

5.4 Kinetic theory

Monatomic gas

Pressure	$p = \frac{1}{3}nm\langle c^2 \rangle$	(5.77)	p pressure n number density $= N/V$ m particle mass $\langle c^2 \rangle$ mean squared particle velocity
Equation of state of an ideal gas	$pV = NkT$	(5.78)	V volume k Boltzmann constant N number of particles T temperature
Internal energy	$U = \frac{3}{2}NkT = \frac{N}{2}m\langle c^2 \rangle$	(5.79)	U internal energy
Heat capacities	$C_V = \frac{3}{2}Nk$	(5.80)	C_V heat capacity, constant V
	$C_p = C_V + Nk = \frac{5}{2}Nk$	(5.81)	C_p heat capacity, constant p
	$\gamma = \frac{C_p}{C_V} = \frac{5}{3}$	(5.82)	γ ratio of heat capacities
Entropy (Sackur–Tetrode equation) ^a	$S = Nk \ln \left[\left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} e^{5/2} \frac{V}{N} \right]$	(5.83)	S entropy $\hbar$ $= (\text{Planck constant})/(2\pi)$ e $= 2.71828\dots$

^aFor the uncondensed gas. The factor $\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2}$ is the quantum concentration of the particles, n_Q . Their thermal de Broglie wavelength, λ_T , approximately equals $n_Q^{-1/3}$.

Maxwell–Boltzmann distribution^a

Particle speed distribution	$\text{pr}(c) \, dc = \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left(\frac{-mc^2}{2kT} \right) 4\pi c^2 \, dc$	(5.84)	pr probability density m particle mass k Boltzmann constant T temperature c particle speed
Particle energy distribution	$\text{pr}(E) \, dE = \frac{2E^{1/2}}{\pi^{1/2}(kT)^{3/2}} \exp\left(\frac{-E}{kT} \right) dE$	(5.85)	E particle kinetic energy $(= mc^2/2)$
Mean speed	$\langle c \rangle = \left(\frac{8kT}{\pi m} \right)^{1/2}$	(5.86)	$\langle c \rangle$ mean speed
rms speed	$c_{\text{rms}} = \left(\frac{3kT}{m} \right)^{1/2} = \left(\frac{3\pi}{8} \right)^{1/2} \langle c \rangle$	(5.87)	c_{rms} root mean squared speed
Most probable speed	$\hat{c} = \left(\frac{2kT}{m} \right)^{1/2} = \left(\frac{\pi}{4} \right)^{1/2} \langle c \rangle$	(5.88)	$\hat{c}$ most probable speed

^aProbability density functions normalised so that $\int_0^\infty \text{pr}(x) \, dx = 1$.

Transport properties

Mean free path ^a	$l = \frac{1}{\sqrt{2}\pi d^2 n}$	(5.89)	l mean free path d molecular diameter n particle number density
Survival equation ^b	$\text{pr}(x) = \exp(-x/l)$	(5.90)	pr probability x linear distance
Flux through a plane ^c	$J = \frac{1}{4}n\langle c \rangle$	(5.91)	J molecular flux $\langle c \rangle$ mean molecular speed
Self-diffusion (Fick's law of diffusion) ^d	$\mathbf{J} = -D\nabla n$	(5.92)	D diffusion coefficient
	where $D \simeq \frac{2}{3}l\langle c \rangle$	(5.93)	
Thermal conductivity ^d	$\mathbf{H} = -\lambda\nabla T$	(5.94)	$\mathbf{H}$ heat flux per unit area
	$\nabla^2 T = \frac{1}{D} \frac{\partial T}{\partial t}$	(5.95)	λ thermal conductivity T temperature
	for monatomic gas $\lambda \simeq \frac{5}{4}\rho l\langle c \rangle c_V$	(5.96)	ρ density c_V specific heat capacity, V constant
Viscosity ^d	$\eta \simeq \frac{1}{2}\rho l\langle c \rangle$	(5.97)	η dynamic viscosity x displacement of sphere in x direction after time t
Brownian motion (of a sphere)	$\langle x^2 \rangle = \frac{kTt}{3\pi\eta a}$	(5.98)	k Boltzmann constant t time interval a sphere radius
Free molecular flow (Knudsen flow) ^e	$\frac{dM}{dt} = \frac{4R_p^3}{3L} \left(\frac{2\pi m}{k} \right)^{1/2} \left(\frac{p_1}{T_1^{1/2}} - \frac{p_2}{T_2^{1/2}} \right)$	(5.99)	$\frac{dM}{dt}$ mass flow rate R_p pipe radius L pipe length m particle mass p pressure

^aFor a perfect gas of hard, spherical particles with a Maxwell-Boltzmann speed distribution.

^bProbability of travelling distance x without a collision.

^cFrom the side where the number density is n , assuming an isotropic velocity distribution. Also known as “collision number.”

^dSimplistic kinetic theory yields numerical coefficients of 1/3 for D , λ and η .

^eThrough a pipe from end 1 to end 2, assuming $R_p \ll l$ (i.e., at very low pressure).

Gas equipartition

Classical equipartition ^a	$E_q = \frac{1}{2}kT$	(5.100)	E_q energy per quadratic degree of freedom k Boltzmann constant T temperature
Ideal gas heat capacities	$C_V = \frac{1}{2}fNk = \frac{1}{2}fnR$	(5.101)	C_V heat capacity, V constant
	$C_p = Nk \left(1 + \frac{f}{2} \right)$	(5.102)	C_p heat capacity, p constant N number of molecules
	$\gamma = \frac{C_p}{C_V} = 1 + \frac{2}{f}$	(5.103)	f number of degrees of freedom n number of moles
			R molar gas constant γ ratio of heat capacities

^aSystem in thermal equilibrium at temperature T .