

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 $f(x_1, \dots, x_n)$ 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

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

See? \blacksquare

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

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

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

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

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

Application in Thermodynamics

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

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

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

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

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

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

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

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

Third Identity. Expressed as

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

Proof. We again invoke cyclic with $x \rightarrow U, y \rightarrow N_j, z \rightarrow S$; 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

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

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.

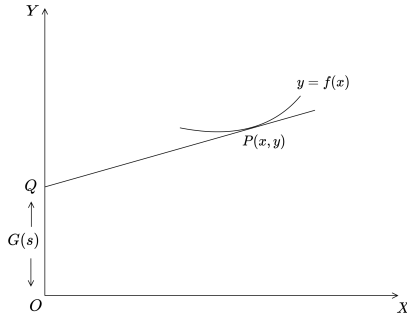


Figure: Geometric interperatation of Legendre transformation

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

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

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

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

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

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

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

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

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

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

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



Figure 1: Gaussian integral solved by polar method.

Important formula. 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

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

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 continous, I can move the partial differentiation outside the integral and turning it into total differentiation

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

Hence

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

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

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

Therefore

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

And I obtain the complete expression for the fish function

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

Now I can evaluate the Gaussian integral

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

and I find

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

Much to my chagrin, it is actually more trouble some than the polar method. Let's us 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 shrimple.

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

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

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

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

Beta Function

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

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

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

Change of order. It is easy to show that

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

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

$$B(p, q) = - \int_1^0 (1 - y)^{p-1} y^{q-1} dy = \int_0^1 y^{q-1} (1 - y)^{p-1} dy$$

$$B(p, q) = B(q, p) \quad \blacksquare$$

Integration Range. The range of integration can be changed with

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

Another form is

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

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

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

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

$$B(p, q) = \int_0^\infty \left(\frac{y}{1 + y}\right)^{p-1} \left(\frac{(1 + y) - y}{1 + y}\right)^{q-1} \frac{1}{(1 + y)^2} dy$$

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

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 $dx = 2 \cos \theta \sin \theta d\theta$

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

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

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

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

Error Function

We define error function as

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

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

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

Here are some of their relations.

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

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

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

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

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

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

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

Complementary error function. Defined as

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

Its relations with the actual error function are as follows.

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

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

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

then

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

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

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

Imaginary error function. We define

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

Here are some relation to the actual error function.

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

Riemann zeta function

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

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

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

$$\begin{aligned}\zeta(2) &= \frac{\pi^2}{6}; & \zeta(4) &= \frac{\pi^4}{90}; & \zeta(6) &= \frac{\pi^6}{945} \\ \zeta(3) &= 1.202; & \zeta(5) &= 1.036; & \zeta(7) &= 1.008\end{aligned}$$

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

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

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, $V \propto T$

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. 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, we give (without the derivation)

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

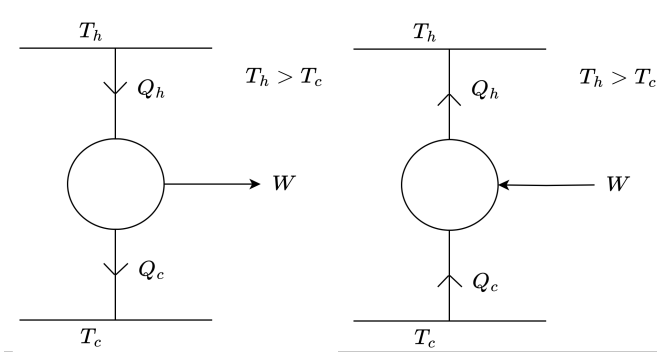


Figure: Carnot engine and reverse Carnot engine.

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.

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.

1. **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 P_B as its pressure.
2. **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

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

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:

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

Since $V_D < V_C$, 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.

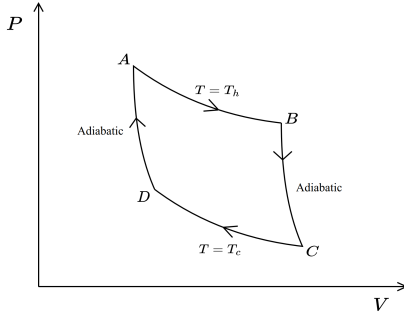


Figure: PV diagram of a cyclic Carnot process.

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

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

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

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

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

$$U(V, T) = C_V T = cNk_B T$$

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:

1. **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.

2. **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 constraints 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 obeys the relation

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

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

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

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

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

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

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

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

Internal energy function. All those 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 particles $N_{i|r}$. We can therefore write the total derivative of U as

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

We then define

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

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

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

It follows that

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

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

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

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

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

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

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

Using the maximum entropy principle, we have

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

Which implies

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

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

Thermodynamics' Potentials

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

Helmholtz Potential

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

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

We define the resulting function as Helmholtz potential or Free energy

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

Partial derivative relation. The differential of F read as

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

Therefore

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

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

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

Partial derivative relation. The differential of F is then

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

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

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

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

Gibbs Potential

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

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

Hence

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

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

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

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

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

It follows that

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

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

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

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

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

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

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

Hence

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

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

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

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

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

And Hence

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

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

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

Them being exact would imply

$$\begin{aligned}\left. \frac{\partial T}{\partial V} \right|_S &= - \left. \frac{\partial P}{\partial S} \right|_V & \left. \frac{\partial S}{\partial V} \right|_T &= \left. \frac{\partial P}{\partial T} \right|_V \\ \left. \frac{\partial S}{\partial P} \right|_T &= - \left. \frac{\partial V}{\partial T} \right|_P & \left. \frac{\partial T}{\partial P} \right|_S &= \left. \frac{\partial V}{\partial S} \right|_P\end{aligned}$$

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.

$$C_V = \left. \frac{\partial Q}{\partial T} \right|_V = \left. \frac{\partial U}{\partial T} \right|_V, \quad \kappa_S = - \frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_S, \quad \alpha_S = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_S$$

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.

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