda) E(\lambda)$$

we have our intensity as

$$I = \frac{1}{4} uc = \frac{1}{4} 7.65 \cdot 10^{-16} T^4 c = 5.57 \cdot 10^{-8} T^4$$

Fermi-Dirac Distribution

Fermi-Dirac Distribution

The distribution of particle obeying the Pauli exclusion principle, also called fermion, is governed by Fermi-Dirac distribution. In general, the number of particle per unit energy interval is given by

$$n(E) = \frac{g(E)}{\exp[(E - \mu)/k_B T] + 1}$$

For free non-relativistic fermion—such as metals, conductor, and electron gases—the density of state is given by

$$g(E) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}$$

then the distribution function simply evaluate into

$$n(E) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{E^{1/2}}{\exp[(E - \mu)/k_B T] + 1}$$

The Fermi-Dirac distribution may be expressed as a product of the Fermi function and the density of state

$$n(E) = f(E, T)g(E)$$

where

$$f(E, T) = \frac{1}{\exp[(E - \mu)/k_B T] + 1}$$

Einstein Derivation

The number of configuration in this case is the number of ways to choose N_E particle from P_E cells

$$\mathcal{P}_E = \binom{P_E}{N_E} = \frac{P_E!}{(P_E - N_E)!N_E!}$$

with the number of cells given by

$$P_E = \frac{2\pi}{\hbar^3} V (2m)^{3/2} \sqrt{E} dE$$

This is the same value that Bose derived. As for the total number of configuration across all interval of energy

$$\mathcal{P} = \prod_{E=0}^{\infty} \mathcal{P}_E$$

To find the distribution function, we need to determine the entropy of such system. Hence, we need to maximize the logarithm of said configuration. To such end, we write the logarithm as

$$\ln \mathcal{P} = \sum_E [P_E \ln(P_E) - P_E - (P_E - N_E) \ln(P_E - N_E) + (P_E - N_E)]$$

$$- N_E \ln(N_E) + N_E]$$

$$\ln \mathcal{P} = \sum_E P_E \ln(P_E) - (P_E - N_E) \ln(P_E - N_E) - N_E \ln(N_E)$$

By Lagrange's method, we consider the following constraints

$$N = \sum_{E=0}^{\infty} N_E, \quad U = \sum_{E=0}^{\infty} EN_E$$

and construct the following function

$$F = \ln \mathcal{P} + \lambda_1 N_E + \lambda_2 E N_E$$

Setting the derivative to zero

$$\ln(P_E - N_E) + 1 - \ln(N_E) - 1\lambda_1 + \lambda_2 E = 0$$

and solving for N_E

$$\frac{P_E - N_E}{N_E} = \exp(\lambda_1 - \lambda_2 E)$$

$$N_E = \frac{P_E}{\exp(\lambda_1 - \lambda_2 E) + 1}$$

The expression for entropy then reads

$$S = \sum_E P_E k_B \ln(P_E) - \sum_E (P_E k_B - N_E k_B)$$

$$\left[\ln(P_E) + \ln \left(\frac{\exp(\lambda_1 - \lambda_2 E)}{\exp(\lambda_1 - \lambda_2 E) + 1} \right) \right]$$

$$- \sum_E N_E k_B [\ln(P_E) - \ln(\exp(\lambda_1 - \lambda_2 E) + 1)]$$

furthermore

$$S = \sum_E (N_E k_B - P_E k_B) \ln \left(\frac{\exp(\lambda_1 - \lambda_2 E)}{\exp(\lambda_1 - \lambda_2 E) + 1} \right)$$

$$+ \ln \sum_E N_E k_B \ln (\exp(\lambda_1 - \lambda_2 E) + 1)$$

additionally

$$S = N k_B (-\lambda_1 - \lambda_2 E) - \sum_E P_E \ln \left(\frac{\exp(\lambda_1 - \lambda_2 E)}{\exp(\lambda_1 - \lambda_2 E) + 1} \right)$$

By using the thermodynamics relation

$$\frac{1}{T} = \frac{\partial S}{\partial U} \Big|_{V,N} = -\lambda_2 k_B \implies \lambda_2 = -\frac{1}{k_B T}$$

and

$$-\frac{\mu}{T} = \frac{\partial S}{\partial N} = -k_B \lambda_1 \implies \lambda_1 = \frac{\mu}{k_B T}$$

Therefore

$$N_E = \frac{2\pi}{h^3} \frac{V(2m)^{3/2} \sqrt{E}}{\exp[(E - \mu)/k_B T] + 1} dE$$

and for the distribution function

$$n_E = \frac{2\pi}{h^3} \frac{V(2m)^{3/2} \sqrt{E}}{\exp[(E - \mu)/k_B T] + 1}$$

Fermi Gas at Zero Temperature

The Fermi function at absolute zero can be written as step function

$$f(E, 0) = \begin{cases} 1 & E < \mu \\ 0 & \mu < E \end{cases}$$

To see how this came to be, observe the behavior of the Fermi function, which depends on the value $E - \mu$, as T approach zero. For $E < \mu$ and $\mu < E$ respectively, we have

$$f(E, 0) = \frac{1}{\exp(-\infty) + 1} \quad \text{and} \quad f(E, 0) = \frac{1}{\exp(\infty) + 1}$$

Since the Fermi-Dirac distribution is a product of Fermi function and density of state, DoS, function, we must have

$$n(E)|_{T=0} = \begin{cases} g(E) & E < \mu \\ 0 & \mu < E \end{cases}$$

Fermi energy. The Fermi energy is the energy of the highest occupied state at absolute zero temperature. It is given by

$$E_F = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{2/3} = \frac{3N}{2g(E_F)}$$

We define the chemical potential at absolute zero as the Fermi energy $\mu \equiv E_F$. To derive the said quantity, we consider the total number of particle

$$\begin{aligned} N &= \int_0^\infty n(E) dE = \int_0^{E_F} g(E) dE \\ &= \int_0^{E_F} \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} dE \\ N &= \frac{V}{3\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E_F^{3/2} \end{aligned}$$

By solving for E_F , we obtain the expression for Fermi energy. Alternatively we can write it in terms of DoS by doing simple algebra

$$\begin{aligned} g(E_F) &= \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E_F^{1/2} \\ &= \frac{3N}{2} \frac{1}{3\pi^2} \frac{V}{N} \left(\frac{2m}{\hbar^2} \right)^{3/2} E_F^{1/2} \\ g(E_F) &= \frac{3N}{2} \frac{E_F^{1/2}}{E_F^{3/2}} = \frac{3N}{2E_F} \end{aligned}$$

Fermi temperature. The Fermi temperature is the temperature where the thermal energy kT can be compared with the Fermi energy E_F . By comparing those two energy, we obtain the value of Fermi temperature

$$T_F = \frac{E_F}{k} = \frac{\hbar^2}{2mk} \left(3\pi^2 \frac{N}{V} \right)^{2/3}$$

Fermi velocity. Like Fermi energy, the Fermi velocity is the highest velocity, or rather speed, of fermion at absolute zero. It is given by

$$v_F = \left(\frac{2E_F}{m} \right)^{1/2}$$

It can be obtained by using the kinetic energy relation $E = mv^2/2$ for the Fermi energy. To be more explicit, we can also write

$$v_F = \frac{\hbar}{m} \left(3\pi^2 \frac{N}{V} \right)^{1/3}$$

Fermi momentum. The Fermi momentum is the highest momentum fermions at absolute zero can possibly have, and it is given by

$$p = \hbar \left(3\pi^2 \frac{N}{V} \right)^{1/3}$$

Fermi wavevector and wavelength. Since the momentum of a free fermion is $p = \hbar k$, we have the Fermi wavevector as $k = p/\hbar$ or

$$k_F = \left(3\pi^2 \frac{N}{V} \right)^{1/3}$$

Using the wave relation $k = 2\pi/\lambda$, we can determine the Fermi wavelength

$$\lambda_F = \frac{2\pi}{(3\pi^2 N/V)^{1/3}}$$

Average energy. At absolute zero, the average energy of fermion is given by

$$\langle E \rangle = \frac{3}{5} E_F$$

It is derived by the following method.

$$\begin{aligned} \langle E \rangle |_{T=0} &= \frac{1}{N} \int_0^\infty E n(E) dE = \frac{1}{N} \int_0^\infty \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{3/2} dE \\ &= \frac{V}{2\pi^2 N} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{2}{5} E_F^{5/2} \\ &= \frac{V}{2\pi^2 N} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{2}{5} \left(\frac{\hbar^2}{2m} \right)^{5/2} \left(3\pi^2 \frac{N}{V} \right)^{5/3} \\ \langle E \rangle |_{T=0} &= \frac{1}{5} \left(\frac{\pi^2 N}{V} \right)^{3/2} \left(\frac{\hbar}{2m} \right) 3^{5/3} = \frac{3^{5/3}}{5} \frac{E_F}{3^{2/3}} = \frac{3}{5} E_F \end{aligned}$$

Average velocity. The average velocity of fermion at absolute zero is given by

$$\langle v \rangle |_{T=0} = \frac{1}{N} \int_0^\infty E n(E) dE$$

It is derived in the following ways.

$$\langle v \rangle |_{T=0} = \frac{1}{N} \int_0^\infty v n(v) dv = \frac{1}{N} \int_0^\infty \frac{V}{2\pi^2} \left(\frac{\hbar}{2m} \right)^{3/2} \left(\frac{m}{2} \right)^{1/2} v^2 mv dv$$

$$\begin{aligned}
&= \frac{V}{\pi^2 N} \left(\frac{m}{\hbar} \right)^3 \frac{1}{4} v_F^4 \\
&= \frac{V}{\pi^2 N} \left(\frac{m}{\hbar} \right)^3 \frac{1}{4} \left(\frac{\hbar}{m} \right)^3 \left(3\pi^2 \frac{N}{V} \right) v_f = \frac{3}{4} v_F
\end{aligned}$$

Fermi Gas at Low Temperature

Unlike at the absolute zero, the Fermi function at low temperature can not be written as step function, instead it decreases smoothly around the Fermi energy. This also implies that the distribution function does not suffer from discontinuity.

At low temperature, there are N_0 fermions occupying Fermi energy state and ΔN fermion occupying the higher energy state. Thus, the number of fermion is $N = N_0 + \Delta N$.

It is convenient to use the Sommerfeld expansion to evaluate Fermi-Dirac distribution at low temperature

$$\int_0^\infty f(E)g(E)dE = \int_0^{E_F} g(E)dE + \sum_{n=1}^{\infty} c_n (kT)^{2n} g^{(2n-1)}(E)_{E_F}$$

In many practical applications, however, we can approximate the integral only using the first term. The so called first-order Sommerfeld expansion expressed as

$$\int_0^\infty f(E)g(E)dE \approx \int_0^{E_F} g(E)dE + \frac{(\pi kT)^2}{6} g'(E)_{E_F}$$

Chemical potential. Recall the integral for fermion at absolute zero

$$N = \int_0^\infty n(E) dE = \int_0^{E_F} g(E) dE$$

We define chemical potential $\mu(T)$ such that the upper limit of the integral is shifted into

$$N = \int_0^{\mu(T)} g(E) dE$$

The number of particle for given T remain the same because chemical is defined in a way such that the number of particle also remain the same. This is also way at absolute zero the chemical energy is defined as Fermi energy $\mu \equiv E_F$. The Fermi function is also approximated to be $f(E) \approx 1$ since the value is mostly 1 up to $E = \mu(T)$.

The expression for chemical potential at low temperature is given by

$$\mu = E_F \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{E_F} \right)^2 \right] = E_F \left[1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right]$$

To derive the expression for chemical potential, we approximate the number of particle using Taylor expansion

$$N = \int_0^\mu g(E) dE \approx \int_0^{E_F} g(E) dE + g(E_F)(\mu - E_F)$$

and using the first order Sommerfeld expansion

$$N = \int_0^\infty f(E)g(E) dE \approx \int_0^{E_F} g(E) dE + \frac{(\pi kT)^2}{6} g'(E)_{E_F}$$

Equating both expression for the number of particle

$$\begin{aligned} g(E_F)(\mu - E_F) &= g'(E) \frac{(\pi kT)^2}{6} \\ \mu - E_F &= \frac{(\pi kT)^2}{6} \frac{g'(E)_{E_F}}{g(E)_{E_F}} \end{aligned}$$

We write the DoS and its derivative as

$$\begin{aligned} g(E) &= \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} \\ g'(E) &= \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{1}{E^{1/2}} = \frac{g(E)}{2E_F} \end{aligned}$$

Hence

$$\begin{aligned} \mu - E_F &= \frac{(\pi kT)^2}{12E_F} \\ \mu &= E_F \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{E_F} \right)^2 \right] \end{aligned}$$

Alternatively, using the Fermi temperature, we can rewrite the expression in terms of Fermi temperature.

Average energy. Given by

$$\langle E \rangle = E_F \left[\frac{3}{5} + \frac{\pi^2}{4} \left(\frac{kT}{E_F} \right)^2 \right] = E_F \left[\frac{3}{5} + \frac{\pi^2}{4} \left(\frac{T}{T_F} \right)^2 \right]$$

To derive this, we use the first order Sommerfeld expansion, however instead the function of $g(E)$, we use $Eg(E)$

$$\int_0^\infty Ef(E)g(E) dE \approx \int_0^{E_F} g(E) dE + \frac{(\pi kT)^2}{6} [Eg(E)]'_{E_F}$$

Since the integral above can be used to determine the average energy, then

$$\begin{aligned} \langle E \rangle &= \frac{1}{N} \int_0^\mu g(E) dE + \frac{(\pi kT)^2}{6} [Eg(E)]'_\mu \\ \langle E \rangle &= \frac{1}{N} \int_0^{E_F} g(E) dE + \frac{1}{N} \int_{E_F}^\mu g(E) dE + \frac{(\pi kT)^2}{6} [Eg(E)]'_\mu \end{aligned}$$

We can approximate the second term as

$$\begin{aligned} \frac{1}{N} \int_{E_F}^\mu g(E) dE &= \frac{1}{N} Eg(E_F)(E_F - \mu) = -\frac{1}{N} \frac{3N}{2} \frac{(\pi kT)^2}{12E_F} \\ \frac{1}{N} \int_{E_F}^\mu g(E) dE &= -\frac{1}{8} \frac{(\pi kT)^2}{E_F} \end{aligned}$$

and the derivative term as

$$\begin{aligned}[Eg(E)]'_{\mu} &= g(\mu) + \mu g'(\mu) \approx g(E_F) + E_F g'(E_F) \\ &\approx g(E_F) + \frac{3}{2}g(E_F) = \frac{3}{2}g(E_F) \\ [Eg(E)]'_{\mu} &\approx \frac{9N}{4E_F}\end{aligned}$$

Thus

$$\langle E \rangle = \frac{3}{5}E_F - \frac{1}{4}\frac{(\pi kT)^2}{E_F} + \frac{3}{8}\frac{(\pi kT)^2}{E_F} = E_F \left[\frac{3}{5} + \frac{\pi^2}{4} \left(\frac{kT}{E_F} \right)^2 \right]$$

Heat capacitance. Inside metal, heat capacitance is the sum of heat capacitance due to phonon, predicted by Debye's model, and due to the free electron, governed by Fermi-Dirac distribution

$$C_V = C_{V\text{ph}} + C_{V\text{el}} = \begin{cases} AT^3 + \gamma T & T < \theta_D \\ 3R + \gamma T & \theta_D < T < T_F \\ \gamma T & T_F < T \end{cases}$$

For the first two case, the first term is the heat capacitance predicted by Debye, while the term γT is predicted by Fermi-Dirac distribution.

To derive the quantity of heat capacitance, we use the thermodynamics define of heat capacitance for constant volume. On differentiating the total energy with respect to temperature, we have

$$\frac{d}{dt} \langle NE \rangle \Big|_{V,N=N_A} = N_A \frac{E_F \pi^2}{2T_F^2} T = N_A \frac{k\pi^2}{2T_F} = 4.93R \frac{T}{T_F}$$

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 ϵ . The permutation of configuration $E_{k|P} \equiv E_1, \dots, E_P$ 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 $(0, \epsilon)$

Macrostate $n_{k P} = (n_0, n_1)$	Microstate $E_{k P} = (E_1, E_2, E_3)$
$(3, 0)$	$(0, 0, 0)$
$(2, 1)$	$(\epsilon, 0, 0), (0, \epsilon, 0), (0, 0, \epsilon)$
$(1, 2)$	$(\epsilon, \epsilon, 0), (\epsilon, 0, \epsilon), (0, \epsilon, \epsilon)$
$(0, 3)$	$(\epsilon, \epsilon, \epsilon)$

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

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

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 $n_{k P} = (n_0, \dots, n_7)$	Number of configuration $D(N, P, n_{k P})$
$(6, 0, 0, 0, 0, 0, 0, 1)$	$\frac{7!}{6!0!0!0!0!0!1!} = 7$
$(5, 1, 0, 0, 0, 0, 1, 0)$	$\frac{7!}{5!1!0!0!0!0!1!0!} = 42$
$(5, 0, 1, 0, 0, 1, 0, 0)$	$\frac{7!}{5!0!1!0!0!1!0!0!} = 42$
$(5, 0, 0, 1, 1, 0, 0, 0)$	$\frac{7!}{5!0!0!1!1!0!0!0!} = 42$
$(4, 2, 0, 0, 0, 1, 0, 0)$	$\frac{7!}{4!2!0!0!1!0!0!0!} = 105$
$(4, 1, 1, 0, 1, 0, 0, 0)$	$\frac{7!}{4!1!1!0!1!0!0!0!} = 210$
$(4, 0, 2, 1, 0, 0, 0, 0)$	$\frac{7!}{4!0!2!1!0!0!0!0!} = 105$
$(4, 1, 0, 2, 0, 0, 0, 0)$	$\frac{7!}{4!1!0!2!0!0!0!0!} = 105$
$(3, 3, 0, 0, 1, 0, 0, 0)$	$\frac{7!}{3!3!0!0!0!0!0!} = 140$
$(3, 2, 1, 1, 0, 0, 0, 0)$	$\frac{7!}{3!2!1!1!0!0!0!0!} = 420$
$(3, 1, 3, 0, 0, 0, 0, 0)$	$\frac{7!}{3!1!3!0!0!0!0!0!} = 140$
$(2, 4, 0, 1, 0, 0, 0, 0)$	$\frac{7!}{2!4!0!1!0!0!0!0!} = 105$
$(2, 3, 2, 0, 0, 0, 0, 0)$	$\frac{7!}{2!3!2!0!0!0!0!0!} = 210$
$(1, 5, 1, 0, 0, 0, 0, 0)$	$\frac{7!}{1!5!1!0!0!0!0!0!} = 42$
$(0, 7, 0, 0, 0, 0, 0, 0)$	$\frac{7!}{0!7!0!0!0!0!0!0!} = 1$

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.

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

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

or

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

where $x = L/(L+N)$.

The number of particle n_k inside configuration above is

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

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

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

In terms of observable quantity, this expression reads

$$n_k = N \left[1 - \exp \left(-\frac{\epsilon}{k_B T} \right) \right] \exp \left[-\frac{k\epsilon}{k_B T} \right]$$

Proof. 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, we can find the desired maximum function. 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

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

Solving for n_k

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

for convenience's sake, we use

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

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

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

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 real™ 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

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

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

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

Using $u = L\epsilon/N$, we $x = L/(L + N)$ as

$$x = \frac{Nu/\epsilon}{Nu/\epsilon + L\epsilon/u} = \frac{u}{u + L\epsilon^2/Nu} = \frac{u}{u + \epsilon}$$

Substituting it inside the expression of n_k

$$n_k = N(1-x)x^k = N \left(1 - \frac{u}{u+\epsilon}\right) \left(\frac{u}{u+\epsilon}\right)^k = \frac{N_\epsilon}{u+\epsilon} \left(1 + \frac{\epsilon}{u}\right)^{-k} \quad \blacksquare$$

I suppose we can also solve x for u

$$\begin{aligned} xu + x\epsilon &= u \\ u(1-x) &= x\epsilon \\ u &= \frac{x\epsilon}{1-x} \end{aligned}$$

Then plug in the equation for average molecular energy

$$\begin{aligned} \frac{\epsilon}{\exp(\epsilon/k_B T) - 1} &= \frac{x\epsilon}{1-x} \\ \frac{1-x}{x} &= \exp(\epsilon/k_B T) - 1 \\ 1 &= x \exp(\epsilon/k_B T) \\ x &= \exp(-\epsilon/k_B T) \end{aligned}$$

Substituting the value of x inside the expression for n_k , we have

$$n_k = N(1-x)x^k = N \left[1 - \exp\left(-\frac{\epsilon}{k_B T}\right)\right] \exp\left[-\frac{k\epsilon}{k_B T}\right] \quad \blacksquare$$

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

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

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

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

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 results:

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.

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 $x = 0.5078125$.

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

Heat, work, and Thermodynamics. In statistical mechanics, heat given to a system corresponds to energy transfer through particle exchange and cause the number of particle per energy level changes. For example, consider particle inside potential box. Suppose we are giving energy without changing the system structure such as volume, shape of the potential, external field, and its Hamiltonian. In thermodynamics lens, we are doing transfer of energy via heat.

In other hand, work represents the energy change due to changes in the energy levels themselves. This could be done by changing the system structure. The change of energy level s due to work W is

$$d\epsilon_s = \frac{W}{E} \epsilon_s$$

Now consider the first thermodynamics in the lens of thermodynamics

$$dE = dQ - PdV$$

and with the lens of statistical mechanics

$$dE = \sum_s [\epsilon_s dn_s + n_s d\epsilon_s]$$

Here we can see that

$$\sum_s \epsilon_s dn_s = dQ \quad \text{and} \quad \sum_s n_s d\epsilon_s = -P dV$$

Next consider the second law. Thermodynamics define entropy as state function where

$$dS \geq \frac{dQ}{T}$$

We use the equal sign for reversible process and inequality for the irreversible process. According to statistical mechanics however, this law reads

$$S = k \ln \Omega$$

According to this law, a system will evolve to the direction with more entropy. This is a consequence of the definition of the entropy: a measure how many microscopic ways a system can realize a given macroscopic state. Naturally, macrostate with more microstate is more probable, thus any given system will evolve toward it.

Finally, we consider the last law. According to this law, the entropy at absolute zero is $S = 0$. This is due to at that temperature, a system will only have one microstate, thus by definition of entropy, $S = 0$.

Change of energy level proof. Consider the energy eigenstate of particle in a potential box

$$\epsilon_s = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2) = \frac{h^2}{8m}B_s V^{-2/3}$$

Its logarithm reads

$$\ln \epsilon_s = \ln \frac{h^2}{8m} B_s - \frac{2}{3} \ln V$$

and its differential

$$\frac{d\epsilon_s}{\epsilon_s} = -\frac{2}{3} \ln V$$

Recall

$$-\frac{2}{3} \ln V = -\frac{P dV}{\frac{3}{2} N k T} = \frac{dW}{E}$$

Hence

$$d\epsilon_s = \frac{dW}{E} \epsilon_s$$

Two Level System

This model describes a system that can only exist in two discrete energy states, which might occur naturally in diatomic molecule. The population number of the excitation state is given by

$$n_2 = \frac{N g_2}{g_2 + g_1 \exp(\Delta\epsilon/kT)}$$

The energy of said system is

$$U = N \epsilon_1 + \frac{N g_2 \Delta\epsilon}{g_2 + g_1 \exp(\Delta\epsilon/kT)}$$

The heat capacitance is written as

$$C_V = N_A k \left(\frac{\Delta\epsilon}{kT} \right)^2 \frac{g_1 g_2 \exp(\Delta\epsilon/kT)}{[g_2 + g_1 \exp(\Delta\epsilon/kT)]^2}$$

In general, the maximum value of C_V occur at

$$e^{-x} = \frac{(x^2 - 2x)g_1}{(2x + x^2)g_2 e^{-x}}$$

where $x = \Delta\epsilon/kT$. In the special case of $g_1 = g_2 = 1$, the C_{Vm} occur at $x_m = 2.4$ and $C_V(x = 2.4) = 0.44 Nk$

Population number derivation. Consider N classical particle with two level of energy g_1 and g_2 . Recall the configuration for classical particle

$$\Omega = N! \prod_s \frac{g_s^{n_s}}{n_s!}$$

On using the Stirling approximation and the Boltzmann entropy

$$S = k \sum_s [n_s \ln g_s + N \ln N - N - n_s \ln n_s + n_s]$$

$$S = k \sum_s \left[n_s \ln \frac{g_s}{n_s} + N \ln N \right]$$

We express the total energy as

$$U = (N - n_2)\epsilon_1 + n_2\epsilon_2 = N\epsilon_1 + n_2\Delta\epsilon$$

where $n_1 = N - n_2$ as the occupation number of the ground state. Here we want to find the distribution function for the second state particle. To do so, we begin by maximizing the Helmholtz potential, since at equilibrium its value is minimum

$$\begin{aligned} F &= E - TS \\ &= (N - n_2)\epsilon_1 + n\epsilon_2 \\ &\quad - kT \sum_s \left[n_s \ln \frac{g_s}{n_s} + N \ln N \right] \\ &= (N - n_2)\epsilon_1 + n\epsilon_2 \\ &\quad - kT \left[(N - n_2) \ln \frac{g_1}{N - n_2} + n_2 \ln \frac{g_2}{n_2} + N \ln N \right] \end{aligned}$$

Then we differentiate it with respect to n_2

$$\begin{aligned} \frac{\partial F}{\partial n} &= -\epsilon_1 + \epsilon_2 - kT \left[-\ln \frac{g_1}{N - n_2} \right. \\ &\quad \left. + (N - n_2) \frac{N - n_2}{g_1} \frac{g_1}{N - n_2} + \ln \frac{g_2}{n_2} - n \frac{n}{g_2} \frac{g_2}{n^2} \right] \\ &= \Delta\epsilon - kT \left[\ln \left(\frac{g_2}{g_1} \frac{N - n_2}{n} \right) \right] \end{aligned}$$

and set it to zero

$$\begin{aligned} kT \left[\ln \left(\frac{g_2}{g_1} \frac{N - n_2}{n} \right) \right] &= \Delta\epsilon \\ \frac{g_2}{g_1} \frac{N - n_2}{n} &= \exp \frac{\Delta\epsilon}{kT} \\ \frac{g_2}{g_1} N &= n_2 \left[1 + \exp \frac{\Delta\epsilon}{kT} \right] \\ n_2 &= \frac{g_2}{g_1} \frac{N}{g_2/g_1 + \frac{g_2}{g_1} \exp(\Delta\epsilon/kT)} \\ n_2 &= \frac{Ng_2}{g_2 + g_1 \exp(\Delta\epsilon/kT)} \end{aligned}$$

Heat capacitance. We this on the expression for energy

$$U = N\epsilon_1 + \frac{Ng_2\Delta\epsilon}{g_2 + g_1 \exp(\Delta\epsilon/kT)}$$

to evaluate its derivative with respect to temperature at constant V and $N = N_A$ to obtain the heat capacitance

$$C_V = \frac{N_A g_2 \Delta\epsilon \left[-g_1(-\Delta/kT^2) \exp(\Delta\epsilon/kT) \right]}{\left[g_2 + g_1 \exp(\Delta\epsilon/kT) \right]^2}$$

$$C_V = N_A k \left(\frac{\Delta\epsilon}{kT} \right)^2 \frac{g_1 g_2 \exp(\Delta\epsilon/kT)}{\left[g_2 + g_1 \exp(\Delta\epsilon/kT) \right]^2}$$

To find the maximum value of C_V we shall differentiate it once more, but we first define $x = \Delta\epsilon/kT$. Then

$$\frac{d}{dx} N_A k x^2 \frac{g_1 g_2 e^x}{[g_2 + g_1 e^x]^2} = 0$$

$$\frac{[(2xe^x + x^2e^x)(g_2 + g_1e^x)^2 - x^2e^x(2(g_2 + g_1e^x)g_1e^x)]}{(g_2 + g_1e^x)^4} = 0$$

$$(2xe^x + x^2e^x)(g_2 + g_1e^x)^2 - 2g_1x^2e^{2x} = 0$$

$$(x^2 - 2x)g_1 - (2x + x^2)g_2e^{-x} = 0$$

$$\frac{(x^2 - 2x)g_1}{(2x + x^2)g_2e^{-x}} = e^{-x}$$

The value of $x \equiv x_m$ that satisfies above equation is the value of x where C_V assumes the maximum value, or $C_V(x_m) \equiv C_{Vm}$.

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

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

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

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

As for Nu constraint

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

We have

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

Hence

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

Now we evaluate the expression permutability measure

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

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 $\epsilon \rightarrow 0$

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

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

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

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

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

As for its derivative,

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

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

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

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

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

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

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

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

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

Solving both for N and equating them

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

$$\begin{aligned} \frac{4u}{3} &= \frac{2m}{\lambda_2 m} \\ \lambda_2 &= \frac{3}{2u} \end{aligned}$$

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

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

Now we evaluate the expression permutability measure

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

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

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

We evaluate this in “spherical” coordinate

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

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

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

then

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

and then

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

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

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

Relation With Thermodynamics

Recall the identity of

$$\begin{aligned} dQ = N du + P dV &\iff dU = dQ + P dV, \quad dN = 0 \\ PV = \frac{2}{3}Nu &\iff PV = Nk_B T, \quad u = \frac{3}{2}k_B T \end{aligned}$$

We then use it to obtain

$$\begin{aligned} \int \frac{dQ}{u} &= \int \frac{N}{u} du + \int \frac{2N}{3V} dV = N \ln u + \frac{2N}{3} \ln V + C \\ &= \frac{2}{3} N \left(\frac{3}{2} \ln u + \ln V \right) + C \end{aligned}$$

and to write it in other way

$$\int \frac{dQ}{u} = \frac{2}{3k_B T} dQ = \frac{2}{3k_B} S_T$$

On equating both of them, we obtain an expression for thermodynamics entropy

$$S_T = Nk_B \left(\frac{3}{2} \ln u + \ln V \right) + C$$

Hence with appropriate value for C , we can obtain the desired link between Boltzmann's permutability measure and thermodynamics entropy

$$S_T = k_B \Omega \equiv S_B \implies \frac{1}{T} = \frac{\partial S_B}{\partial U}$$

In terms of macroscopic properties, the Boltzmann entropy written as

$$S_B = Nk_B \left[\frac{3}{2} \ln \frac{U}{N} + \ln \left(\frac{V}{N} \right) + \frac{3}{2} \ln \left(\frac{4\pi}{3m} \right) + \frac{3}{2} \right]$$

which is extensive; unlike thermodynamics entropy, which require proper constant.

Discrete model. Recall the expression for logarithm of maximum configuration \mathcal{P}_m in terms of x . By Boltzmann definition of entropy, we have

$$S_B = k_B \ln(\mathcal{P}_{\max}) = Nk_B \left[\ln \left(\frac{1}{1-x} \right) + \frac{x}{1-x} \ln \left(\frac{1}{x} \right) \right]$$

Substituting the value of x

$$\begin{aligned} S_B &= Nk_B \left[\ln \left(\frac{1}{1-u/(u+\epsilon)} \right) + \frac{u/(u+\epsilon)}{1-u/(u+\epsilon)} \ln \left(\frac{1}{u/(u+\epsilon)} \right) \right] \\ &= Nk_B \left[\ln \left(\frac{u+\epsilon}{\epsilon} \right) + \frac{u}{\epsilon} \ln \left(\frac{u+\epsilon}{u} \right) \right] \\ &= Nk_B \left[\ln \left(1 + \frac{u}{\epsilon} \right) + \frac{u}{\epsilon} \ln \left(1 + \frac{\epsilon}{u} \right) \right] \\ &= Nk_B \left[\ln \left(1 + \frac{u}{\epsilon} \right) + \frac{u}{\epsilon} \ln \left\{ \frac{\epsilon}{u} \left(\frac{u}{\epsilon} + 1 \right) \right\} \right] \\ S_B &= Nk_B \left[\left(1 + \frac{u}{\epsilon} \right) \ln \left(1 + \frac{u}{\epsilon} \right) - \frac{u}{\epsilon} \ln \left(\frac{u}{\epsilon} \right) \right] \end{aligned}$$

Using this we can determine another expression of u in terms of ϵ

$$\begin{aligned} \frac{1}{T} &= Nk_B \frac{\partial}{N\partial u} \left[\left(1 + \frac{u}{\epsilon} \right) \ln \left(1 + \frac{u}{\epsilon} \right) - \frac{u}{\epsilon} \ln \left(\frac{u}{\epsilon} \right) \right] \\ &= k_B \left[\frac{\partial}{\partial \alpha} (\alpha \ln \alpha) \frac{\partial}{\partial u} \left(1 + \frac{u}{\epsilon} \right) - \frac{1}{\epsilon} \frac{\partial}{\partial u} (u \ln u - u \ln \epsilon) \right] \\ &= k_B \left[\left\{ \ln \left(1 + \frac{u}{\epsilon} \right) + 1 \right\} \frac{1}{\epsilon} - \frac{1}{\epsilon} \{ \ln(u) + 1 - \ln(\epsilon) \} \right] \\ \frac{1}{T} &= \frac{k_B}{\epsilon} \left[\ln \left(1 + \frac{u}{\epsilon} \right) - \ln \left(\frac{u}{\epsilon} \right) \right] \\ \frac{\epsilon}{k_B T} &= \ln \left(\frac{\epsilon}{u} + 1 \right) \end{aligned}$$

Raising e to the power of it, we have

$$\begin{aligned} \exp \left(\frac{\epsilon}{k_B T} \right) &= \frac{\epsilon}{u} + 1 \\ u \left[\exp \left(\frac{\epsilon}{k_B T} \right) - 1 \right] &= \epsilon \\ u &= \frac{\epsilon}{\exp(\epsilon/k_B T) - 1} \end{aligned}$$

As an aside, using $\epsilon = h\nu$ would result in Planck's entropy and average molecular energy to S_B and u respectively.

Equilibrium Distribution

Ensembles

The maximum entropy principle state that thermal equilibrium is described by such probability distribution of microstates for which the statistical entropy is maximum subject to the constraints on the system. The constraints of general interest are the ones pertaining to whether the system exchanges energy and/or particles with its environment. Those constraints define three types of ensembles:

1. **Microcanonical.** Represents a system which is isolated and exchanges neither energy nor particles with the environment. System has fixed N, V, E .
2. **Canonical.** Represents a system which exchanges energy but not particles with the environment, as in system connected with heat bath. System has fixed N, T, V .
3. **Grand Canonical.** Represents a system which exchanges energy as well as particles with the environment. System has fixed μ, V, T .

Partition function

For canonical ensembles, the partition function is defined as follows

$$Z \equiv \sum_i e^{-E_i/kT}$$

where i denote the index for the microstates of the system. And

$$Z \equiv \sum_s g_s e^{-E_s/kT}$$

In the context of quantum statistical mechanics, g_s denotes the degeneracy of the E_s energy, while in the context of classical quantum mechanics it denotes Number of distinguishable configurations with energy E_s . In quantum system, s refers to the s -th energy level, while in classical system it refers to the s -th microstates.

The generalized partition function for a gas of N identical classical non-interacting particles in three dimensions, the partition function is

$$Z = \frac{1}{N! h^{3N}} \int \prod_{i=1}^N e^{-\beta \mathcal{H}(\mathbf{q}_i, \mathbf{p}_i)} d^{3N} \mathbf{q}_i d^{3N} \mathbf{p}_i$$

Alternatively

$$Z = \frac{Z_{\text{single}}^N}{N!}$$

where

$$Z_{\text{single}} = \frac{1}{h^3} \int e^{-\beta \mathcal{H}(\mathbf{q}, \mathbf{p})} d^3 \mathbf{q} d^3 \mathbf{p}$$

Using this expression, we obtain the partition function for the ideal gas

$$Z = \frac{1}{N!} \left(\frac{V}{\Lambda^3} \right)^N \quad \text{where} \quad \Lambda = \left(\frac{h^2}{2\pi mkT} \right)^{1/2}$$

with the single partition function itself as $Z_{\text{single}} = V/\Lambda^3$. Thus, note the difference of N ensemble partition function with the single particle partition function.

Derivation. For an ideal gas, the Hamiltonian is just kinetic energy

$$\mathcal{H}(p_i) = \frac{p_i^2}{2m}$$

which is also a function of momentum only. Then the partition function is written as

$$\begin{aligned} Z &= \frac{1}{N!h^{3N}} \int \exp \left(-\beta \sum_{i=1}^N \frac{p_i^2}{2m} \right) d^{3N}\mathbf{p}_i \int d^{3N}\mathbf{q}_i \\ Z &= \frac{V^N}{N!h^{3N}} \left[\int \exp \left(-\beta \frac{p^2}{2m} \right) d^3\mathbf{p} \right]^N \end{aligned}$$

Recall that $p^2 = p_x^2 + p_y^2 + p_z^2$ and $d^3\mathbf{p} = dp_x \, dp_y \, dp_z$

$$\begin{aligned} Z &= \frac{V^N}{N!h^{3N}} \left[\int \exp \left(-\frac{p^2}{2mkT} \right) d\mathbf{p} \right]^{3N} \\ &= \frac{V^N}{N!h^{3N}} (2\pi mkT)^{3N/2} \\ Z &= \frac{V^N}{N!h^{3N}} \left(\frac{2\pi mkT}{h^2} \right)^{3N} \end{aligned}$$

Then using the definition of the thermal de Broglie wavelength $\Lambda = (h^2/2\pi mkT)^{1/2}$

$$Z = \frac{1}{N!} \left(\frac{V}{\Lambda^3} \right)^N \quad \text{with} \quad Z_{\text{single}} \equiv \frac{V}{\Lambda^3}$$

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Another derivation. Recall the definition of partition function and the degeneracy of the classical particles

$$Z = \sum_s g_s e^{-E_s/kT} \quad \text{and} \quad g(E) \, dE = 2\pi V \left(\frac{2m}{h^2} \right)^{3/2} E^{1/2} \, dE$$

At high T , we can assume the summation sign changes into integral due to kT being larger compared to the typical energy level spacing ΔE . Then

$$\begin{aligned} Z &= 2\pi V \left(\frac{2m}{h^2} \right)^{3/2} \int E^{1/2} \exp \left(\frac{E}{kT} \right) \, dE \\ Z &= 2\pi V \left(\frac{2m}{h^2} \right)^{3/2} \left[(kT)^{3/2} \frac{\sqrt{\pi}}{2} \right] \end{aligned}$$

$$Z = V \left(\frac{2\pi m k T}{h^2} \right)^{3/2}$$

In terms of thermal de Broglie wavelength

$$Z = \frac{V}{\Lambda^3}$$

This is the partition function for the single particle; for many identical particles then, the partition function is simply the partition function for single particle raised to the power of the number of particle N and multiplied by $1/N!$ to avoid the Gibbs paradox.

To understand the reasoning, consider the classical configuration Ω_{MB} . Here we treat the particle as truly distinguishable, yet they cause the Gibbs paradox due to over counting of the microstate. When we are dividing by $N!$ we treat Ω_{MB} as a permutation and the corrected configuration Ω'_{MB} as the combination. To obtain Ω'_{MB} , we are then dividing Ω_{MB} by $N!$.

Probability

On using the defined partition function, the probability P_i that our system is in microstate i with energy E_i is

$$P_i = \frac{1}{Z} e^{-E_i/kT}$$

Derivation. Probability of the system being in i -th state is proportional to the number of ways the reservoir can arrange itself with that its own energy

$$P_i \propto \Omega_R(E_T - E_i)$$

since $E_R = E_T - E_i$. By Boltzmann definition of entropy

$$\Omega_R(E_T - E_i) = \exp \left[\frac{S_R(E_T - E_i)}{k} \right]$$

Then

$$P_i \propto \exp \left[\frac{S_R(E_T - E_i)}{k} \right]$$

We know that $E_i \ll E_R$, thus $E_i \ll E_T$ and we can expand the reservoir entropy using Taylor expansion

$$S_R(E_T - E_i) \approx S_R(E_T) - \frac{\partial S_R(E_T)}{\partial E} E_i$$

Using the relation $\partial S / \partial E = 1/T$

$$S_R(E_T - E_i) \approx S_R(E_T) - \frac{E_i}{T}$$

So

$$P_i \propto \exp \left[\frac{S_R}{k} \right] \exp \left[-\frac{E_i}{kT} \right]$$

Since $e^{S_R/k}$ is a constant which does not depend on the microstate i , we can define it as the normalization constant

$$\sum_i P_i = C \sum_i e^{-E_i/kT} = 1$$

which can be evaluated as

$$C = \frac{1}{\sum_i e^{-E_i/kT}} = \frac{1}{Z}$$

Therefore

$$P_i = \frac{e^{-E_i/kT}}{Z}$$

Physical Quantities

We shall derive some physical quantities using partition function and prove them in the case of ideal gas by comparing them to the known ideal gas law.

Average energy. Expressed as

$$\langle E \rangle = \frac{kT^2}{Z} \frac{\partial Z}{\partial T} = kT^2 \frac{\partial}{\partial T} \ln Z = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z$$

with $\beta = 1/kT$ as thermodynamics constant.

Derivation. Average energy is just the expectation value

$$\langle E \rangle = \sum_i P_i E_i = \frac{1}{Z} \sum_i E_i e^{E_i/kT}$$

To evaluate the summation, consider

$$\frac{\partial Z}{\partial T} = \frac{\partial}{\partial T} \sum_i e^{E_i/kT} = \frac{1}{kT^2} \sum_i E_i e^{E_i/kT}$$

This is simply the previous series. Thus,

$$\langle E \rangle = \frac{kT^2}{Z} \frac{\partial Z}{\partial T}$$

To obtain the next expression, we express the derivative term as

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

To prove this expression, we are going to consider the case of ideal gas. Using the partition function of ideal gas for the case of single particle and multiparticle will result with the known result $E = 3kT/2$ for single particle and $E = 3NkT/2$

$$\langle E \rangle = kT^2 \frac{\partial}{\partial T} \ln V \left(\frac{2\pi mkT}{h^2} \right)^{3/2} = \frac{3}{2} kT$$

and

$$\langle E \rangle = T^2 \frac{\partial}{\partial T} \ln \frac{V^N}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} = \frac{3}{2} NkT$$

Energy Fluctuation. Energy fluctuation refers to statistical deviations of the energy of a system from its average value. This also referred as the variance $(\Delta E)^2 = \sigma^2$. Another similar definition is the standard deviation $\Delta E = \sigma$

$$(\Delta E)^2 = kT^2 C_V \quad \text{and} \quad \Delta E = T \sqrt{kC_V}$$

Derivation. Recall

$$\frac{\partial Z}{\partial \beta} = -\frac{1}{Z} \sum_s E_s e^{-E_s \beta}, \quad \frac{\partial^2 Z}{\partial \beta^2} = \frac{1}{Z} \sum_s E_s e^{E_s \beta}$$

We can use these expressions to write the variance σ^2 and standard deviation σ . The variance is evaluated by

$$\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$$

From this, we need to determine the square average energy

$$\langle E \rangle^2 = \frac{1}{Z} \sum_s E_s e^{E_s \beta} = \frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2$$

and the average of energy squared

$$\langle E^2 \rangle = \frac{1}{Z} \sum_s E_s^2 e^{E_s \beta} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta}$$

Thus, we have the expression for variance

$$\langle (\Delta E)^2 \rangle = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta} - \frac{1}{Z} \left(\frac{\partial Z}{\partial \beta} \right)^2$$

But this is just

$$\frac{\partial \epsilon}{\partial 2\beta} = \frac{\partial}{\partial \beta} \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) = \frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2 - \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}$$

Therefore

$$\langle (\Delta E)^2 \rangle = -\frac{\partial}{\partial \beta} \langle E \rangle$$

Calculating the derivative we have

$$\langle (\Delta E)^2 \rangle = -\frac{\partial \langle E \rangle}{\partial T} \frac{\partial T}{\partial \beta} = \frac{C_V}{k\beta^2} = kT^2 C_V$$

Entropy. Expressed as follows.

$$S = NkT \ln \frac{V}{\Lambda} + \frac{E}{T}$$

This expression however, suffer from the Gibbs paradox. The expression for entropy that does not suffer from it usually expressed by Sackur-Tetrode equation

$$S = Nk \left(\ln \frac{V}{N\Lambda^3} + \frac{5}{2} \right)$$

Derivation. Consider the logarithm of the configuration for the classical particle

$$\Omega = N! \prod_s \frac{g_s^{n_s}}{n_s!} \implies \ln \Omega = N \ln N + \sum_s \ln \frac{g_s}{n_s}$$

Notice that

$$\frac{g_s}{n_s} = \frac{g_s}{g_s \exp(\alpha - \beta E_s)} = \exp(-\alpha + \beta E_s)$$

Thus

$$\begin{aligned} \ln \Omega &= N \ln N - \sum_s n_s \alpha + \sum_s n_s \beta E_s \\ \ln \Omega &= N \ln \frac{N}{e^\alpha} + \frac{E}{kT} \end{aligned}$$

Also notice that

$$\frac{N}{e^\alpha} = \sum_s \frac{n_s}{e^\alpha} = \sum_s \frac{\exp(\alpha + \beta E_s)}{\exp \alpha} = \sum_s \exp \frac{E_s}{kT} = Z_{\text{single}}$$

Therefore

$$S = NkT \ln Z + \frac{E}{T}$$

To derive the corrected version, consider the configuration number of the semi-classical particle

$$\Omega = \prod_s \frac{g_s^{n_s}}{n_s!}$$

Its logarithm reads

$$\ln \Omega = \sum_s n_s \ln g_s - n_s \ln n_s + n_s = \sum_s n_s + n_s \ln \frac{g_s}{n_s}$$

Using the previous result for g_s/n_s and N/e^α

$$\begin{aligned} \ln \Omega &= \sum_s n_s + n_s \left(\frac{E_s}{kT} - \alpha \right) \\ &= N + N \ln \frac{Z_{\text{single}}}{N} + \frac{E}{kT} \\ \ln \Omega &= N + N \ln \frac{V}{N \Lambda^3} + \frac{3}{2} N \end{aligned}$$

Thus

$$S = Nk \left(\ln \frac{V}{N \Lambda^3} + \frac{5}{2} \right)$$

Helmholtz Potential. On using the definition of $F = E - TS$, we have

$$F = -NkT \ln Z$$

which is the wrong result derived from wrong entropy. For the correct one, we have

$$F = -NkT \left(\ln \frac{V}{N \Lambda^3} + 1 \right)$$

or in terms of multiparticle partition function

$$F = -kT \ln Z$$

Derivation. The case single particle partition function is quite trivial, while for the case of multi particle one we can simply expand the definition

$$F = -kT \ln \frac{V^N}{N! \Lambda^{3N}} = -kT \left(N \ln \frac{V}{\Lambda^3} - N \ln N + N \right)$$

$$F = -NkT \left(\ln \frac{V}{N\Lambda^3} + 1 \right)$$

Pressure. For the case of the wrong and the corrected partition function respectively

$$P = NkT \frac{\partial}{\partial V} \ln Z \quad \text{and} \quad P = kT \frac{\partial}{\partial V} \ln Z$$

Derivation. Consider the first law of thermodynamics

$$dE = dQ - P dV$$

and the differential of the Helmholtz potential

$$dF = dE - T dS - S dT$$

Thus

$$dF = -P dV - T dT \implies P = -\frac{\partial F}{\partial V} \Big|_T$$

On using the expression for Helmholtz potential, we can express pressure in terms of partition function.

We can obtain the ideal gas law using both the wrong and corrected version. For the case of the wrong version, we use the single particle partition function

$$P = NkT \frac{\partial}{\partial V} \ln \frac{V}{\Lambda^3} = \frac{NkT}{V}$$

While for the corrected version, we use the many particles partition function

$$P = kT \frac{\partial}{\partial V} \ln \frac{V^N}{N! \Lambda^{3N}} = \frac{NkT}{V}$$

Gibbs Paradox

This problem occurs for the expression of entropy which does not takes into account the indistinguishability of particles. To illustrate this problem, consider two ensembles of ideal gas with the same E, V, N, T, P, S which sat side-by-side. No macroscopic changes occur, as the system is in equilibrium. But if the formula for entropy is not extensive, the entropy of the combined system will not be $2S$

$$S_T = 2NkT \ln \frac{2V}{\Lambda} + \frac{E}{T} = 2NkT \ln \frac{2V}{\Lambda} + \frac{2E}{T} + 2NkT \ln 2 = 2S + 2NkT$$

If the entropy is extensive, however, it will produce total entropy of $2S$

$$S_T = 2Nk \left(\ln \frac{2V}{2N\Lambda^3} + \frac{5}{2} \right) = 2S$$

Rotational Partition Function

Rotational partition function Z_{rot} relates the rotational degrees of freedom f to the rotational part of the energy and defined as

$$Z_{\text{rot}} = \sum_J g_J e^{-E_J/kT}$$

where $g_J = 2J + 1$ is the degeneracy of energy level E_J . Its contribution only become significant at temperatures above the molecule's characteristic rotational temperature θ_{rot} , for diatomic molecule

$$\theta_{\text{rot}} = \frac{\hbar^2}{\mu r^2 k}$$

Molecule's Z_{rot} depends on the structure of said molecule, since different molecules have different degrees of freedom; for example

1. **Monatomic gas.** Noble gas such as He and Ar have $f = 0$; thus $Z_{\text{rot}} = 1$, $E_{\text{rot}} = 0$, and $C_{V_{\text{rot}}=0}$.
2. **Linear molecule.** Examples are diatomic and linear triatomic. For this type of molecules, their $f = 2$, with one axis parallel to the bond and the other perpendicular to it. Thermodynamically, $E_{\text{rot}} = NkT$, and $C_{V_{\text{rot}}=N_A k} = 3N_A k/2$.
3. **Nonlinear polyatomic.** They have 3 degrees of freedom: one for each three-dimensions. With $E_{\text{rot}} = 3NkT/2$, their $C_{V_{\text{rot}}} = 3N_A k/2$.

In general, the expression for the rotational partition function is

$$Z_{\text{rot}} = \sum_J (2J + 1) \exp \left[-\frac{\theta_{\text{rot}}}{T} J(J + 1) \right]$$

This expression, then, can be simplified for the case of high and low temperature.

Derivation. Recall that in the case of electron, the magnetic quantum number m_l is only allowed to have the values $-l \leq m_l \leq l$, thus $g_l = 2l + 1$. In the same principle, $g_J = 2J + 1$ In quantum mechanics, the rotational energy is defined

$$E_J = \frac{1}{2I} \langle \hat{J}^2 \rangle$$

Recall also the orbital angular of electron $L = \sqrt{\hbar^2 l(l+1)}$, in the case of total angular momentum then $\hat{J}^2 = J(J+1)\hbar^2$, here however it acts as operator. Then we can write the rotational energy as

$$E_J = \frac{J(J+1)\hbar^2}{2\mu r^2}$$

Substituting those expressions into the partition function

$$Z_{\text{rot}} = \sum_J (2J + 1) \exp \left[-\frac{\hbar^2}{2\mu r^2 k} \frac{1}{T} J(J + 1) \right]$$

On using the definition of the rotational temperature

$$Z_{\text{rot}} = \sum_J (2J + 1) \exp \left[-\frac{\theta_{\text{rot}}}{T} J(J + 1) \right]$$

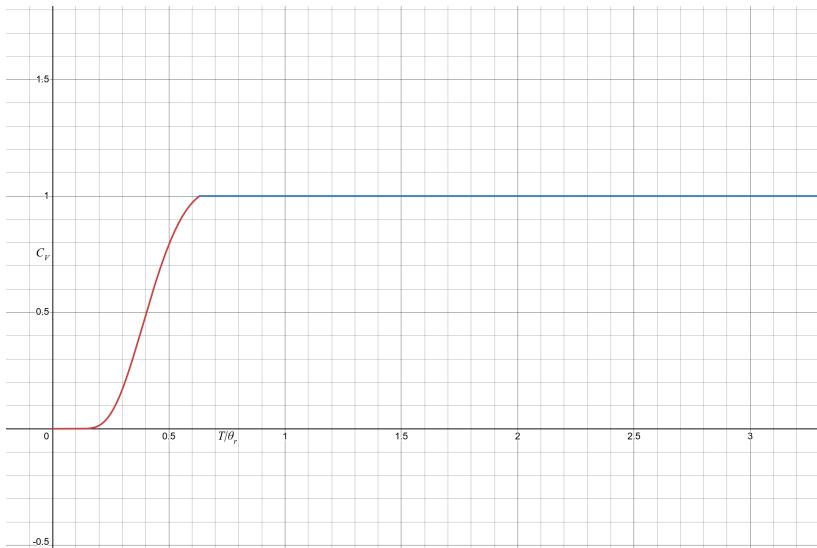


Figure: C_V obtained by approximating Z_{rot} at low temperature and high temperature

High temperature approximation. At high temperature, we can approx the summation of Z_{rot} by integral

$$Z_{\text{rot}} = \int_J (2J+1) \exp \left[-\frac{\theta_{\text{rot}}}{T} J(J+1) \right] dJ$$

Changing the variable into $u = 2J+1$ and $du = d(2J+1)dJ$, we have

$$Z_{\text{rot}} = \int_J \exp \left[-\frac{\theta_{\text{rot}}}{T} u \right] du = \frac{T}{\theta_{\text{rot}}} \exp \left[-\frac{\theta_{\text{rot}}}{T} u \right] \Big|_0^\infty = \frac{T}{\theta_{\text{rot}}}$$

Certain state will be over counted if we did not take into account the symmetry number σ . For example consider hetero nuclear diatomic molecule, where if we rotate the molecule in 180 deg results in a different orientation–atom A on the left and on the right. This means that we over count the configuration, thus we divide by $\sigma = 2$ to fix it

$$Z_{\text{rot}} = \frac{T}{\sigma \theta_{\text{rot}}}$$

For the case of homo nuclear molecules, $\sigma = 1$.

The energy can be evaluated into

$$E = \frac{kT^2}{T/\sigma \theta_{\text{rot}}} \frac{d}{dT} \frac{T}{\sigma \theta_{\text{rot}}} = kT$$

and its heat capacitance

$$C_V = R$$

Low temperature approximation. At low temperature, only low states J are occupied, thus we can approximate the Z_{rot} by its few first terms

$$Z_{\text{rot}} = 1 + 3 \exp \left(-\frac{2\theta_{\text{rot}}}{T} \right)$$

The energy can be evaluated into

$$\begin{aligned} E &= \frac{kT^2}{1 + 3 \exp\left(-\frac{2\theta_{\text{rot}}}{T}\right)} \frac{d}{dT} 1 + 3 \exp\left(-\frac{2\theta_{\text{rot}}}{T}\right) \\ &= \frac{kT^2}{1 + 3 \exp\left(-\frac{2\theta_{\text{rot}}}{T}\right)} \left(\frac{2\theta_{\text{rot}}}{T^2}\right) 3 \exp\left(-\frac{2\theta_{\text{rot}}}{T}\right) \\ E &= \frac{6k\theta_{\text{rot}}}{\exp\left(\frac{2\theta_{\text{rot}}}{T}\right) + 3} \end{aligned}$$

and the heat capacitance

$$\begin{aligned} C_V &= 6R\theta_{\text{rot}}(-1) \left[\exp\left(\frac{2\theta_{\text{rot}}}{T}\right) + 3 \right]^{-2} \left(-\frac{2\theta_{\text{rot}}}{T^2}\right) \exp\left(\frac{2\theta_{\text{rot}}}{T}\right) \\ C_V &= \frac{12(\theta_{\text{rot}}/T)^2 \exp(2\theta_{\text{rot}}/T)}{\left[\exp(\theta_{\text{rot}}/T) + 3\right]^2} \end{aligned}$$

Vibration Partition Function

The vibrational partition function refers to the vibrational components of a system canonical partition function. For the case of diatomic molecule, their vibrational degrees of freedom is one, however their total energy is $E = kT$ since they have both kinetic and potential energy based on the motion and the stretching of the bond. Assuming the diatomic molecule as harmonic oscillator, the partition function can be written as

$$Z_{\text{vib}} = \frac{\exp(\theta_v/2T)}{1 - \exp(\theta_{\text{vib}}/T)}$$

where $\theta_{\text{vib}} \equiv h\nu/kT$ denote the vibrational temperature. Then the average energy

$$\langle E \rangle = k\theta_{\text{vib}} \left[\frac{1}{2} + \frac{1}{\exp(\theta_{\text{vib}}/T) - 1} \right]$$

and the heat capacitance

$$C_V = \frac{(\theta_{\text{vib}}/T)^2 e^{\theta_{\text{vib}}/T}}{(e^{\theta_{\text{vib}}/T})^2} R$$

Derivation. The energy eigenstate of harmonic oscillator is

$$E_n = \left(n + \frac{1}{2}\right) h\nu$$

Then the partition function reads

$$Z_{\text{vib}} = \sum_n \exp\left(-\frac{n + 1/2}{kT} h\nu\right)$$

Using the defined rotational temperature

$$Z_{\text{vib}} = \exp\left(\frac{\theta_{\text{vib}}}{2T}\right) \sum_n \exp\left(-\frac{n\theta_{\text{vib}}}{T}\right)$$

$$Z_{\text{vib}} = \frac{\exp(-\theta_{\text{vib}}/2T)}{1 - \exp(\theta_{\text{vib}}/T)}$$

Thus the average energy can be evaluated into

$$\begin{aligned}\langle E \rangle &= kT^2 \frac{\partial}{\partial T} \left[-\frac{\theta_{\text{vib}}}{2T} - \ln \left(1 - e^{\theta_{\text{vib}}/T} \right) \right] \\ &= kT^2 \left[\frac{\theta_{\text{vib}}}{2T^2} - \ln \left(1 - e^{-\theta_{\text{vib}}/T} \right) \right] \\ &= kT^2 \left[\frac{\theta_{\text{vib}}}{2T^2} + \frac{1}{1 - e^{-\theta_{\text{vib}}/T}} \left(\frac{\theta_{\text{vib}}}{T^2} \right) e^{-\theta_{\text{vib}}/T} \right] \\ \langle E \rangle &= k\theta_{\text{vib}} \left[\frac{1}{2} + \frac{1}{e^{\theta_{\text{vib}}/T} - 1} \right]\end{aligned}$$

For the heat capacitance, we differentiate the expression for average energy respect to temperature

$$\begin{aligned}C_V &= k\theta_{\text{vib}} \frac{\partial}{\partial T} \left[\frac{1}{2} + \frac{1}{e^{\theta_{\text{vib}}/T} - 1} \right] \\ &= N_A k\theta_{\text{vib}} (-1)(e^{\theta_{\text{vib}}/T} - 1)^{-2} \left(-\frac{\theta_{\text{vib}}}{T^2} \right) e^{\theta_{\text{vib}}/T} \\ C_V &= \frac{(\theta_{\text{vib}}/T)^2 e^{\theta_{\text{vib}}/T}}{(e^{\theta_{\text{vib}}/T} - 1)^2} R\end{aligned}$$

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