

# Thermodynamics

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## 1 Maxwell-Boltzmann distribution

**Derivation.** The probability  $P_i$  that a particle occupies a state with energy  $E_i$  is proportional to the Boltzmann factor:

$$P_i \propto \exp\left(-\frac{E_i}{kT}\right)$$

Along one dimension, we have  $E = mv_x^2/2$ , so the probability of any velocity  $v_x$  is

$$f(v_x) = \sqrt{\frac{m}{2\pi kT}} \exp\left(-\frac{mv_x^2}{2kT}\right)$$

where the distribution is normalized so that  $\int_{-\infty}^{\infty} f(v_x) dx = 1$ . Since the component velocities are independent,

$$f(v_x, v_y, v_z) = f(v_x)f(v_y)f(v_z) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2kT}\right)$$

Finally, we integrate over the sphere  $v^2 = v_x^2 + v_y^2 + v_z^2$

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

**RMS speed.**  $v_{\text{rms}} = \sqrt{v^2}$ . For conciseness, let  $\alpha = m/2kT$ .

$$v_{\text{rms}} = \sqrt{\int_0^{\infty} f(v) v^2 dv} = \sqrt{\left(\frac{\alpha}{\pi}\right)^{3/2} 4\pi v^2 e^{-\alpha v^2} v^2 dv} = \sqrt{\frac{4}{\sqrt{\pi}} \alpha^{3/2} \int_0^{\infty} v^4 e^{-\alpha v^2} dv}$$

Now change to variable  $x = \alpha v^2$  so that  $v = \frac{x}{a}$  and  $dv = \frac{1}{2\alpha v} dx$ .

$$v_{\text{rms}} = \sqrt{\frac{4}{\sqrt{\pi}} \alpha^{3/2} \int_0^{\infty} v^4 e^{-x} \frac{1}{2\alpha v} dx} = \sqrt{\frac{2}{\alpha \sqrt{\pi}} \int_0^{\infty} x^{3/2} e^{-x} dx}$$

The Gamma function  $\Gamma(z) = \int_0^{\infty} x^{z-1} e^{-x} dx$  satisfies  $\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$  and  $\Gamma(z+1) = z\Gamma(z)$ , so

$$v_{\text{rms}} = \sqrt{\frac{2}{\alpha \sqrt{\pi}} \Gamma\left(\frac{5}{2}\right)} = \sqrt{\frac{2}{\alpha \sqrt{\pi}} \left(\sqrt{\pi} \cdot \frac{1}{2} \cdot \frac{3}{2}\right)} = \sqrt{\frac{3}{2\alpha}} = \sqrt{\frac{3kT}{m}}$$

**Most probable speed.**  $f'(v_p) = 0 \Rightarrow v_p = \sqrt{\frac{2kT}{m}}$ .

**Average speed.**  $\bar{v} = \int_0^{\infty} v f(v) dv = \sqrt{\frac{8kT}{\pi m}}$ .

## 2 Thermodynamics

**Zeroth law.** If two systems are in thermal equilibrium with a third system, they are in thermal equilibrium with each other, i.e. temperature  $T$  is transitive.

**Thermal expansion.** The length of a metal bar or the height of a column of mercury increases at higher  $T$  according to  $\frac{d\ell}{dT} = \alpha\ell \Rightarrow \ell = \ell_0 e^{\alpha(T-T_0)}$ . The Taylor expansion

$$f(x) = f(x_0) + \frac{f'(x_0)}{1}(x - x_0) + \dots$$

gives a linear approximation  $\ell \approx \ell_0 + \alpha\ell_0\Delta T$  or

$$\Delta\ell \approx \alpha\ell_0\Delta T$$

Similarly,  $V \approx (1 + \alpha\Delta T)^3 V_0 \approx (1 + 3\alpha\Delta T)V_0$ , so

$$\Delta V \approx \beta V_0 \Delta T, \text{ where } \beta = 3\alpha$$

This defines the empirical temperature scale used in thermometers.

**Ideal gas law.** Consider a side of a cube containing an ideal gas, which has perfectly elastic collisions.  $F = \frac{dp}{dt} = \frac{2m\bar{v}_x}{2L/\bar{v}_x} = \frac{m\bar{v}_x^2}{L}$  and  $P = \frac{F}{A} = \frac{m\bar{v}_x^2}{L^3} = \frac{mv^2}{3V}$ , so

$$PV = \frac{2}{3}KE = NkT$$

This shows that temperature is an absolute scale which measures internal energy.

**Equipartition theorem.** We have assumed that KE is only due to translational motion in three dimensions. But diatomic molecules have two more degrees of rotational KE =  $\frac{1}{2}I\omega^2$ . Since these terms are also quadratic, we may generalize our results to  $d$  degrees of freedom:

$$KE = \frac{d}{2}NkT$$

**First law:** energy is conserved. Energy may be transferred on two levels: microscopic, as heat transferred into the gas, or macroscopic, as work done by the gas. Thus,

$$\Delta U = Q - W$$

Note that  $W = \int F dx = \int PA dx = \int P dV$  is the area under a PV diagram.

**Second law.** Total entropy always increases:  $\Delta S = \int \frac{dQ}{T} \geq 0$

Clausius statement: no process is possible whose sole effect is to transfer heat from a cold to a hot reservoir, since otherwise  $dS = \frac{dQ}{Q_H} + \frac{-dQ}{Q_L} < 0$ .

Kelvin-Planck statement: no process is possible to convert heat entirely into work, since otherwise the work could be used to heat a warmer reservoir.

**Third law:**  $S = 0$  for a perfect crystal at  $T = 0$ , i.e. entropy is an absolute quantity. However,  $\Delta S$  also goes to 0, so it is impossible to reach this state in a finite number of steps.

### 3 Thermal processes

**Isothermal:**  $\Delta T = 0 \Rightarrow \Delta U = 0$ .  $Q = W = \int_{V_0}^V \frac{nRT}{V} dV = nRT \ln \frac{V}{V_0}$ .

This shows that  $Q = nC\Delta T$  is not valid for gases with  $\Delta V \gg 0$ . Instead, gases have a specific heat at constant volume  $C_V$  and a specific heat at constant pressure  $C_P$ . Isothermal processes may be computed as a combination of isovolumetric and isobaric processes.

**Isovolumetric:**  $\Delta V = 0 \Rightarrow W = 0$ .  $Q = \Delta U = \frac{d}{2}nR\Delta T$ , so  $C_V = \frac{d}{2}R$ .

Note that  $\Delta U = nC_V\Delta T$  always holds for any process.

**Isobaric:**  $\Delta P = 0$ .  $Q = \Delta U + W = \frac{d}{2}nR\Delta T + nR\Delta T$ , so  $C_P = \left(\frac{d}{2} + 1\right)R$ .

$C_P > C_V$  since under isobaric conditions, some of the heat is used to do work.

**Adiabatic:**  $Q = 0 \Rightarrow \Delta S = 0$ . We have the differential ideal gas law  $P dV + V dP = nR dT$  and  $nC_V dT = dU = -dW = -PdV \Rightarrow nC_V dT + P dV = 0$ , so  $\frac{dP}{P} + \frac{C_V+R}{C_V} \frac{dV}{V} = 0$ . Thus,

$$PV^\gamma \text{ is constant, where } \gamma = \frac{C_P}{C_V} = \frac{d+2}{d}$$

Adiabatic curves are steeper than isothermal curves on the PV diagram since  $T$  changes.

### 4 Heat engines

**Efficiency**  $\eta = \frac{W}{Q_{\text{in}}} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} < 1$ .

**Carnot's theorem.** Reversible processes have are quasistatic (carried out infinitely slowly as a series of equilibrium states) and frictionless. All reversible engines between constant temperatures have the same efficiency (Carnot's theorem), while irreversible engines have a lower efficiency.

**Carnot cycle.** Consists of isothermal expansion  $ab$ , adiabatic expansion  $bc$ , isothermal compression  $cd$ , and adiabatic compression  $da$ . Since  $dQ = T dS$ ,

$$\eta = 1 - \frac{Q_H}{Q_L} = 1 - \frac{T_L \Delta S}{T_H \Delta S} = 1 - \frac{T_L}{T_H}$$