

Pressure is force per unit area, $d\vec{F} = -pd\vec{A}$, where the direction of \vec{A} is outward along the surface normal.

The compressibility of a fluid $k = -(1/V)\partial V/\partial p$. $k = 1/p$ for an ideal gas, but is much smaller for ordinary liquids, which can be regarded as approximately incompressible ($k \approx 0$).

Pressure variation in a column of incompressible liquid $p(z) = p_0 + \rho g(h - z)$ where h is the height of the column. The gradient of the pressure gives the *force per unit volume* $\vec{f} = -\nabla p$. The volume integral of $\int_V \vec{f} dV$ is the hydrostatic force on the material in the enclosed volume.

Pascal's principle: An external pressure is transmitted undiminished to all parts of a fluid in equilibrium. Note that this is a statement about the pressure, not the force.

Archimedes principle: The bouyant force on an object in a fluid is the weight of the excluded fluid.

Force on curved surface: The force from a fluid with (constant) pressure p on a hemisphere of radius R is $\vec{F} = \oint_S pd\vec{A} = \pi pR^2$. In general, if the pressure is constant, this force depends only on the cross sectional area perpendicular to the line of action of the force.

Divergence Theorem: For any vector field $\vec{u}(\vec{r})$, the flux of \vec{u} through a closed surface \mathcal{S} is $\oint_S \vec{u} \cdot d\vec{A} = \int_V \vec{\nabla} \cdot \vec{u} dV$. This means the total flow of \vec{u} through the closed surface is the sum of the net flows from each point (aka the *divergence* of \vec{u}) contained in the volume bounded by the surface. (Worked example: a calculation of the Archimedes force from the pressure of a fluid at the boundary of an immersed object).

Surface Tension: The surface energy of a fluid is $U_s = \gamma A$ where A is the surface area and γ is the surface tension. $[\gamma] = \text{J/m}^2 = \text{N/m}$. The latter is useful for formulating the surface tension force using the contact "line".

Equation of Continuity: For a steady flow bounded by a container of varying cross sectional area A , the volume flow rate $\Phi = vA$ is constant.

Equation of Motion: The force density $\vec{f} = \rho\partial\vec{v}/\partial t + \rho(\vec{v} \cdot \vec{\nabla})\vec{v}$, where the second term is called the "convective derivative." For steady flow we have $\vec{f} = \rho(\vec{v} \cdot \vec{\nabla})\vec{v}$. In these expressions \vec{v} is the average velocity of all the particles found in a fixed volume element of the fluid.

Note: for steady flow in a circular channel $(\vec{v} \cdot \vec{\nabla})\vec{v} = -(v^2/r)\hat{r}$ in each volume element. This gives the net "centripetal acceleration" of the particles in the volume element. Since the flow is steady $\partial\vec{v}/\partial t = 0$.

Bernoulli's Law: For steady, incompressible and irrotational flow, $(1/2)\rho v^2 + \rho g z + p = \text{constant}$. This is the work energy theorem for steady flow in a fluid.

Torricelli's Law: The flow velocity from a liquid column of height h is the free fall velocity $v = \sqrt{2gh}$.

The viscous force transmitted across a surface \mathcal{A} of a flowing liquid is $F/\mathcal{A} = \eta\dot{\epsilon}$ where $\dot{\epsilon}$ is the strain rate and η is the viscosity.

Poiseuille's Law: The flow velocity of a viscous fluid in a circular pipe with radius R and length ℓ is *nonuniform*

$$v(r) = \frac{\Delta p}{4\eta\ell} (R^2 - r^2) \quad (1)$$

and the volume flow rate is proportional to R^4

$$\Phi = \frac{\pi R^4 \Delta p}{8\eta\ell} \quad (2)$$

Stokes' Law: A sphere of radius R moving at velocity v relative to a fluid with viscosity η experiences a viscous drag force $F_v = 6\pi\eta Rv$.

The pressure from a gas on the walls of its container is calculated from kinetic theory $p = 2n\langle K \rangle/3$ where n is the number of particles per unit volume and $\langle K \rangle$ is the mean kinetic (translational) kinetic energy. This gives a microscopic basis for the ideal gas equation of state $p\mathcal{V} = NkT = N_m\mathcal{R}T$ where k is Boltzmann's constant, and \mathcal{R} is the gas constant.

Two Equilibria: Mechanical equilibrium between two otherwise isolated systems that are free to exchange volumes is established when the pressures are equal. Thermal equilibrium between two systems that can exchange energy is established when the temperatures are equal.

Heat I: When two otherwise isolated systems at different temperatures are in thermal contact, heat flows from the high temperature to low temperature system. This is a nonequilibrium state. Warning: do not confuse temperature and heat.

Heat II: The heat capacity of an object is the ratio of the heat required to raise the temperature by ΔT to the temperature change, $C = Q/\Delta T$ in the limit that $\Delta T \rightarrow 0$. The heat capacity is an extensive quantity that is proportional to the total number of particles in the system. It is useful to re-express this as a specific heat $c = C/N$ or a molar heat capacity $c^m = C/N_m$. For compressible states (like a gas) we need to specify the thermodynamic state of the system while the heat is added, by distinguishing between the specific heats at constant volume and at constant pressure.

Specific Heats for Ideal Gases For a monatomic ideal gas, only the translational motions contribute to the thermal energy so that the molar heat capacity $c_v^m = 3R/2$ where R is the universal gas constant. By the equipartition theorem each "thermally accessible" degree of freedom contributes $kT/2$ to the internal energy so that, for example, an ideal diatomic gas has a molar heat capacity $c_v^m = 5R/2$. In general the heat capacity can depend on the temperature since at high temperature more internal motions become thermally accessible.

Heat III: The rate of flow of heat \dot{Q} through a rectangular parallelepiped of cross sectional area \mathcal{A} and width d is

$$\dot{Q} = \frac{k\mathcal{A}\Delta T}{d} \quad (3)$$

where k is the thermal conductivity, and ΔT is the temperature difference across the width of the parallelepiped.

Three Maxwell Distributions: For a one dimensional ideal gas, the velocity distribution $f_1(v_x)$ is

$$f_1(v_x) = n_1 \sqrt{\frac{m}{2\pi kT}} \exp\left(-\frac{mv_x^2}{2kT}\right) \quad (4)$$

where n_1 gives the one dimensional density (number of particles per unit length). $f_1(v_x)\Delta v_x$ gives the number of particles per unit length with velocities between v_x and $v_x + \Delta v_x$. For a three dimensional gas this generalizes to

$$f(v_x, v_y, v_z) = n \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2kT}\right) \quad (5)$$

where n is the three dimensional density (number of particles per unit volume). The distribution of molecular *speeds* $g(v)$ can be derived from this, giving

$$g(v) = 4\pi n \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT} \quad (6)$$

$g(v)\Delta v$ gives the number of particles per unit volume with *speeds* between v and $v + \Delta v$. The most probable speed occurs when $dg/dv = 0$, so $v_p = \sqrt{2kT/m}$. The mean square speed $\langle v^2 \rangle$ is obtained by an average over this distribution

$$\langle v^2 \rangle = \frac{\int_0^\infty dv v^2 g(v)}{\int_0^\infty dv g(v)} = \frac{3kT}{m} \quad (7)$$

(Note: the proof of the last equality is assigned as a homework problem.)

Boltzmann Factor: In thermal equilibrium at temperature T the probability to find a molecule in a state with energy E (note this is the sum of its kinetic and potential energies) is proportional to the ‘‘Boltzmann factor’’ $\exp(-E/kT)$. This means that in equilibrium very high energy states $E \gg kT$ have exponentially small probabilities.

Useful Gaussian Integrals:

$$\begin{aligned} \int_{-\infty}^{\infty} \exp(-\alpha x^2) dx &= \sqrt{\pi/\alpha} \\ \int_0^{\infty} \exp(-\alpha x^2) x dx &= 1/2\alpha \\ \int_{-\infty}^{\infty} \exp(-\alpha x^2) x^{2n} dx &= (-1)^n \frac{d^n}{d\alpha^n} \sqrt{\frac{\pi}{\alpha}} \\ \int_0^{\infty} \exp(-\alpha x^2) x^{2n+1} dx &= (-1)^n \frac{d^n}{d\alpha^n} \frac{1}{2\alpha} \end{aligned} \quad (8)$$

First Law of Thermodynamics: $\Delta U = Q + W$ where U is the internal energy, Q is the heat flow to the system ($Q < 0$ is heat flow out and $Q > 0$ is heat flow in) and W is the work done *on the system*. For a compressible system $dW = -pdV$.

More on Heat Capacities: $Q = C\Delta T$, but for a compressible system, we need to distinguish the thermodynamic state of the system while the heat is added. Thus C_V is the heat capacity at constant *volume* ($= 3Nk/2$ for an ideal monatomic gas) and C_p is the heat capacity at constant *pressure* ($= 5Nk/2$) for an ideal monatomic gas. Any quasistatic change of state can be reconstructed from combinations of infinitesimal constant volume and constant pressure changes of state. It is useful to define the dimensionless thermodynamic parameter $\gamma = C_p/C_V$.

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State Functions A state function depends only on the equilibrium thermodynamic state of a system, not its history. An example is the internal energy, which for an ideal gas depends only on the temperature and the total number of molecules, i.e. $U(T) = 3NkT/2$ for an ideal monatomic gas of N atoms. The internal energy cannot change in any cyclic process that returns the system to its initial equilibrium state.

Path Functions Heat added to/extracted from and work done to/by a thermodynamic system in a quasistatic change of state can depend on the “path” that connects the initial and final states. In particular the total work done on, and heat transferred to a thermodynamic system in a quasistatic cycle can be nonzero.

Some Quasistatic Changes of State

Isothermal Compression/Expansion (Ideal Gas): $p\mathcal{V} = \text{constant}$, $\Delta U = 0$, $W = -NkT \log(\mathcal{V}_f/\mathcal{V}_i)$, $Q = NkT \log(\mathcal{V}_f/\mathcal{V}_i)$.

Isobaric Compression/Expansion (Ideal Gas): $\Delta U = Q + W$, $W = -p\Delta\mathcal{V}$, $Q = C_p\Delta T$.

Adiabatic Compression/Expansion (Ideal Gas): $p\mathcal{V}^\gamma = \text{constant}$ (or $T\mathcal{V}^{\gamma-1} = \text{constant}$), $Q = 0$, $\Delta U = W = (p_f\mathcal{V}_f - p_i\mathcal{V}_i)/(\gamma - 1)$. These formulas hold for a reversibly adiabatic change of state (we refer to this change as *fast but not too fast*).

Entropy: is a quantitative measure of the disorder of an equilibrium thermodynamic state. It is an extensive quantity, proportional to the number of atoms/molecules in a system. *Disorder* in this context is a logarithmic measure of the number of states that store the total thermal energy U in equilibrium at temperature T . Entropy is a state function, i.e. an equilibrium thermodynamic state has a definite entropy. For example, the entropy of the ideal gas at temperature T , pressure p and volume \mathcal{V} is

$$S = Nk \log(U^{3/2}\mathcal{V}) + \text{constant} \quad (9)$$

where the constant is called the chemical constant (it is independent of T and \mathcal{V}). Other formulas can be derived for other thermodynamic systems. The change of entropy during a thermodynamic change of state depend only on the initial and final states, and not on the history during the change of state. The change of entropy can be evaluated by direct calculation from equation (9) (we call this the *state function method*) or by evaluating the integral *the heat formula*

$$\Delta S(a \rightarrow b) = \left[\int_a^b \frac{dQ}{T} \right]_{\text{quasistatic}} \quad (10)$$

on any quasistatic (reversible) path that connects the states a and b . This latter method is the *classical* definition of the change in entropy (it predates the statistical interpretation.)

Second Law of Thermodynamics: Only processes with $\Delta S_{\text{tot}} \geq 0$ occur in thermodynamic systems. To properly use this formula *be sure to include the changes of entropy of the reservoirs with which the system interacts!* Note that the entropy of a single part of an interacting system (sometimes called a subsystem) can decrease in a thermodynamic change of state (an example is the entropy change of a gas in an isothermal compression). Reversible processes obey the equality $\Delta S_{\text{tot}} = 0$. In practice there are no truly reversible processes, since every quasistatic change involves many infinitesimal departures from and relaxations back to equilibrium states (and every such relaxation is a one way process where $\Delta S > 0$).

Two adiabatic expansions. A reversibly adiabatic expansion has $Q = 0$, and using the heat formula has $\Delta S = 0$. This is called an isentropic change. An adiabatic free expansion (for example breaking the partition between a confined gas and a vacuum) involves the relaxation from an initial highly nonequilibrium state to a final equilibrium state. This is an irreversible process that has $\Delta S \neq 0$ despite the fact that $Q = 0$. Notice that the heat formula cannot be applied (directly) to this process since the system evolves through a sequence of nonequilibrium intermediate states to which equation (10) is inapplicable.

Short course in Thermodynamics

- (a) Understand the three step cycle: isothermal (slow) compression, reversible adiabatic (fast but not too fast) expansion, and reheating at constant volume to return to initial state.
- (b) Understand the difference between the reversible adiabatic expansion and the adiabatic free expansion (and be able to calculate the change of entropy for each.)
- (c) Understand that a thermodynamic cycle can *partially* convert *heat* into *work*. No cycle can completely convert heat into work. This is the *Kelvin statement* of the second law of thermodynamics.

Efficiency of Thermodynamic Cycles The efficiency of a cyclic thermodynamic process is $\eta = W/Q_{\text{in}}$ where W is the net work done and Q_{in} is the heat absorbed. The optimum efficiency is realized by a theoretical cycle called the *Carnot cycle* that extracts heat from a high temperature reservoir at temperature T_{high} does work and discharges heat to a low temperature reservoir T_{low} . The Carnot cycle is a reversible cycle that absorbs heat only at its highest operating temperature and discharges heat only at its lowest operating temperature. The Carnot cycle has an efficiency $\eta = W/Q_{\text{in}} = (Q_{\text{in}} - Q_{\text{out}})/Q_{\text{in}} = 1 - T_{\text{low}}/T_{\text{high}}$.