

## 5.4 Kinetic theory

### Monatomic gas

|                                                |                                                                                              |        |                                                                                                                         |
|------------------------------------------------|----------------------------------------------------------------------------------------------|--------|-------------------------------------------------------------------------------------------------------------------------|
| Pressure                                       | $p = \frac{1}{3}nm\langle c^2 \rangle$                                                       | (5.77) | $p$ pressure<br>$n$ number density = $N/V$<br>$m$ particle mass<br>$\langle c^2 \rangle$ mean squared particle velocity |
| Equation of state of an ideal gas              | $pV = NkT$                                                                                   | (5.78) | $V$ volume<br>$k$ Boltzmann constant<br>$N$ number of particles<br>$T$ 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) | $\gamma$ ratio of heat capacities                                                                                       |
| Entropy (Sackur–Tetrode equation) <sup>a</sup> | $S = Nk \ln \left[ \left( \frac{mkT}{2\pi\hbar^2} \right)^{3/2} e^{5/2} \frac{V}{N} \right]$ | (5.83) | $S$ entropy<br>$\hbar$ = (Planck constant)/( $2\pi$ )<br>$e$ = 2.71828...                                               |

<sup>a</sup>For 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,  $\lambda_T$ , approximately equals  $n_Q^{-1/3}$ .

### Maxwell–Boltzmann distribution<sup>a</sup>

|                              |                                                                                                                    |        |                                                                                                                         |
|------------------------------|--------------------------------------------------------------------------------------------------------------------|--------|-------------------------------------------------------------------------------------------------------------------------|
| 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) | $\text{pr}$ probability density<br>$m$ particle mass<br>$k$ Boltzmann constant<br>$T$ temperature<br>$c$ 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) | $c_{\text{rms}}$ 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                                                                                           |

<sup>a</sup>Probability density functions normalised so that  $\int_0^\infty \text{pr}(x) \, dx = 1$ .



## Transport properties

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

<sup>a</sup>For a perfect gas of hard, spherical particles with a Maxwell-Boltzmann speed distribution.

<sup>b</sup>Probability of travelling distance  $x$  without a collision.

<sup>c</sup>From the side where the number density is  $n$ , assuming an isotropic velocity distribution. Also known as “collision number.”

<sup>d</sup>Simplistic kinetic theory yields numerical coefficients of  $1/3$  for  $D$ ,  $\lambda$  and  $\eta$ .

<sup>e</sup>Through a pipe from end 1 to end 2, assuming  $R_p \ll l$  (i.e., at very low pressure).

## Gas equipartition

|                                      |                                              |         |                                                                                                                        |
|--------------------------------------|----------------------------------------------|---------|------------------------------------------------------------------------------------------------------------------------|
| Classical equipartition <sup>a</sup> | $E_q = \frac{1}{2}kT$                        | (5.100) | $E_q$ energy per quadratic degree of freedom<br>$k$ Boltzmann constant<br>$T$ 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<br>$N$ number of molecules                                                           |
|                                      | $\gamma = \frac{C_p}{C_V} = 1 + \frac{2}{f}$ | (5.103) | $f$ number of degrees of freedom<br>$n$ number of moles<br>$R$ molar gas constant<br>$\gamma$ ratio of heat capacities |

<sup>a</sup>System in thermal equilibrium at temperature  $T$ .

