

# Chapter 1

## Thermodynamics

### 1.1 Introduction

A **state variable** is a quantity that depends only on the state of a system. There are two kinds of state variables. **Intensive** variables do not scale with system size while **extensive** variables do scale. Combining systems in equilibrium preserves intensive state variables but adds extensive variables.

$$\Delta U = Q_{in} - W_{out}$$

The **First Law of Thermodynamics** states that the change in internal energy is equal to the amount of heat that is delivered to the system minus the work done by the system on the environment. From physics, we know  $W = F\Delta h = pA\Delta h = p\Delta V$  (think about a piston). Graphing pressure vs. volume, the area under the curve defines work, so work does not just depend on the initial and final states but the path taken. Thus, work is not a change in a state variable. Note that this is not a change in work so  $dW$  is inappropriate. So,  $\cancel{d}W$  or  $\delta W$  sometimes used to still indicate that the work is small but not a change. Note that if we rearrange to  $\frac{W}{P} = \Delta V$ , this is a change in a state variable, so pressure is an **integrating denominator** for work.

### 1.2 Ideal Gas Law

The gas molecules colliding is what imparts a force and gives the gas a pressure. These collisions can be considered as elastic. Consider a piston; the momentum imparted on the piston in time  $\Delta t$  is  $\sum_{v_z > 0} 2mv_z n_{hit}$  where  $n_{hit}$  is the number of molecules with a positive  $v_z$  that hit the piston in time  $\Delta t$ .

$$= \sum_{v_z > 0} 2mv_z \frac{Av_z \Delta t}{V} Np_{v_z}$$

where  $p_{v_z}$  is the probability that the z component of a molecule is  $v_z$ . So,

$$p = \frac{F}{A} = \frac{\Delta\rho}{A\Delta t} = 2\frac{N}{V} \sum_{v_z > 0} mv_z^2 p_{v_z}$$

Using symmetry,

$$= \frac{N}{V} \sum_{v_z} mv_z^2 p_{v_z}$$

Assuming that the gas is **isotropic**, same in all directions, we can simplify the following. Note that gravity does act only in the z directions, however this effect is negligible.

$$= \frac{N}{3V} \sum_v mv^2 p_v = \frac{2N}{3V} \sum_v \frac{1}{2} mv^2 p_v = \frac{2N}{3V} \langle K \rangle$$

Rearranging,

$$pV = N \cdot \frac{2}{3} \langle K \rangle$$

Popularly,

$$pV = nRT = N \frac{R}{\eta} T = N k_B T$$

Remember that  $n$  is in moles while  $N$  is a constant.  $k_B$  is known as the Boltzmann Constant and is  $1.3806488(13) \times 10^{-23} \frac{J}{K}$ . Equating,

$$\langle K \rangle = \frac{3}{2} k_B T$$

Notice this 3 comes from the 3 directions that the particle can travel in. This is known as the **Equipartition of energy**. Overall, for  $l$  degrees of freedom,

$$U = \frac{l}{2} N k_B T = \frac{l}{2} pV$$

For monotomic gases,  $l = 3$  but diatomic gases can spin if the temperature is high enough.

### 1.3 Heat Capacity

The heat capacity  $C$  is the heat required per Kelvin increase in temperature,  $\frac{Q}{\Delta T}$ . Note that  $C$  is extensive, so we can divide by mass. At **isobaric** (constant pressure) conditions,

$$\Delta U = \frac{l}{2} p \Delta V = Q - p \Delta V \Rightarrow Q = \left( \frac{l}{2} + 1 \right) p \Delta V$$

So,

$$C_p = \left( \frac{3}{2} + 1 \right) N k_B$$

At **isochoric** (constant volume) conditions,  $W = 0$  and  $\Delta U = Q$ . Using ideal gas,

$$C_V = \frac{l}{2} N k_B$$

At **isothermal** (constant temperature), heat capacity doesn't make sense neither do non-infinitesimal changes in volume. So,

$$W = \int p dV = \int_{V_i}^{V_f} N k_B T \frac{dV}{V} = N k_B T \ln \frac{V_f}{V_i}$$

Additionally,  $\Delta U = 0 \Rightarrow Q = W$ , so isothermic processes are 100% efficient. An **adiabatic** or **isentropic** (constant entropy) has not heat flow. Here  $Q = 0 \Rightarrow \Delta U = -W$ . Substituting,

$$\frac{l}{2} d(pV) = -pdV \Rightarrow \left( \frac{l}{2} + 1 \right) p dV = -\frac{l}{2} V dp$$

Rearranging,

$$\frac{\frac{l}{2} + 1}{\frac{l}{2}} \frac{dV}{d} = -\frac{dp}{p}$$

Note that this ratio is  $\frac{C_p}{C_v} = \frac{c_p}{c_v} = \gamma$  and is the ratio of specific heats (gamma is not Euler-Mascheroni). Integrating,

$$\gamma \ln V = -\ln P + \text{const}$$

$$pV^\gamma = \text{const}$$

The speed of sound through an ideal gas is

$$\text{speed of sound} = \sqrt{\frac{\gamma R T}{\text{molar mass}}}$$

A **Carnot cycle** uses only isothermal and adiabatic processes. The efficiency of this cycle

$$e_c = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}$$

It is the most efficient possible for an engine between these temperature extremes.

## 1.4 Laws of Thermodynamics

The **Zeroth Law** states that if  $A$  is in thermal equilibrium with  $B$  and  $B$  is in TE with  $C$ , then  $A$  is in TE with  $C$ . The **First Law** states that energy is conserved.

## 1.5 Lagrange Multipliers

Lagrange multipliers are a technique for optimize a multivariate scalar function under a constraint. Suppose we need to maximize  $f(x, y)$  under the constraint  $g(x, y) = 0$ . Note that if we draw level curves of  $f(x, y)$ , we see that to optimize this,  $\nabla f = \lambda \nabla g$ . We can build a function

$$F(x, y; \lambda) = f(x, y) + \lambda g(x, y)$$

Taking derivatives,

$$F_x = f_x(x, y) + \lambda g_x(x, y) = 0$$

$$F_y = f_y(x, y) + \lambda g_y(x, y) = 0$$

$$F_\lambda = g(x, y) = 0$$

Note that the derivative with respect to  $\lambda$  is the constraint. Solving these three equations with three variables should optimize  $f(x, y)$  under  $F_\lambda = g(x, y) = 0$ .

## 1.6 Pfaffian Expressions

We know  $dU = Q - W$ . But, work is *not* an exact differential and it cannot be understood as a change in a state variable. Instead, the work is a sum of state variables times changes in state variables. A **Pfaffian Expression** is a sum of multiples of differentials. Consider the Pfaffian expression  $(1 - xy)dx - x^2dy$ . By Clairaut's,  $\frac{\partial Q}{\partial x} = -2x \neq \frac{\partial P}{\partial y} = -x$ . So, The expression cannot be the differential of some function,  $\neq df$ .

### 1.6.1 Integrating Denominator

However, if we divide the expression by  $e^{xy}$ ,  $\frac{\partial Q}{\partial x} = \frac{\partial P}{\partial y} = (x^2y - 2x)e^{-xy}$ . This is an **integrating denominator** as it makes the expression an exact differential. The integrating denominator allows us to write a Pfaffian expression in terms of an exact differential. For work,  $P$  is an integrating denominator as  $\frac{W}{P} = -dV$ .

### 1.6.2 Canatheodory

A mathematician named **Canatheodory** tells us that a Pfaffian expression admits an integrating denominator iff there are points in the state space in every neighborhood of our initial point *inaccessible* to the initial point while the Pfaffian expression = 0. Notice that every expression in 2 dimensions has an integrating denominator. An example that doesn't have an integrating denominator is  $ydx + dy - dz$ . Suppose we start at  $(0, 0, 0)$ . We can transition to the following point while keeping the Pfaffian expression = 0.

$$(0, 0, 0) \rightarrow (a - \frac{c-b}{b}, 0, 0) \rightarrow (a - \frac{c-b}{b}, b, b) \rightarrow (a, b, c)$$

With  $b \neq 0$  (special case), any point  $(a, b, c)$  is accessible. So, there is no integrating denominator.

## 1.7 Maximum Entropy

Suppose  $N$  atoms with total energy  $E$  have  $m$  accessible states with energies  $\{\epsilon_k\}_{k=1}^m$ . Determine the occupation numbers  $\{n_k\}_{k=1}^m$  that extremize the entropy  $S = k_B \ln \Omega = k_B \ln \frac{N!}{\prod_{k=1}^m n_k!}$ . So, we maximize  $\ln N! - \sum_{k=1}^m \ln n_k!$  subject to  $\sum_{k=1}^m n_k = M$ . Using Lagrange Multipliers,

$$F = \ln N! - \sum_{k=1}^m \ln n_k! + \lambda \left( N - \sum_{k=1}^m n_k \right) + \beta \left( E - \sum_{k=1}^m \epsilon_k n_k \right)$$

We can consider all  $n_k$  to be independent of each other. Taking a derivative,

$$\frac{\partial F}{\partial n_j} = -\frac{\partial}{\partial n_j} \ln n_j! - \lambda - \beta \epsilon_j = 0$$

Using Sterling's Approximation,

$$\frac{\partial}{\partial n} \ln n! \approx \frac{\partial}{\partial n} \left( n \ln n - n + \frac{1}{2} \ln(2\pi n) \right) = \ln n + \frac{1}{2n}$$

Plugging in,

$$\frac{\partial F}{\partial n_j} \approx \ln n_j - \lambda - \beta \epsilon_j = 0$$

In thermal equilibrium,  $\ln n_j + \beta \epsilon_j = -\lambda$  and  $\ln(n_j e^{\beta \epsilon_j})$  is independent of  $j$ . So,  $n_j \propto e^{-\beta \epsilon_j}$ . This is known as the **Boltzmann Factor**.

### 1.7.1 Thermal Contact

Suppose two systems are in thermal contact and System 1 gives  $\epsilon_j - \epsilon_k$  energy to System 2 by moving a single atom from state  $k$  to state  $j$ . Then,  $\Delta E_2 = \epsilon_j - \epsilon_k$ . For entropy,

$$\begin{aligned} \Delta S_2 &= k_B \ln \frac{N!}{n_1 \cdots (n_k - 1)! (n_j + 1)! \cdots n_m!} - k_B \ln \frac{N!}{n_1 \cdots n_k! \cdots n_j \cdots n_m!} \\ &= k_B \ln \left( \frac{n_k! n_j!}{(n_k - 1)! (n_j + 1)!} \right) = k_B \ln \frac{n_k}{n_j + 1} \end{aligned}$$

Since the occupation numbers are extremely large, we can approximate and use the Boltzmann factor,

$$\approx k_B \ln \frac{n_k}{n_j} = k_B \beta (\epsilon_j - \epsilon_k) = k_B B \Delta E_2$$

If this is a reversible process,  $\Delta E_2 = Q$  so

$$\boxed{k_B \beta Q = \Delta S}$$

Note that  $k_B B$  is an integrating denominator for heat and is the same for systems in thermal equilibrium. So,

$$k_B \beta = \frac{1}{T} \Rightarrow \boxed{\beta = \frac{1}{k_B T}}$$

### 1.7.2 Finding Entropy

Let  $N = 3 \times 10^{20}$  atoms be in three accessible states  $\epsilon_1 = 0, \epsilon_2 = \epsilon, \epsilon_3 = 4\epsilon$  and let  $E = \frac{1}{2}N\epsilon$ . Entropy is

$$S = k_B(\ln N! - \ln n_1! - \ln n_2! - \ln n_3!)$$

Using Stirling's Approximation and simplifying,

$$S \approx k_B \left( - \sum_{k=1}^3 n_k \ln \frac{n_k}{N} + \frac{1}{2} \ln \frac{N}{4\pi^2 n_1 n_2 n_3} \right)$$

## 1.8 State Variable Derivatives

We know  $dU = Q - W$ . From previous analysis, we know  $\frac{W}{p} = dV$  and  $\frac{Q}{T} = S$ .

$$dU = TdS - pdV$$

From multivariate calculus, we know  $df = \nabla f \cdot d\vec{r}$ . So,  $U = U(S, V)$ ,  $T = \left(\frac{\partial U}{\partial S}\right)_V$ , and  $p = -\left(\frac{\partial U}{\partial V}\right)_S$ . Using Clairaut's,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

This is known as a **Maxwell relation**. The following values are easiest to measure.

$$B = -\left(\frac{\partial p}{\partial V/V}\right)_T = -V\left(\frac{\partial p}{\partial V}\right)_T$$

The **isothermal bulk modulus** is the pressure required for a fractional volume change.

$$\alpha = \left(\frac{\partial V/V}{\partial T}\right)_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

The **isobaric thermal expansion coefficient** is the fractional volume change per temperature change.

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_P$$

The **heat capacity** at constant pressure is the heat required per change in temperature.

### 1.8.1 Other Potentials

We know  $U = U(S, V)$ . What if we wanted something that is naturally in terms of  $S$  and  $p$ ? Consider  $H = U + pV$ . Then,  $dH = dU + pdV + Vdp = TdS + Vdp$  (this  $H$  is known as the **enthalpy**). From the regular representation of  $dU$ ,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

From the differential of enthalpy,

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

The **Helmholtz free energy** is defined as  $A = U - TS$ . This gives  $dA = -SdT - pdV$  and

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

The **Gibb's free energy** is defined as  $G = U - TS + pV$  giving  $dG = -SdT + Vdp$  and

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\alpha V$$

### 1.8.2 Example

Suppose we wanted to find  $\left(\frac{\partial P}{\partial T}\right)_V$ . We consider  $V$  as a function of  $p$  and  $T$ .

$$dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_P dT$$

Manipulating the three values,

$$= -\frac{V}{B} dp + \alpha V dT$$

Since the value we want to find occurs at constant volume we set LHS to 0 and solve giving  $\alpha B$ .

## 1.9 Systems

### 1.9.1 Absolute Maximum Entropy

Using Lagrange multipliers, we can see that without regard for the total energy  $\beta = 0$ . Then,  $n_j \propto e^{-\beta \epsilon_j} = 1$ . So, the occupation numbers are evenly distributed.

### 1.9.2 Three Accessible States

Consider  $N$  atoms in thermal equilibrium with 3 accessible states of energies  $0, \epsilon, 3\epsilon$ . Then, by the Boltzmann factor,

$$N = A + Ae^{-\beta\epsilon} + Ae^{-3\beta\epsilon} = A(1 + x + x^3)$$

If the total energy is  $N\epsilon$ ,

$$N\epsilon = A(0 + x\epsilon + x^3 \cdot 3\epsilon) \Rightarrow 1 + x + x^3 = x + 3x^3$$

We can find the roots of this equation to solve for the occupation numbers. Manipulating the Boltzmann factor, we get

$$T = -\frac{1}{\ln x} \cdot \frac{\epsilon}{k_B}$$

### 1.9.3 Temperature

In Thermodynamics, temperature is defined as follows.

$$T = \left( \frac{\partial U}{\partial S} \right)_V$$

It is the integrating denominator for heat.

$$dS = \frac{Q}{T}$$

Consider two substances exchanging heat ( $T_1$  passes heat  $Q$  to  $T_2$ ).

$$\Delta S_1 = -\frac{Q}{T_1}, \Delta S_2 = \frac{Q}{T_2}$$

$$\Delta S = Q \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

If  $T_2 < T_1$ , the change in entropy is positive and the process is **spontaneous**. Considering energy and entropy, we see that maximal entropy occurs at some point. In lasers, energy is added so that the occupation numbers in the excited states are larger than those in the regular states. For positive  $T$ ,  $k_B T$  is a measure of how much ambient energy is available at some temperature  $T$ . Note from the definition of temperature given above, temperature can be negative theoretically though this is hard in practice. Processes that require less than  $k_B T$  can take place freely, but processes that require more than this do not happen.



## 1.10 Velocity/Speed Distribution

In classical mechanics, there are a continuum of energy states. Let's consider non-relativistic velocities only. Atoms of mass  $m$  with speed  $\vec{v}$  require energy  $\frac{1}{2}mv^2$ . Additionally, the probability of velocity  $\vec{v} \propto e^{-\frac{1}{2}\beta mv^2}$ . However, since the velocity is a continuum, the probability of an atom having exactly some velocity is 0. Instead consider the probability of some velocity between  $\vec{v}$  and  $\vec{v} + d\vec{v}$ . So, instead we can write the probability as  $\propto e^{-\frac{1}{2}\beta mv^2} dv_x dv_y dv_z$ . A **phase space** represent a set of quantities that determine the state of the object. Note this is a volume in phase space. Solving for the constant of proportionality  $A$ ,

$$\begin{aligned} 1 &= A \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} dv_z e^{-\frac{1}{2}\beta mv^2} \\ &= A \left( \int_{-\infty}^{\infty} dv_x e^{-\frac{1}{2}\beta mv_x^2} \right) \left( \int_{-\infty}^{\infty} dv_y e^{-\frac{1}{2}\beta mv_y^2} \right) \left( \int_{-\infty}^{\infty} dv_z e^{-\frac{1}{2}\beta mv_z^2} \right) \end{aligned}$$

Recognizing these integrals as Gaussian integrals,

$$= A \left( \sqrt{\frac{2\pi}{\beta m}} \right)^3$$

Solving for  $A$ ,

$$P(\vec{v}, d\vec{v}) = \left( \frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} e^{-\frac{1}{2}\beta mv^2} d^3v$$

This is known as the **Maxwell-Boltzmann velocity distribution**. This gives us a Gaussian distribution with highest value at 0. To get a speed distribution, we multiply by the volume of phase space associated with speed between  $v$  and  $v + dv$ .

$$P(v, dv) = \left( \frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} e^{-\frac{1}{2}\beta mv^2} \cdot 4\pi v^2 dv$$

This is known as the **Maxwell-Boltzmann speed distribution**. Consider the expectation value of the speed. We can do this by integrating. In the integral, we first substitute  $u = \sqrt{\beta m} v$  to scale it:

$$\begin{aligned} \left( \frac{\beta m}{2\pi} \right)^{\frac{3}{2}} e^{-\frac{u^2}{2}} \cdot 4\pi \cdot \frac{u^2}{\beta m} \cdot \frac{du}{\sqrt{\beta m}} &= \sqrt{\frac{2}{\pi}} e^{-\frac{u^2}{2}} u^2 du \\ \langle v \rangle &= \int_0^{\infty} \sqrt{\frac{2}{\pi}} e^{-\frac{u^2}{2}} u^2 du = \sqrt{\frac{2k_B T}{\pi m}} \int_0^{\infty} u^3 e^{-\frac{u^2}{2}} du \end{aligned}$$

Using  $s = \frac{u^2}{2}$ , we can get,

$$\langle v \rangle = \sqrt{\frac{2k_B T}{\pi m}} \int_0^{\infty} 2s e^{-s} ds = \sqrt{\frac{8k_B T}{\pi m}}$$

We can also find the expected value of the square of the speed.

$$\langle v^2 \rangle = \int_0^\infty \sqrt{\frac{2}{\pi}} e^{-\frac{u^2}{2}} \cdot u^2 \cdot \frac{u^2}{\beta m} du = \sqrt{\frac{2}{\pi}} \cdot \frac{k_B T}{m} \cdot \int_0^\infty u^4 e^{-\frac{u^2}{2}} du$$

We know  $\int_0^\infty e^{-\alpha u^2} = \frac{1}{2} \sqrt{\frac{\pi}{\alpha}}$ . Taking two derivatives with respect to  $\alpha$ ,

$$\boxed{\langle v^2 \rangle = \sqrt{\frac{3k_B T}{m}}}$$

This is commonly known as the **rms speed** (root-mean-square). The most probable speed is where  $u^2 e^{-\frac{u^2}{2}}$  is maximum. Taking derivatives, we can find  $u = \sqrt{s}$ . So, the **most probable speed** is

$$v_{mp} = \sqrt{\frac{2k_B T}{m}}$$

Notice that the substitution being used is

$$u = \sqrt{Bm} v = \sqrt{\frac{\text{molar mass}}{RT}} v$$

## 1.11 Rayleigh Jeans Law

Let's analyze the number of different states an electromagnetic wave has. Waves can be described in terms of their wave number  $k$  as  $\sin(kx - \omega t)$ . Consider some distance  $L$  that is an integer number of wavelengths. In other words,

$$\sin(kx - \omega t) = \sin(k(x + L) - \omega t) \Rightarrow kL = 2\pi n \Rightarrow k_n = \frac{2\pi n}{L}$$

To count this, we just sum

$$\sum \Delta n \rightarrow \sum \frac{L \Delta k}{2\pi}$$

This is the number of states between  $k$  and  $k + \Delta k$ . Similarly, in three dimensions,

$$\frac{L^3 d^3 k}{(2\pi)^3}$$

Notice that this is a volume in phase space. We can see that the **state density** is  $\frac{d^3 k}{(2\pi)^3}$ . So the energy of waves with wave number between  $k$  and  $k + dk$  is

$$E = 2 \cdot 4\pi k^2 \cdot \frac{d^3 k}{(2\pi)^3} \cdot k_B T$$

This 2 comes from polarization, the  $4\pi k^2$  comes from the volume of phase space between  $k$  and  $k + dk$ , and the  $k_B T$  gives us the energy for each state. It turns

out this is easier to write in terms of the wavelength,  $k = \frac{2\pi}{\lambda}$ . So, the energy density required by EM waves with wavelength between  $\lambda$  and  $\lambda + d\lambda$  is

$$\frac{8\pi k_B T}{\lambda^4} d\lambda$$

This is the **Rayleigh-Jeans Law**.

## 1.12 Ultraviolet Catastrophe

To get the total amount of energy that an EM waves need, we would integrate the Rayleigh-Jeans Law quantity over  $\lambda$ . However, this is not integrable around 0, so it seems that EM waves require "all" energy at any temperature other than  $T = 0$ . The theory supports this, but experimental data does not. This is what is known as the **Ultraviolet Catastrophe**. Plank resolved this by changing the energy per state from  $k_B T$  to

$$\frac{h \cdot \frac{c}{\lambda}}{e^{\beta \cdot \frac{hc}{\lambda}} - 1}$$

Notice that for large  $\lambda$ , the expansion of the exponent gives us  $\approx k_B T$ . Here,  $c$  is the speed of light in a vacuum.  $h$  is Planck's constant which, at the time, was fit to experimental data. Many theorists prefer working with this in terms of frequency,  $\nu$ :  $\lambda\nu = c \Rightarrow \lambda = \frac{c}{\nu}$ . Plugging this in, the energy per state is

$$\Rightarrow \frac{h\nu}{e^{\beta h\nu} - 1} = h\nu e^{-\beta h\nu} \cdot \frac{1}{1 - e^{-\beta h\nu}} = h\nu (e^{-\beta h\nu} + e^{-2\beta h\nu} + \dots)$$

This is an infinite sum of Boltzmann factors associated with energies of  $nh\nu$ . The reason this solves the catastrophe is that there is a minimum amount of energy  $h\nu$  to excite an EM wave. If  $h\nu \ll k_B T$ , the EM waves are easily excited, but if opposite, they are hard to excite. For EM waves, the **photons** are occupying these states. With this resolution, let's get the total energy density in EM waves in thermal equilibrium.

$$= \int_0^\infty 2 \cdot \frac{h\nu}{e^{\beta h\nu} - 1} \cdot \frac{4\pi\nu^2}{c^3} d\nu$$

Using  $u = \beta h\nu$ ,

$$= \frac{8\pi}{(\beta hc)^3} \cdot \frac{1}{\beta} \int_0^\infty \frac{u^3}{e^u - 1} du$$

Notice this is the zeta-gamma integral.

$$= \frac{8\pi}{(\beta hc)^3} \cdot \frac{1}{\beta} \cdot \Gamma(4) \cdot \zeta(4) = \boxed{\frac{8\pi^5 k_B^4}{15h^3 c^3} T^4}$$

For low temperatures, the energy is contained in the matter. But as temperature increases, the energy in EM waves will overtake the matter until it is radiation dominated. Each photon carries energy  $h\nu$ , so the photon density is

$$= \int_0^\infty 2 \cdot \frac{1}{e^{\beta h\nu} - 1} \cdot \frac{4\pi\nu^2 d\nu}{c^3} = \frac{8\pi}{(\beta h\nu)^3} \int_0^\infty \frac{u^2 du}{e^u - 1} = \boxed{\frac{16\pi}{(hc)^3} \zeta(3) k_B^3 T^3}$$

### 1.13 Stefan-Boltzmann Law

Consider a surface and the amount of radiation escaping the surface. So, the energy that escapes in time  $\Delta t$  is,

$$2 \cdot \frac{h\nu}{e^{\beta h\nu} - 1} \cdot \frac{d^3 k}{(2\pi)^3} \cdot dS \cdot c \cos \phi \Delta t$$

Here,  $\phi$  is the angle between  $\vec{k}$  and  $\vec{n}$ . The angular integration gives

$$\int_0^{\frac{\pi}{2}} \sin \phi d\phi \int_0^{2\pi} \cos \theta d\theta = \pi$$

So, the original integral is

$$\begin{aligned} &= 2 \int_0^\infty \frac{h\nu}{e^{\beta h\nu} - 1} \cdot \frac{\pi k^2 dk}{(2\pi)^3} dS \cdot c \Delta t = 2\pi \int_0^\infty \frac{h\nu}{e^{\beta h\nu} - 1} \cdot \frac{\nu^2 d\nu}{c^3} dS \cdot c \Delta t \\ &= (\text{total energy density}) \frac{c}{4} \cdot dS \Delta t \end{aligned}$$

The total power emitted will then be

$$\frac{2\pi^5 k_B^4}{15h^3 c} \cdot AT^4$$

This is the **Stefan-Boltzmann constant**.