



MIXTURE SETTLING

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MIXTURE SETTLING

All kind of mixtures (molecular solutions, colloids, and multiphase systems) tend to be stratified under the influence of external force fields (like gravity, centrifugation, or electromagnetic fields), although single-phase fluids (e.g. gas mixtures) tend towards a small segregation, whereas multi-phase systems like a gas/liquid mixture usually separate completely. Settling here means spatial concentration non-uniformity (i.e. stratification), with levels of constant concentration perpendicular to the force field direction, and non-uniformity ranging from small concentration gradients to different phases separated by interfaces. Notice, however, that in a more restricted sense, settling may refer to the process by which suspended solid particulates settle to the bottom of a liquid and form a sediment.

We only consider here mixture settling (segregation, stratification, demixing, or related terms) by the effect of gravity (acting downwards along the z coordinate), and the two basic settling variables: the stratification profile at equilibrium, and the speed of settling towards it. Gravity is omnipresent on our usual environment, the Earth surface, but can be counterbalanced in a spaceflight, where, aided with a centrifuge, the whole range of gravity intensities can be established to better analyse settling profiles and speeds (it must be warned, however, that at very low gravity levels, the lack of constancy in its intensity and direction may render the space environment too noisy for experiments on [microgravity](#)).

Furthermore, we only consider segregation of components already existing in the mixture in the same phase as the mixture, i.e. we do not consider chemical reactions or [nucleation](#) of a different phase (e.g. as when vapours segregate from a boiling liquid, or as when water vapour condenses or separates from humid air in dew), neither coagulation (forming a solid out of a liquid), although flocculation (particle aggregation) is considered below, in *Coalescence and rain*.

The main causes of species segregation in a mixture are:

- Thermodynamic equilibrium state under a force field, where a balance between the tendency to minimize the energy of a system (i.e. to fall), and the tendency of the system to get disperse, is reached.
- Non-equilibrium states due to transient processes from initial non-equilibrium (e.g. exhaling breathed air into fresh air, pouring milk over tea). After some time, a well-mixed equilibrium will be reached (if there are no other disturbances).
- Non-equilibrium states due to forced steady processes at system boundaries, as when CO₂ is being produced by fermentation in cellars or in brewing.

EQUILIBRIUM OF STRATIFIED SYSTEMS

Any thermodynamic system, be it a mixture or a pure component, if isolated from its surroundings, tends to evolve towards a unique distribution of its conservative magnitudes called the equilibrium state, defined by the maximisation of a distribution function called entropy, and identified by the following consequences (see Chap. 2: [Entropy](#)):

1. The temperature field is uniform in any system at equilibrium (i.e. independent of any force field).
2. The macroscopic velocity field matches that of a solid body (there are no relative velocities, i.e. all velocities are zero in an appropriate reference frame).
3. The chemical potential, μ_i , for each of the pure chemical components, i , varies in the direction of the applied field (here vertically downwards, g ; constant laterally), as:

$$\frac{d(\mu_i + M_i g z)}{dz} = 0 \quad (1)$$

where M_i is the molar mass of species i .

Equation (1) may be developed in terms of the intrinsic variables in $\mu_i(T, p, x_i)$ as:

$$\frac{\partial \mu_i}{\partial T} \frac{dT}{dz} + \frac{\partial \mu_i}{\partial p} \frac{dp}{dz} + \frac{\partial \mu_i}{\partial x_i} \frac{dx_i}{dz} + M_i g = 0 \quad (2)$$

that we now proceed to analyse term by term. The term dx_i/dz is the one wanted: the concentration profile at equilibrium segregation. As said before, $dT/dz=0$ at equilibrium. The term dp/dz will be worked out from the Gibbs-Duhem equation (Chap. 2), $0=SdT-Vdp+\sum n_i d\mu_i$, that, combined with Eq. (1) yields:

$$0 = S \frac{dT}{dz} - V \frac{dp}{dz} + \sum n_i \frac{d\mu_i}{dz} \rightarrow 0 = -V \frac{dp}{dz} - \sum (n_i M_i) g = -V \frac{dp}{dz} - mg \quad (3)$$

better known as the hydrostatic equation in a fluid in the form $dp/dz=-\rho g$. The other terms in (2), the dependence of the chemical potential on pressure and composition will be evaluated assuming an ideal mixture (Chap. 7: [Mixtures](#)); thence $\partial \mu_i / \partial p = V/n$ and $\partial \mu_i / \partial x_i = RT/x_i$, with $R=8.3 \text{ J}/(\text{mol}\cdot\text{K})$, so that, substitution in (2) finally yields:

$$0 - \frac{V}{n} \frac{\sum (n_i M_i) g}{V} + \frac{RT}{x_i} \frac{dx_i}{dz} + M_i g = 0 \rightarrow \frac{d \ln(x_i)}{dz} = \frac{(\sum x_i M_i - M_i) g}{RT} \quad (4)$$

The last equation directly relates our target, dx_i/dz (the concentration profile at equilibrium) with the forces driving it: the applied field, g , and the discrimination in the mixture measured by the difference between the molar mass of the mixture, $\sum x_i M_i$, and that of the species segregating, M_i . We now further define the system under study.

Except for the ideal-mixture model used above to pass from (3) to (4), the development has been general and applicable to any mixture in any phase, e.g. the nitrogen/oxygen gas mixtures (air), alcohol/water mixtures, water droplets and dust particles in air, air bubbles in water, vapour bubbles in water, even to red cells in blood in the ideal limit.

[Analytical chemistry](#) deals with instruments and methods used to separate, identify, and quantify matter (see e.g. [gas analysis](#)). Recall that, besides mole fractions $x_i=n_i/n$, mass fractions $y_i=m_i/m$, and volume fractions $\alpha_i=V_i/V$, may be used to determine the state of a two-phase mixture.

GAS SEGREGATION IN THE ATMOSPHERE

We know that the Earth's atmosphere is stratified in [layers](#); from bottom up (horizontal variations are much smaller): troposphere, stratosphere, mesosphere, ionosphere, thermosphere... But why not just a monotonous vertically-thinning air layer?

The shortest answer is that atmospheric stratification is due to solar radiation, which is selectively absorbed at some altitudes:

- At high altitudes, say $z > 90$ km, the ionizing tail in the solar spectrum (UV and below wavelengths) dissociates and ionizes air molecules, and temperature there is very large.
- At intermediate altitudes, around $z = 35$ km, the UV radiation dissociate O_2 to form a layer of ozone (O_3), shielding the lower layers from these life-damaging radiations. Temperature in this region has a local maximum due to this UV absorption, serving as separation of the stratosphere (downwards) from the mesosphere (upwards).
- At low altitudes, say $z < 20$ km, in a cloudless sky the atmosphere is almost transparent to solar radiation, which is absorbed at the surface (almost totally at the oceans' surface, to a lesser fraction at land, and in a minimal amount over glaciers).

In spite of these alternating thermal layers (see Fig. 1 for the International Standard Atmosphere model, [ISA](#)), an isothermal atmosphere model may be a good approximation to find pressure and density values aloft; e.g. up to 100 km altitude, the ISA model has a $T_{\min} = 187$ K and a $T_{\max} = 288$ K, i.e. an average $(187 + 288)/2 = 238$ K. It is shown [aside](#) that an exponential-model ('em') atmosphere with constant $T_{em} = 239$ K, with pressure $p(z) = p_{em} \exp(-z/z_{em})$, density $\rho(z) = \rho_{em} \exp(-z/z_{em})$, and parameters $z_{em} = 7$ km, $\rho_{em} = 1.4$ kg/m³, and $p_{em} = 96$ kPa, is a good approximation up to 90 km except for close to the ground.

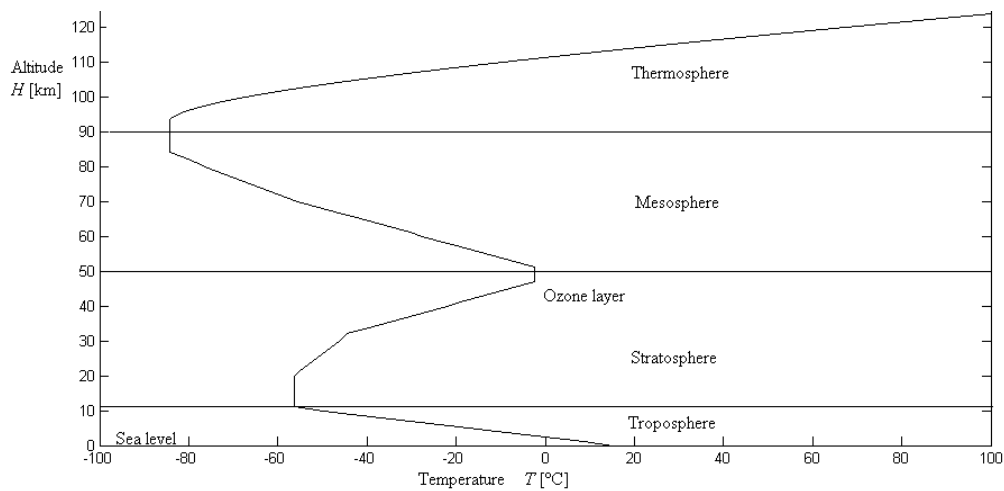


Fig. 1. Vertical thermal structure of Earth's atmosphere (extended ISA model).

But the above layered and exponentially-uniform models only refer to p - T values. Air composition happens to be almost uniform up to 100 km altitude ([homosphere](#)) due to turbulent mixing, roughly with 79 % of N_2 and 21 % of O_2 molar. Major deviations are, from bottom up, a maximum of 3 % of water vapour at the Earth's surface, some 5 ppm of O_3 at around $z=30$ km altitude, and a maximum of 4 % of atomic oxygen at $z=30$ km altitude.

However, this uniformity in air composition is a dynamic state (a permanent mixing process driven by non-uniform solar radiation). What would air-composition be in a static atmosphere?

- Would light gases like helium and hydrogen ascend, and heavy ones like carbon dioxide will fall to the bottom, all due to gravity (buoyancy)? No; there are light components at the bottom (mainly water vapour) and heavy components at the top (e.g. more-abundant components at $z=100$ km are: 77 % N_2 , 18 % O_2 , 4 % O, 1 % Ar, 0.02 % CO_2 , 0.001 % H...). N_2 is the main component up to $z=180$ km, atomic oxygen (O) taking over in the 180..460 km range, then helium (He) in the 460..800 km range, and finally atomic hydrogen (H) upwards, but this is due to solar absorption and not to buoyancy.
- Would air composition be uniform at equilibrium because gases mix perfectly? No; all mixtures under a force field segregate more or less at equilibrium, tending to balance the tendency to minimize energy (i.e. to fall), with the tendency of matter to get dispersed (i.e. to increase entropy). If the mixture has not reached equilibrium, either because of a long relaxation time or because of disturbing boundary conditions, its composition may be anyway.

In summary:

- The atmosphere at large (up to nearly $z=100$ km, and there is only 0.3 ppm of its mass further upwards) has almost a uniform composition (leaving humidity aside), not because of equilibrium but because of convection driven by solar radiation (e.g. according to (4), if it were at equilibrium, with 21 % of O_2 at $z=0$, the atmosphere would only have 6 % O_2 at $z=100$ km).
- Air masses of 'normal' size (say of $\ll 1$ km vertical extent) have almost uniform composition when at equilibrium; e.g. in a 100 m height air column, if there is 1 % of argon at the bottom ($M_{Ar}=0.040$ kg/mol, against $M_{N_2}=0.028$ kg/mol), there would be 0.995 % Ar at the top, at equilibrium, according to (4). But we can easily alter air composition locally by releasing different gases (e.g. by blowing

with our mouth over a quick-response CO₂ detector, we will see a sudden change from some $x_{\text{CO}_2}=0.05\%$ to up to $x_{\text{CO}_2}=4\%$, and back to say $x_{\text{CO}_2}=1\%$ after exhalation, depending on breath and mixing details).

Note on CO₂ stratification

Concerning the last described experiment (human breath over a close-up CO₂ detector), one can easily understand that the result is not dependent on orientation (horizontal, vertically up, or downwards) because the exit direction of the jet is dictated by mouth orientation. Taking the CO₂ detector further away while blowing horizontally, we would see the CO₂ fraction decreasing by mixing with entrained air from the surroundings, but, will the outgoing jet remain horizontal?, or it will turn downwards because CO₂ is heavier than air?, or upwards because the jet is warmer than air? The result might be tested with a local CO₂ detector, but would be simpler and more conclusive if an image of the whole CO₂-field near the head of the breathing person would be seen at once (e.g. using a moiré reflectometer to detect changes in air refractive index, or using a special infrared camera to detect CO₂ absorption in a narrow band near $\lambda=4\ \mu\text{m}$ as used in many exhaust-gas analysers, or preparing an artificial exhaler with a similar jet but made visible by adding a propylene-mist or a coloured additive). The end result is that exhaled air is lighter than room air and the jet bends upwards, as seen when a mist of condensed vapour makes exhalation visible in cold winter mornings, though it depends on temperature and composition details; e.g. if room air is at 100 kPa and 20 °C with $\rho=pM/(RT)=10^5\cdot 0.029/(8.3\cdot 293)=1.19\ \text{kg/m}^3$, the exhalation at say 35 °C and 4 % CO₂ has $\rho=pM/(RT)=10^5\cdot(0.04\cdot 0.044+0.96\cdot 0.029)/(8.3\cdot 293)=1.16\ \text{kg/m}^3$ and tends to bend upwards.

Fermentation, the anaerobic decomposition of organic matter, produces CO₂ that, in confined spaces (e.g. cellar tanks, caves) tends to accumulate at the lower levels, sometimes to deadly concentrations. Those places are also humid and fouled because water vapour and other distasteful gases and vapours are also released from decomposing organic matter, but we cannot smell CO₂ and a 10% of it will kill us without warning (by [hypercarbia](#)).

Of course, a pure CO₂ jet issuing horizontally (or vertically, as in the [Lake Nyos disaster](#)) tends to bend downwards while it is concentrated (diffusing afterwards), but this is not why CO₂ is used in some fire extinguishers; a nitrogen jet will extinguish the fire almost the same, because the basis is the same: to blow out air near the fire by an inert gas jet for oxygen starvation. In fact, N₂ jets are safer to people than CO₂ jets: we can breathe air with up to 85 % N₂ (if the rest is oxygen), but will die in a minute with 10 % CO₂ no matter how much oxygen is present. The reason why CO₂ is used in fire extinguishers is its compactness; e.g. you may have 5 kg of liquid CO₂ in a 7 L capacity bottle with a total mass of 14 kg allowing portable use (i.e. with a CO₂ density of $\rho=5/0.007=700\ \text{kg/m}^3$), kept safely up to 65 °C in a bottle of 20 MPa strength; however, an N₂ bottle with the same strength will only admit 1.3 kg of N₂ to be safe up to 65 °C. That is why N₂ fire extinguishers are not portable and only used in special [applications](#).

PARTICLE SEGREGATION IN THE ATMOSPHERE

We change here to a discrete (particulate) model of a mixture, and consider a binary mixture of a minority component i , the solute, made of spherical particles ('p') of diameter d , in a majority component that we

take as a pure fluid 'f', the solvent. Applying (4) to the volume of a particle, $V_p = \pi d^3/6$, with the molar mass for particles being $M_i = N_A \rho_p V_p$, and similarly for the fluid, we have:

$$\frac{d \ln(x_i)}{dz} = \frac{(\sum x_i M_i - M_i) g}{RT} = \frac{N_A (\rho_f - \rho_p) \frac{\pi d^3}{6} g}{RT} = cd^3 \quad (5)$$

where $N_A = 6.022 \cdot 10^{23}$ 1/mol is Avogadro's constant, ρ_f and ρ_p are the densities of the solvent (fluid) and the solute (particles), and c is a coefficient here introduced to single-out the particle-size effect. The characteristic length of the segregation profile may be defined as the height at which the molar fraction reduces to a half, which from (5) is:

$$L_{1/2} = \frac{\ln(1/2)}{cd^3} \quad (6)$$

showing that, for given substances (solvent and solute) and ambient conditions (temperature and gravity), the larger the solute particles, d , the smaller the characteristic segregation length, $L_{1/2}$, i.e. the steeper the solute-concentration slope, dc/dz , so that a measure of this slope may be used to find the size of particles.

A possible application of measuring the segregation length is in finding a value for [Avogadro's constant](#). Avogadro in 1811 just established the hypothesis that equal volumes of gases contain equal number of molecules, but the first quantitative calculation is due to Loschmidt in 1865 from thermal conductivity and kinetic theory of gases, and the most renown is due to [Perrin](#) in 1909 (Nobel Prize 1926) from equilibrium segregation profiles (the most precise is based on direct atomic-size measurements by X-ray diffraction of crystals); substituting (5) in (6) finally yields a direct relation between the unknown Avogadro's number and the easily measurable particle size chosen and segregation length within a fluid:

$$L_{1/2} = \frac{\ln(1/2)}{cd^3} = \frac{RT \ln(1/2)}{N_A (\rho_f - \rho_p) \frac{\pi d^3}{6} g} \rightarrow N_A = \frac{RT \ln(1/2)}{L_{1/2} (\rho_f - \rho_p) \frac{\pi d^3}{6} g} \quad (7)$$

Example 1. Compute Avogadro's number from the following experiment: a colloidal suspension of solid particles in water has been prepared; the particles have $d = 0.45 \pm 0.1 \mu\text{m}$ and $\rho_p = 1255 \pm 10 \text{ kg/m}^3$, and the concentration of particles falls to a half in a $L_{1/2} = 46 \pm 2 \mu\text{m}$ height in water at $T = 15 \pm 1 \text{ }^\circ\text{C}$.

Sol. Direct substitution in (7) yields:

$$N_A = \frac{8.3 \cdot 288 \cdot \ln(1/2)}{(46 \pm 2) 10^{-6} (998 - 1255 \pm 10) \frac{\pi [(0.45 \pm 0.1) 10^{-6}]^3}{6} 9.8} = (3 \pm 3) \cdot 10^{23} \text{ particles/mol}$$

not a bad approximation to the exact value of $N_A = 6.022 \cdot 10^{23}$ particles/mol, [adopted on 2019](#).

We are assuming a many-particles mixture, but it is worth considering for a moment the thermodynamics of the degenerate mixture composed of just one single particle in a host fluid medium (composed of many particles, assumed to be smaller than the guest one). Particles may be treated individually (interaction

effects with the rest less than 1 %) if their concentration is low ($V_p/V < 0.01$) and their size much smaller than the container, say $d/D_{\text{tank}} < 0.001$. In the equilibrium state, entropy maximisation implies that the large particle cannot have a privileged position; i.e., its position should be uniformly spread in time over the available volume, a stressed thermodynamic view of the normal system with many particles uniformly spread in the available space ([ergodic hypothesis](#)).

Let us try to follow the motion of one particle, and consider only one dimension for simplicity. If at a certain instant, $t=0$, the particle is found at position $x=0$ with speed $\dot{x} = v_0$, its motion will be described by $m\ddot{x} = F(t)$ (known as [Langevin equation](#)), with $F(t)$ being the force on the large particle due to collisions with the many small particles surrounding it, and that may be assumed to have a random value at every instant, with vanishing time-average. But the averaged kinetic energy of the large particle in equilibrium with the medium must be $(1/2)m\langle v^2 \rangle = (3/2)kT$ according to the [kinetic theory of gases](#), where $k=R/N_A=1.38 \cdot 10^{-23}$ J/K is Boltzmann's constant, with the result that $\langle x^2 \rangle = (3kT/m)t^2$, since time is monotonically increasing; i.e. although the mean position does not change with time, $\langle x \rangle = 0$, the random distance to the original position spreads out with a typical deviation $\sigma_x = \sqrt{\langle x^2 \rangle} = \sqrt{3kT/m} t$, i.e. growing linearly with time, and the root-mean-square of its speed is $\dot{x}_{\text{rms}} = \sqrt{3kT/m} = \sqrt{3RT/M}$, e.g. $\dot{x}_{\text{rms},N_2} = \sqrt{3RT/M} = \sqrt{3 \cdot 8.3288/0.028} = 506$ m/s for a N_2 molecule in air or water at 288 K (the medium has little influence), but $5 \cdot 10^{-3}$ m/s for a 1 μm fine-dust-particle, or $20 \cdot 10^{-6}$ m/s for a 30 μm pollen-particle, and much smaller for much larger particles. The conclusion is clear: at any finite temperature, at equilibrium, particles cannot stay quiescent; very small particles (like molecules in the air) move at swift speeds (but the particles are invisible), particles visible to the naked eye move so slowly that their motion is invisible, but appropriately-small particles can be watched moving under the microscope, at equilibrium. This microscopic motion is called [Brownian motion](#); mass diffusion can be seen as a macroscopic manifestation of Brownian motion.

The analysis above is only valid for small times, $t \ll (\rho_p/\rho_f)d^2/(18\nu_f)$, where ‘p’ refers to the large particle and ‘f’ to the fluid (ν_f being its kinematic viscosity). For larger times, fluid drag must be added to the equation of motion, which in the viscous limit ([Stokes flow](#)) takes the form $m\ddot{x} = F(t) - 3\pi\mu_f d\dot{x}$, with μ_f being the fluid’s dynamic viscosity, and d the particle diameter. Hence, for large times $t \gg (\rho_p/\rho_f)d^2/(18\nu_f)$, but before interaction with the walls, the motion is such that $\langle x^2 \rangle = (kT/(3\pi\mu_f d))t$, i.e. the typical diffusive motion $\langle x^2 \rangle = D_i t$ with a diffusion coefficient $D_i = kT/(3\pi\mu_f d)$, a relation known as [Stokes-Einstein equation](#) (to be more directly deduced below).

But before analysing dynamic states in segregation, it is worth revisiting the many different kinds of disperse systems.

CLASSIFICATION OF DISPERSE SYSTEM

Disperse systems can be classified according to the connecting medium (the matrix, i.e. gas dispersions, liquid dispersion, solid dispersions), and according to the size of particles dispersed, Fig. 2. Instead of a generic practical description, we intend to focus on the effect of particle size in the equilibrium concentration in a gravity field.

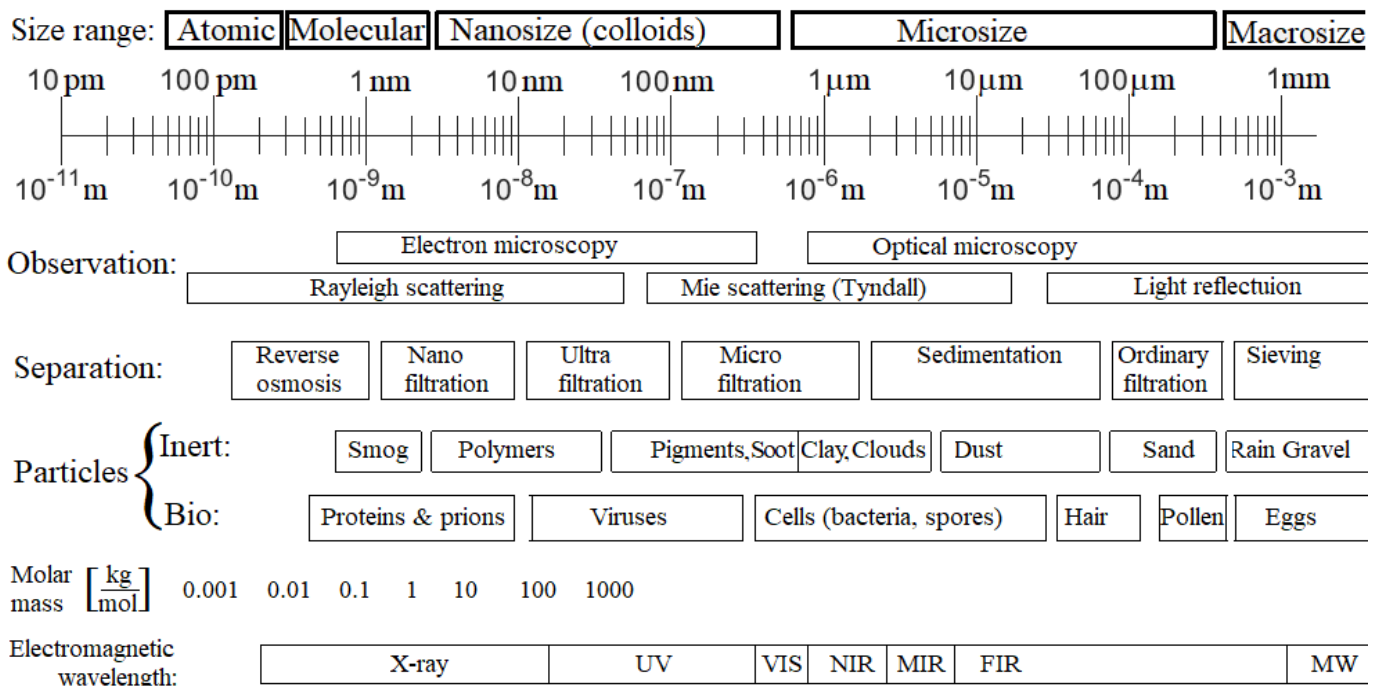


Fig. 2. Range of particle size (mean diameter, in log-scale), type of visualization, method of separation, typical systems, molar mass [kg/mol], and corresponding electromagnetic wavelength.

Particle size can be measured directly: down to 10^{-4} m by naked eye, down to 10^{-7} m by optical microscopy, and down to 10^{-10} m by electron microscopy; but size can also be measured indirectly by light scattering. Besides mean particle size, size distribution is important; [dispersity](#) is a more general measure of the heterogeneity of mixtures, not only related to particle size, but to particle shape, mass, composition, and so on, with a crude classification in:

- Uniform dispersity (also called monodisperse systems), where particles are almost of the same size, or of almost the same molar mass, or of the same kind.
- Non-uniform dispersity, where particles of different sizes, shapes, mass... are noticeable.

An order of magnitude analysis of the particle-size effect on segregation, provides deep insight on the concentration profile at equilibrium. Taking $g=9.8$ m/s², $T=288$ K and $|\rho_f-\rho_p|\sim 10^3$ kg/m³ (good for gas bubbles in water, for drops and dust in air, and for dust in water), the order of magnitude for the coefficient c in (5) is $|c|\sim 10^{24}$ m⁻⁴, and consequently, the correspondence between [particle size](#) and segregation scale is as follows:

- For $d\approx 10^{-10}$ m, (the smallest size of interest, corresponding to single atoms, ions and small molecules), the characteristic segregation length (6) is $L_{1/2}\approx 10^6$ m, too large a vertical distance for any practical purpose on Earth since 10^5 m is already an upper limit for the atmosphere (only 0.3 ppm of its mass further upwards), and the assumption of equilibrium is also untenable. This model may be applied however to make a guess of the settling of oxygen in air, resulting that, for an equilibrium atmosphere, if we take $x_{O_2}=0.21$ at sea level, at 10^4 m it would be $x_{O_2}=0.18$ (if it were at equilibrium). There are solid membranes selective to particles of this size (the solvent), giving way to osmotic processes; chemical affinity between membrane and solvent, instead of porous size, is what matters.
- For $d\approx 10^{-9}$ m, i.e. molecules up to $M_i=0.4$ kg/mol (e.g. for amino acids $M_i\approx 0.12$ kg/mol, for sugar $M_i=0.342$ kg/mol); $L_{1/2}\approx 10^3$ m, i.e. too large for any practical engineering purpose. From 10^{-10} m $< d < 10^{-8}$ m, mixtures are transparent (in the visible band, $\lambda_{VIS}=0.4..0.7$ μm), do not settle, and

they are called molecular mixtures or solutions. For very thick layers, molecular mixtures take a bluish colour because of Rayleigh scattering, a symmetric scattering (same back and forth) in the limit $d \ll \lambda$ with a small overall intensity proportional to λ^{-4} (that is why air and water are transparent at short distances and blue at the large), with a polar pattern proportional to $\cos^2\theta$ for polarised radiation and $1 + \cos^2\theta$ for un-polarised radiation. In this limit there is also some Raman scattering, which does not preserve the wavelength (Rayleigh, Mie and Tyndall scattering have the same frequency as the light source).

- For $d \approx 10^{-8}$ m, i.e. small macromolecules up to $M_i = 20$ kg/mol, and hence $L_{1/2} \approx 1$ m; e.g. small viruses, the muscle protein myoglobin (with $M_i = 17$ kg/mol having some $17/0.12 = 142$ aminoacids), or ovalbumin (with $M_i = 45$ kg/mol). These mixtures are slightly turbid (turbidity is measured by absorption (turbidimetry) or by scattering (nephelometry), they do not settle, but an opacity gradient can be seen in large systems, and are considered colloidal mixtures.
- For $d \approx 10^{-7}$ m, i.e. large macromolecules with $M_i > 40$ kg/mol, and hence $L_{1/2} \approx 10^{-3}$ m; e.g. human hemoglobin ($M_i = 65$ kg/mol), collagen ($M_i = 345$ kg/mol), DNA ($M_i \approx 4000$ kg/mol, $d \approx 0.24$ μm), fine soot, fine smoke, soot, paint pigments. These mixtures are whitish turbid, do not settle (except by ultracentrifugation or electrical migration), and are also called colloidal mixtures. There are also many large molecules that do not dissolve in water, like cellulose, starch and polystyrene, staying as larger clusters. Below 10^{-6} m, the optical microscopy does not work well (the electron microscope is used), but, with appropriate illumination, single particles of some 10^{-7} m can be seen, although not in real magnitude, due to Mie scattering (when $d \sim \lambda$, an incident light beam makes electrons to vibrate and emit light of the same frequency but stronger to the rear than to the front, and independent of λ , i.e. white if illuminated with a white light).
- For $d \approx 10^{-6}$ m, and hence $L_{1/2} \approx 10^{-6}$ m, i.e. smoke and pigments, mist, fog and thin clouds, fat micelle in water (milk, salad dressing, cream liqueurs), and small cells like bacteria. Milk is basically a dispersion of fat globules in an aqueous solution of lactose and casein micelles, but globule-size varies with species from 0.2 μm to 15 μm ; raw cow milk globules are 2.4 μm , but decrease to 0.4 μm in homogenised milk. These mixtures are opaque, do not settle or do it too slowly (except by centrifugation or electrical migration), their edges are clearly discerned, and single particles can be seen under the microscope. They are named colloidal mixtures up to $d \approx 10^{-6}$ m, and dispersions or suspensions if larger. It is astonishing that clouds in the sky, being formed by liquid droplets or frozen crystals a thousand times heavier than surrounding air, do not fall at all (up to the mid-19th century, many scientists thought that clouds were made of water bubbles instead of condense water, in spite of the rainbow explanation in terms of water drops, dating from the 12th century); not less amazing is the fact that, in 1 m^3 of a typical cloud, there is more mass of H_2O dissolved as vapour in the air than condensed in the typical thousands of millions of condensed particles per cubic metre (10^9 part/ m^3), which only add some 1 g/m^3 (small enough for airplanes to penetrate a well-defined cloud without any impact, but large enough to block the Sun). Condensed water vapour emanating from hot water or humid gas streams, sometimes named 'white smoke' is basically harmless, contrary to smoke (particularly in this size range that is easily carried into the lungs).
- For $d \approx 10^{-5}$ m, $L_{1/2} \approx 10^{-9}$ m; i.e. dust (flour, talc, ash), thick clouds, typical cells (e.g. red blood cells are 6.7 μm in diameter and 2 μm thick), protozoa, pollen. These mixtures are opaque, settle slowly, and are called suspensions, and single particles can be clearly seen under the microscope, slowly jiggling

(the [Brownian motion](#)), or by contrast (Tyndall scattering, a symmetric scattering for $d \gg \lambda$). High-pressure fuel injection in diesel engines produce a spray of droplets with an asymmetric size-distribution centred around 6..9 μm , with a tail extending up to 100 μm .

- For $d \approx 10^{-4}$ m (e.g. human hair, fine sand, mud), the characteristic segregation length (6) must be $L_{1/2} \approx 10^{-9}$ m because it cannot be smaller than molecular sizes. These mixtures are called heterogeneous and settle quickly; single particles can be seen by the naked eye. Mixtures with larger particles (powders and granules) usually appear stratified as separate phases, but can be maintained in suspension by entrainment in a fluid flow ([fluidized bed](#)), or appear in full solid form more or less compacted (e.g. [soil](#), granite).

In summary, according to the size of the disperse particles, fluid systems can be classified as:

- Solutions (or true solutions, or molecular solutions), with $d < 10^{-8}$ m. The fluid appears transparent, with invisible particles to both direct and transverse light. Membrane separation can be performed with special semi-permeable membranes and a high pressure jump, and is called reverse osmosis.
- Colloids (sometimes called homogeneous suspensions), with $d \subset 10^{-8}..10^{-6}$ m. The fluid appears whitish, with particles not seen in true size (scattering). The word colloid was coined by Thomas Graham, from Gr. *kolla*, glue; when he was studying glue and other gels in late 19th c. Colloids can be separated with a suitable membrane under pressure (ultrafiltration). According to the phases involved, colloids are grouped as:
 - Aerosols, i.e. solid or liquid particles dispersed in a gas. Solids: smoke, ice (e.g. cirrus-clouds, fluid ice). Liquids: fogs and mists (e.g. water in air, water in vapour). Apart these gas-matrix colloids, and solid-matrix dispersions not contemplated (e.g. steels), all other dispersions have a liquid matrix.
 - Sols, i.e. solid particles dispersed in a bulk liquid: paints, sulfur in water. Long macromolecules may increase viscosity so much that a semi-solid gel is formed.
 - Gels, i.e. liquid particles dispersed in a liquid lamella structure (both substances may contribute to the molecular three-dimensional network): gelatine, jelly.
 - Emulsions, i.e. liquid particles dispersed in a bulk liquid: milk (fat in whey), mayonnaise (oil in water), blood, egg-white. Many emulsions are formed from two immiscible liquids stabilised by an emulsifier (usually a polymer, like fatty acids or poly-alcohols).
 - Fizzes, i.e. gas bubbles dispersed in a bulk liquid, e.g. air in water (not so uncommon in tap water), carbon dioxide in water (from natural fermentation like in beer, or added like soda water), vapour in water, etc.
 - Foams, i.e. gas bubbles dispersed in a liquid lamella structure. Pure liquids cannot foam, and all foams are unstable in the long term, but surface-active macromolecules can stabilise them. Solid foams are gas dispersions in a three-dimensional polymeric network, which may be closed as in polystyrene foam ('white cork') or open as in polyurethane foams (upholstery); metal and concrete foams are also possible.
- Suspensions (or heterogeneous suspensions), $d \subset 10^{-6}..10^{-4}$ m, opaque, distinguishable particles slowly settling. Fine solid particles are easily filtrated with simple porous media (clay, fine sand). Fine gas bubbles can also be separated with porous media, but this time the filter must be on the top and not at the bottom (in any case the filter is in the direction of motion).

- Heterogeneous system, $d > 10^{-4}$ m, settled. Can be separated in an ordinary screen mesh. Heterogeneous systems are more readily formed amongst condensed substances with low fluidity, since the large density difference between a gas and a condensed substance quickly tends to separate them in two unmixed phases. However, shaking or some large relative motion can force the gas phase to disperse in a condensed phase.

According to the dispersion medium, mixtures are classified as:

- In gases, solid or liquid particles form mixtures called [aerosols](#); e.g. of liquid aerosol: sprays, clouds of droplets; e.g. of solid aerosols: smoke, dust, clouds of ice crystals. Gases are perfectly miscible with other gases.
- In liquids, gas bubbles may form [liquid foams](#), like in beer or whipped cream; liquid globules form [emulsions](#), like in milk and mayonnaise; solid clusters form [sols](#), like paint and mud. Some liquids are perfectly miscible, forming liquid solutions like water and alcohol. Most gases, liquids, and solids, are partially miscible with a liquid (up to a saturation concentration), forming true solutions.
- In solids, a gas forms a [solid foam](#), a liquid forms a [gel](#), and a solid forms a solid sol (e.g. alloys, tinted glass, gemstones; a few metals perfectly mix forming solid solutions instead of solid sols). Solid foams can be of closed gas bubbles (like in expanded polystyrene foam or ‘white cork’), or open-cell foams (like in polyurethane upholstery, although there are closed-cell structural polyurethane materials); in fact solid foams may be partially closed-cell and open-cell, like bread or pumice, taking some time to be soaked by water. [Porosity](#) is the fraction of the volume of voids over the total volume of a solid, but, for porous flow, the effective porosity is just the accessible void from the surface (open cells); related to porosity, [permeability](#) refers to resistance to fluid flow. A [gel](#) is a solid jelly-like soft material that can have properties ranging from soft and weak to hard and tough. In spite of its name, [aerogel](#) is not a gel but a solid foam made from a gel.

GENERATION OF DISPERSIONS

Mixing (at least partially, see [Solubility](#)) is often a natural process (i.e. it does not require an energy expenditure), driven by gradients in chemical potential, helped (or hindered) by gradients in temperature, and by convective currents (velocity gradients). In these cases, natural mixing can be accelerated for our convenience. On the other hand, there are artificial mixtures that naturally tend to demix (e.g. large condensed particles suspended in a gas). In both cases we may want to force the mixing.

Dispersions can be naturally or artificially generated in two ways:

- From a uniform phase, by homogeneous or heterogeneous nucleation, like in boiling in a pure liquid or a liquid mixture, condensation of humid air, undercooling a solid-in-liquid solution, depressurizing a gas-in-liquid solution, electrolysis of a liquid, etc.
- From a separated two-phase system, by mixing both phases, either by injection of one phase into the other (droppers, bubblers), by spraying (aspirating a liquid in a venturi throat, or entraining a gas in a liquid ejector), or by shaking (mechanically, ultrasonically). [Sonication](#) is the act of applying sound energy to agitate particles in a sample, either to break down large particles (i.e. to produce nanoparticles, as in milk homogenization), or to detach them from solids walls (e.g. ultrasonic cleaning), or for extracting some organic compounds from plants. On the other hand,

in the injection process, the detachment mechanism controls the size and frequency of particles generated. In a quiescent ambient, a droplet detaches when its weight overcomes surface tension forces, more or less as bubbles do (changing weight by floatability) when injecting a gas into a liquid (for instance, the bubble diameter is $d=[3\sigma D/(4g\Delta\rho)]^{3/2}$, where σ is surface tension, D the orifice diameter, g gravity and $\Delta\rho$ the density difference; a relative motion of the liquid, either co-flowing or in cross-flow, decreases bubble size and increases detachment frequency).

Applications of disperse systems are varied, most of them related to their very high heat and mass transfer rates, and chemical reactivity, because of their very large contact area. Waste-water cleaning and ore-extraction by flotation are just two major applications of disperse systems.

The basic processes to separate some species from a mixture are:

- Forcing the mixture through a selective membrane (see [Membrane separation](#), aside).
- Forcing a phase change in the mixture, e.g. salts usually remain after boiling a liquid mixture. Distillation is the most important separation technique (the traditional Chemistry icon).
- Contact with a selective absorber, e.g. carbon dioxide is absorbed in aqueous lime solutions, moisture in hygroscopic salts.
- Forcing a selective segregation by an imposed field, e.g. many macromolecules get charged in solution, depending on pH, and can be forced to move by imposing an electric field, E , until the electric force zeE balances the friction force ([electrophoresis](#)).

Suspensions of large particles (say $d>10^{-5}$ m) naturally separate under gravity by sedimentation or flotation, but can be difficult to achieve under microgravity, as Apollo astronauts suffered when drinking fizz-like water generated in fuel cells; now there are drugs, surface catalysers, and micro-structured walls to get rid of bubbles. Even on ground, it often happens that tiny air bubbles form at the wall of a glass of tap water, after a time; the reason in this case is that tap water is usually colder than ambient air, hence dissolving more gases, which are slowly released and coalesce at the microscopic imperfections on the glass (heterogeneous nucleation is easier than homogeneous nucleation in the bulk).

SPEED OF SOUND IN DISPERSIONS

The [speed of sound](#), c , is the speed of propagation of small perturbations in material media, which can be found experimentally by timing over a given length, or deduced theoretically as:

$$c = \sqrt{\left. \frac{\partial p}{\partial \rho} \right|_s} = \sqrt{\frac{1}{\kappa_s \rho}} = \begin{cases} \overset{PLM}{=} \sqrt{\frac{1}{\kappa_s \rho}} \approx \sqrt{\frac{E}{\rho}} \\ \overset{PGM}{=} \sqrt{\gamma RT} \end{cases} \quad (8)$$

where specific limits are deduced for the perfect liquid (or solid) model, PLM, and the perfect gas model, PGM, with κ_s being the isentropic compressibility coefficient (approximately the inverse of Young's modulus, E), ρ density, and γ ratio of thermal capacities. The speed of sound grows with material rigidity; e.g. in air, $c = \sqrt{\gamma RT} = \sqrt{1.4 \cdot 287 \cdot 288} = 340$ m/s (265 m/s in CO₂, 470 m/s in water vapour, 1320 m/s in H₂); in water $c = 1/\sqrt{\rho \kappa} = 1/\sqrt{10^3 \cdot (0.45 \cdot 10^{-9})} = 1500$ m/s; in steel $c \approx 5000$ m/s (this is for longitudinal-vibration

waves; solids can support shear forces and thus transversal-vibration waves, too; substituting in (8) the bulk modulus E by the shear modulus G , one has $c_{tr} = \sqrt{G/\rho} \approx 3000$ m/s in steel). Low-density highly-compressible materials are good acoustic absorbers (rigid solids have larger sound speeds, do not absorb sound appreciably, but are also good sound barriers ‘to the rear’ because they reflect most of the acoustic power at their surface).

In a [non-dispersive](#) medium (i.e. a single phase pure substance or mixture of similar species), the speed of sound is independent of sound frequency, so the speeds of energy transport and sound propagation are the same for all frequencies. Air, a mixture of oxygen and nitrogen, constitutes a non-dispersive medium. However, air does contain a small amount of CO₂ which is a dispersive medium, and causes dispersion to air at ultrasonic frequencies (>28 kHz); similar to light dispersion, in acoustic dispersive media, each frequency component propagates at its own speed, called the [phase velocity](#), while the energy of the disturbance propagates at the [group velocity](#).

The measure of sound speed in a homogeneous single-phase (mind that ‘homogeneous’ in disperse systems often means ‘uniform distribution’) binary mixture (A+B) can be used to find its composition. In ideal mixtures sound speed is a monotonous function of composition (i.e. changes with molar fraction from c_A at $x_B=0$ to c_B at $x_B=1$, without extrema in between). The generic relation for gas mixtures is:

$$c_{\text{mix}} \stackrel{\text{same } \gamma}{=} \sqrt{\frac{\gamma R_u T}{\sum_{i=1}^c x_i M_i}}, \text{ otherwise find } \gamma \text{ from: } \frac{1}{1 - \frac{1}{\gamma_{\text{mix}}}} = \sum_{i=1}^c \frac{x_i}{1 - \frac{1}{\gamma_i}} \quad (9)$$

Example 2. A helium/argon mixture has a sound speed of (500±5) m/s at (20±1) °C. What is the argon molar fraction?

Sol.: Both being monoatomic, $c_{p_mol} = 5R/2 = 20.8$ J/(mol·K), $\gamma = 5/3$, $c^2 = \gamma R_u T / (x_{\text{He}} M_{\text{He}} + x_{\text{Ar}} M_{\text{Ar}})$, and hence $x_{\text{Ar}} = (33 \pm 1)$ %.

In stratified fluids, the sound speed profile may have local extremes, confining sound propagation in layers, as happens in the [ocean](#); in most ocean regions temperature decreases with depth, and the profile of the speed of sound with depth decreases to a minimum at a depth of several hundred metres, but, below the minimum, sound speed increases again, as the effect of increasing pressure overcomes the effect of decreasing temperature.

SOUND SPEED IN TWO-PHASE SYSTEMS

In multiphase fluids (e.g. in gas-liquid mixtures and foams), sound speed is always lower than the speed of sound in the individual phases. It usually grows with the gas volume fraction over total volume, $\phi = V_G/V_T$, also known as void fraction or porosity, or with the gas mass fraction, w , which for a gas/liquid mixture are related by (we use explicit symbols for the vapour mass fraction, w_V , and the liquid mass fraction, w_L , but $w_V + w_L = 1$):

$$\phi_G \equiv \frac{V_G}{V_L + V_G} = \frac{\frac{w_G}{\rho_G}}{\frac{w_L}{\rho_L} + \frac{w_G}{\rho_G}} = \frac{\frac{w_G RT}{p}}{1 - w_G + \frac{w_G RT}{p}} \quad (10)$$

The case of a pure substance in the whole two-phase range of liquid-vapour equilibrium, LVE, from fizz to mist is illustrative. The sound speed can be theoretically deduced by establishing the density function for the mixture, $\rho = \rho(T, p, w_v)$, and differentiating to pressure at constant entropy, as stated in (8), with the result:

$$c = \frac{\frac{ph_{LV}}{RT} \left(\frac{w_L}{\rho_L} + \frac{w_v RT}{p} \right)}{\sqrt{w_L c_L T + w_v c_p T + \frac{w_w h_{LV}^2}{RT} - 2w_v h_{LV}}} \quad \left\{ \begin{array}{l} c \stackrel{w_v \rightarrow 0}{=} \frac{ph_{LV}}{\rho_L RT \sqrt{c_L T}} \\ c \stackrel{w_v \rightarrow 1}{=} \frac{h_{LV}}{\sqrt{c_p T + \frac{h_{LV}^2}{RT} - 2h_{LV}}} \end{array} \right. \quad (11)$$

where p is the LVE-pressure, $p_v(T)$. For pure water in LVE at $p=100$ kPa, $T=99.6$ °C (372.8 K), $\rho_L=960$ kg/m³, $h_{LV}=2.26 \cdot 10^6$ J/kg, $R=462$ J/(kg·K), $c_L=4200$ J/(kg·K), $c_p=2000$ J/(kg·K), and the sound speed falls from the liquid value of $c=1544$ m/s, abruptly to $c=1.1$ m/s as soon as the first bubbles appears in a uniform L-V mixture (i.e. at $w=0^+$, although the model is not valid so close to $w=0^+$ that compression drives the state outside the two-phase region); sound speed then increases in the LVE region with w_v , almost proportional to $\sqrt{w_v}$, up to $c=444$ m/s at $w=1^-$, suddenly jumping to the ideal vapour value at $w=1^+$, $c=(\gamma RT_1)^{1/2}=(1.3 \cdot 462 \cdot 373)^{1/2}=472$ m/s, as depicted in Fig. 3 as a function of enthalpy, h , what allows a continuous evolution during phase transitions (that w cannot provide).

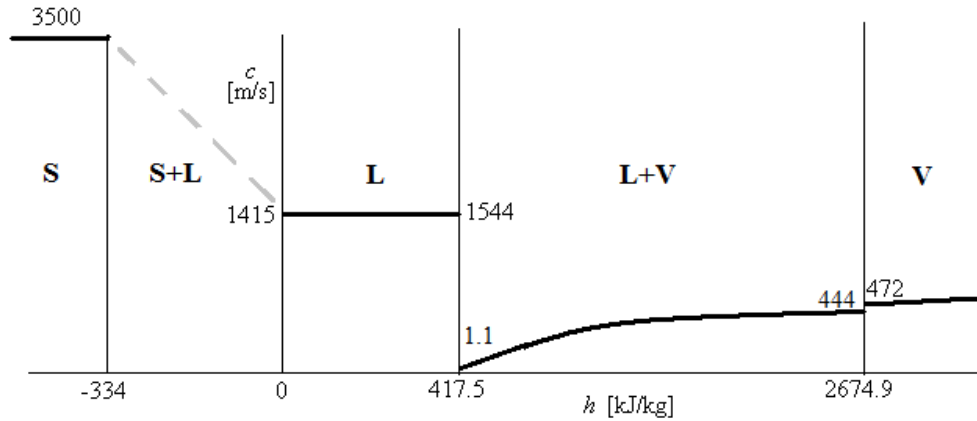


Fig. 3. Sound speed c (in [m/s]) in the different phases of water at 0.1 MPa as a function of enthalpy h (in [kJ/kg] relative to pure liquid state at the triple point). Sound speed is around 3500 m/s in the solid state (ice), varies in an unknown way during solid-to-liquid phase changing, attains the 1415 m/s of pure liquid water at 0 °C, slightly increasing to 1544 m/s at 100 °C, suddenly falling to 1.1 m/s as soon as the first steam bubbles appear (a fizz), then growing to 444 m/s when the last drops remain before total vaporization (a mist) at 100 °C where the perfect gas model yields 472 m/s for steam.

Instead of the homogeneous equilibrium model (HEM) just described, if one assumes that there is no phase change in the isentropic compression/expansion in the sound waves, what is known as homogeneous frozen model (HFM), the result is very different; e.g. in the middle of the L+V region in Fig. 3, sound speed is still very small, but in the fizz limit it tends to infinity, and in the mist limit it matches the pure-vapour value.

Perhaps the simplest sound-speed model was proposed by Wood in 1941 for homogeneous gas-liquid mixtures, based on the assumption of a linear dependence of mixture compressibility with its components compressibility weighted by their volume fraction (a similar relation to mixture density, $\rho = \phi_G \rho_G + \phi_L \rho_L$, namely:

$$\kappa_s = \phi_G \kappa_{sG} + \phi_L \kappa_{sL} \quad (12)$$

and consequently

$$\begin{aligned} \frac{1}{c^2} = \rho \kappa_s &= (\phi_G \rho_G + \phi_L \rho_L)(\phi_G \kappa_{sG} + \phi_L \kappa_{sL}) = (\phi_G \rho_G + \phi_L \rho_L) \left(\phi_G \frac{1}{\rho_G c_G^2} + \phi_L \frac{1}{\rho_L c_L^2} \right) \rightarrow \\ \rightarrow c &= \left[(\phi_G \rho_G + \phi_L \rho_L) \left(\frac{\phi_G}{\rho_G c_G^2} + \frac{\phi_L}{\rho_L c_L^2} \right) \right]^{-1/2} \end{aligned} \quad (13)$$

that relates sound speed in liquid foams (and homogeneous gas-liquid mixtures in general) to sound speed in the liquid phase and in the gas phase, appropriately weighted with respective volumetric fractions ($\phi_G + \phi_L = 1$) and respective densities. Notice that Wood's model matches at both ends of the two-phase mixtures (no discontinuities at liquid saturation and gas saturation points). An approximation of (13) often used for audible frequencies in air/water mixtures, in the range of volume fraction $0.02 < \phi < 0.98$, is $c = (c_{\min}/2) / \sqrt{\phi(1-\phi)}$ with $c_{\min} = 20$ m/s (Pierre et al, 2016).

Notice that, in order for the speed of sound to be regarded as a physical characteristic of a two-phase medium as a whole, the diameter of the particles of the dispersed phase, d , and their mean separation, D , must be much smaller than the wavelength of sound waves, λ , i.e. $d \ll \lambda$ and $D \ll \lambda$, where, for a typical sound speed in a water/gas mixture, $c = 20$ m/s, and a typical sound frequency $f = 1$ kHz, $\lambda = c/f = 20/10^3 = 20$ mm, but for an ultrasound frequency of 1 MHz $\lambda = 20$ μ m).

On the other hand, two-phase systems show acoustic [dispersion](#), i.e. sound propagation (speed and absorption) varies greatly according to the frequency of the wave; e.g. in a liquid foam, say with $\phi_G = 0.8$ (80 % gas volume fraction), at low frequencies, the speed of sound is very low (say 20 m/s) because the sound is slowed down by the coordinated motion of the films and channels, but is not blocked; at high frequencies, the speed of sound is larger (say 200 m/s), although only the films move, thus also allowing the sound to travel through the foam; but at intermediate frequencies, the films move in opposite direction to air, and the sound is therefore blocked in the bubbles over a wide range of frequencies.

Concerning sound reflection, when a pressure wave encounters another medium with the surface normal to the propagation direction of the wave, a portion of that wave is reflected at the interface and some is transmitted into the new medium. A portion of the transmitted energy is absorbed and the rest is transmitted through the material. For a wave traveling through medium 1 and encountering medium 2, the ratio of the intensity of the reflected wave to the incident wave is:

$$\frac{I_r}{I_i} = \left(\frac{\rho_1 c_1 - \rho_2 c_2}{\rho_1 c_1 + \rho_2 c_2} \right)^2 \quad (14)$$

where I_i is the incident power intensity [W/m^2], and ρ and c the density and speed of sound in each medium. The larger the difference in the characteristic resistance between the two media, the more energy is reflected. A high number of internal reflections can transfer energy to the solid structure through frictional losses and efficiently absorb sound.

NON-EQUILIBRIUM IN DISPERSE SYSTEMS

Besides equilibrium parameters, the evolution of non-equilibrium disperse systems is governed by new dynamic variables. The creation, growth, transport, decay and extinction of disperse systems are all non-equilibrium processes. We focus here to two basic transport processes:

- Diffusion of species in a quiescent medium (fluid or solid) due to non-uniformity of the extended chemical potential (1) due to a concentration gradient, often assumed to apply only to very small dispersed particles, say true solutions ($d < 10^{-9}$ m) and colloids (10^{-9} m $< d < 10^{-6}$ m).
- Sedimentation of relatively large particles, say $d > 10^{-6}$ m, in a quiescent fluid due to gravity, although the fall of larger particles is usually analysed with the typical fluid-dynamic approach.

The relative motion of chemical species in a mixture is termed [Mass transfer](#), mainly studied as a chemical subject, except perhaps for humid air, a most important mixture traditionally considered in mechanical engineering to (e.g. air conditioning, cooling towers).

We will focus on non-equilibrium processes without phase change just for simplicity, but mass transfer with phase change is very common, as when water-vapour emanates from a glass of water. In these cases, one has to consider chemical potentials instead of concentrations, limits of solubility, interfacial balances, and associated energy sources or sinks that deeply distort the pure-diffusion process (e.g. water evaporation takes almost 2.5 MJ/kg to change from liquid to vapour, causing temperature drops of about 0.1..0.5 K, which originate convective currents in the nearby air of 1..5 cm/s, overcoming the diffusive mixing). The influence of temperature is often crucial in mass transfer with phase change; e.g. even if Earth's atmosphere has a uniform dry-air composition from 0 to 90 km altitude, its water-vapour content decays exponentially from an average mass fraction (really [humidity ratio](#)) of 7 g/kg at the surface (7 g/kg at mid latitudes, but 17 g/kg near the Equator and 3 g/kg near the Poles) to almost 0 at about 10 km (at mid latitudes; 16 km near the Equator and 7 km near the Poles); air can only dissolve water-vapour up to the saturation limit, $w_{\text{sat}} = M_{\text{va}} / (p/p^*(T) - 1)$, with $M_{\text{va}} = 0.622$, so that at sea level with $p = 100$ kPa and $T = 15$ °C ($p^*(T) = 1.7$ kPa) $w_{\text{sat}} = 11$ g/kg, but at 10 km altitude with $p = 26$ kPa and $T = -50$ °C ($p^*(T) = 3.95$ Pa) $w_{\text{sat}} = 0.1$ g/kg,

DIFFUSION

Thermodynamics teaches us that an isolated system of particles tend to get dispersed, i.e. all gradients tend to die away: species diffuse against concentration gradients, momentum is diffused by velocity gradients, and thermal energy diffuses against temperature gradients. Diffusion is the transport mechanism that acts in a quiescent medium, or relative to moving fluid particles, contrary to the transport by bulk motion, termed convection (a moving [fluid parcel](#) carries on its mass all its species components, its momentum, and its

energy). In the case of solids, we assume that there are no convective currents, but in the case of fluids it is really difficult to have pure diffusion because minute thermal or mechanical perturbations yield uncontrolled convective currents that jeopardize diffusion measurements (to avoid that, one has to procure a thermally and mechanically stable fluid layer, i.e. colder and denser at the bottom under gravity).

The first systematic experimental study of diffusion was performed by Thomas [Graham](#) in 1831 on gases; he demonstrated that "...gases of different nature, when brought into contact, do not arrange themselves according to their density, the heaviest undermost, and the lighter uppermost, but they spontaneously diffuse, mutually and equally, through each other, and so remain in the intimate state of mixture for any length of time." Based on Graham's research on gases (and on his own experiments with salt solutions), Adolf Fick established in 1855 his famous [diffusion law](#) in a similar way to Fourier's law for heat conduction (1822) and Ohm's law for electric current (1827):

$$\frac{\dot{m}_{di}}{A} \vec{n} = \vec{j}_{di} = -D_i \nabla \rho_i \quad (15)$$

meaning that mass-diffusion of species i by unit area in the normal direction, named \vec{j}_{di} , is directly proportional and opposite to the density gradient of species i , $\nabla \rho_i$, or a similar equation in terms of the amount of substance, n_i , and concentration gradient, ∇c_i , instead in term of mass, i.e. $(\dot{n}_{di}/A) \vec{n} = \vec{j}'_{di} = -D_i \nabla c_i$, with the same value of the diffusion coefficient or [diffusivity](#), D_i [m^2/s], but different dimensions for \vec{j}_{di} [(kg/s)/ m^2] in (15), and for \vec{j}'_{di} [(mol/s)/ m^2].

Notice that (15) is only valid for mass diffusion within a homogeneous media without phase changes or chemical reactions, otherwise the more general equation in molar terms:

$$\frac{\dot{n}_{di}}{A} \vec{n} = \vec{j}'_{di} = -\frac{D_i c_i}{RT} \nabla (\mu_i + M_i g z) \quad (16)$$

should be used, according to (1), although we will continue with (15). Notice also that mass diffusion gives way to a macroscopic (bulk) motion, with a bulk velocity, \vec{v} , that should be defined in massic terms in accordance to the momentum balance, $\vec{v} = \sum \rho_i \vec{v}_i / \sum \rho_i$, and not in molar terms, $\vec{v}' = \sum c_i \vec{v}_i / \sum c_i$. In that way, the diffusion velocity \vec{v}_{di} is defined by:

$$\rho_i \vec{v}_{di} = \rho_i (\vec{v}_i - \vec{v}) = \vec{j}_{di} = -D_i \nabla \rho_i \quad (17)$$

If there is a convective flux $\vec{j} \equiv \rho \vec{v}$ (not associated to gradients in concentration but to bulk transport at speed \vec{v}), then the net flux of species i is $\vec{j}_i = y_i \vec{j} + \vec{j}_{di}$, or $\rho_i \vec{v}_i = \rho_i \vec{v} + \rho_i \vec{v}_{di}$.

Diffusion of matter can be viewed as the overall random thermal motion of atoms, molecules, or other particles, in gases, liquids, and solids; the random motion of a single particle is the Brownian motion. The random collisions, transport species (and their momentum and energy) from high concentration to low concentration regions. The kinetic theory of gases shows that the transport of all additive conservative magnitudes (mass of species, components of momentum, and energy) comes from the same process and,

once appropriately scaled, are numerically of the same order of magnitude, $D_i = \nu = a = 10^{-5} \text{ m}^2/\text{s}$ ($0.5 \cdot 10^{-5} \text{ m}^2/\text{s}$ to $2 \cdot 10^{-5} \text{ m}^2/\text{s}$) in a gas at room conditions, D_i being the diffusion coefficient of a gaseous species i in the gaseous mixture, ν the kinematic viscosity of the mixture, and a the thermal diffusivity of the mixture, all of them growing with temperature approximately as $T^{3/2}$, and decreasing with pressure approximately as $1/p$, being almost independent of gravity. And, of course, [diffusivity values](#) depend on the species and the medium considered (relative size of particles, particle shape, and strength of particle interactions).

For diffusion in condense matter there are not such rules, and the diffusion coefficient is typically of order $D_i = 10^{-9} \text{ m}^2/\text{s}$ for normal liquids mixtures and $D_i = 10^{-12} \text{ m}^2/\text{s}$ for macromolecules in liquid and for solids (diffusion coefficient in liquids can be computed from Brownian motion measurement by Stokes-Einstein equation). For instance, for sucrose $M = 0.342 \text{ kg/mol}$ $D_i = 460 \cdot 10^{-12} \text{ m}^2/\text{s}$, for myoglobin $M = 17 \text{ kg/mol}$ $D_i = 100 \cdot 10^{-12} \text{ m}^2/\text{s}$, for haemoglobin $M = 68 \text{ kg/mol}$ $D_i = 70 \cdot 10^{-12} \text{ m}^2/\text{s}$, for collagen $M = 345 \text{ kg/mol}$ $D_i = 7 \cdot 10^{-12} \text{ m}^2/\text{s}$.

Unlike the measurements of viscosity or thermal conductivity, for which standardized techniques and equipment are readily available, the measurements of mass diffusivity is more difficult, due to difficulties in measuring point values of concentration and other issues which complicate this transport process. There are several methods to make the measurement of the diffusion coefficient for liquid solutions. The simplest apparatus, used till today, is the one set up by Clack on 1921. The apparatus consists of a very thin vertical capillary tube connecting two reservoirs, the lower one with a more concentrated dispersion than the upper one, to avoid buoyancy. The liquid in both reservoirs is kept stirred to procure a constant composition near the tube ends. After the quasi-steady state is attained, measuring how the concentration in one reservoir changes with time yields D_i . This is a direct method, but slow.

Dimensional analysis shows that, in terms of the diffusion coefficient, D_i , and the characteristic length of the gradient, L , the order of magnitude for the speed of diffusion, V_{dif} , and the order of magnitude for the relaxation time by diffusion, t_{dif} , are:

$$V_{\text{dif}} \approx \frac{D_i}{L} \quad \text{and} \quad t_{\text{dif}} \approx \frac{L^2}{D_i} \quad (18)$$

For a gaseous mixture for instance, a concentration gradient through a 1 mm layer (a typical boundary layer thickness), has a typical diffusion time of $\Delta t = L^2/D_i = (10^{-3})^2/10^{-5} = 0.1 \text{ s}$, and a typical diffusion speed of $V_{\text{dif}} = D_i/L = 10^{-5}/10^{-3} = 10^{-2} \text{ m/s}$, whereas a concentration gradient through a 0.1 m gas layer (a typical test-tube length), has $\Delta t = (10^{-1})^2/10^{-5} = 10^3 \text{ s}$ and $V_{\text{dif}} = D_i/L = 10^{-5}/10^{-1} = 10^{-4} \text{ m/s}$, showing that diffusion is only effective for very small systems, even in this case of gases, that are much more mobile than condense matter.

Notice that we only consider here mass diffusion due to a concentration gradient, what might be called concentration-phoresis in analogy to other mechanisms of mass diffusion like thermo-phoresis (Soret effect), piezo-phoresis (diffusion due to a pressure gradient), or electrophoresis (diffusion due to a gradient of electrical potential applied to ionic media).

SEDIMENTATION

Sedimentation is the tendency for particles in suspension (of size $d > 10^{-5}$ m) to drift within and settle out of a fluid due to an external force field, which adds a directional component to the omnipresent diffusive motion (along the force field in the case of gravity, perpendicular to it in the case of the Lorentz force, for instance). Sedimentation motion is usually laminar (elementary fluid streams do not mix), but may become turbulent for large particles if they attain high speeds, contrary to diffusion, always a very slow process.

If a mixture at rest has not the equilibrium concentration profile, sedimentation motion starts to build up, i.e. accelerates, until eventually a quasi-steady state is reached. Finally, the moving particles hit the ground surface (or get trapped against a filter). Most often, the steady state of sedimentation, called the terminal velocity (maximum speed), is the key parameter to evaluate settling times, although transients may be important in some cases.

TERMINAL VELOCITY

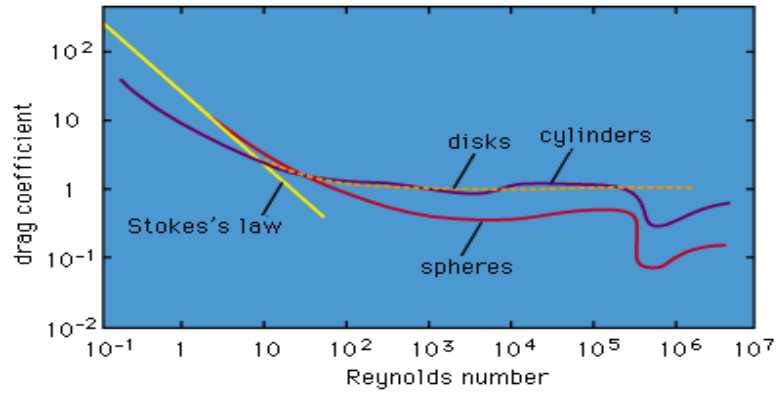
For the case of the gravity field and our previous model for disperse systems of isolated spherical particles (solid, liquid or gas) within a fluid medium (gas or liquid), we can compute the terminal velocity (i.e. the relative speed particle/medium) by a force balance between the applied field and the fluid drag. The general law of motion for a particle of mass m_p , for the vertical component of coordinate z (upright) is:

$$m_p \ddot{z} = -m_p g + \frac{m_p}{\rho_p} \rho_f g - F_D \quad (19)$$

showing that the acceleration is produced by the balance of the gravitational force (the weight, $m_p g$), the Archimedes push ($V_p \rho_f g$, i.e. the resultant pressure force at the frontier due to the presence of the applied force field), and the drag force (F_D , the resultant pressure force at the frontier due to the particle relative motion to the fluid). The latter is traditionally written in terms of the dynamic pressure ($\frac{1}{2} \rho_f V^2$) as:

$$F_D = c_D A \frac{1}{2} \rho_f V^2 \quad (20)$$

where V ($V = \dot{z}$) is the relative velocity, ρ_f the density of the fluid medium, A the frontal area of the particle in its relative motion (for spherical objects $A = \pi d^2/4$), and c_D the so-called drag coefficient. Experiments with different type of particles show how this drag coefficient depends on Reynolds number, $Re = Vd/\nu$, which is the main flow parameter, although there are others effects to take into account, like surface roughness, incoming turbulence intensity, and particle shape (see Fig. 4).



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Fig. 4. Drag coefficient for steady motion of some solid shapes in a fluid, and Stokes law.

The usual approximations for spherical, isolated, particles are:

- [Stokes' law](#) (1851) for slow laminar motion (creeping flow): $c_D=24/Re$ ($F_D=3\pi\mu dV$), very good for $Re<1$ (may be used up to $Re=10$).
- Constant drag coefficient for high speed laminar boundary-layer flow (smooth sphere) with turbulent wake (after flow separation around 80° from the centreline): $c_D\approx 0.5$, applicable for $100<Re<2\cdot 10^5$. An empirical transition law applicable in the $1<Re<10^3$ range may be $c_D=(24/Re)(1+0.15\cdot Re^{0.7})$.
- At about $Re=2\cdot 10^5$ for smooth surfaces ($Re=0.8\cdot 10^5$ for rough surfaces), the laminar boundary-layer flow makes a transition to turbulent layer, delaying flow separation to about 120° from the centreline, with a sharp decrease in drag coefficient to $c_D=0.1$, what is named drag crisis, and then increases to about $c_D=0.4$ for $Re>10^6$ as the turbulent wake widens.

The terminal velocity is obtained substituting these drag laws in (20) and then in (19) with zero acceleration (i.e. in $F_D=V_p\Delta\rho_f g)=\Delta\rho_f g \pi d^3/6$), finally yielding:

$$\text{for } Re<10, \quad V = \frac{\Delta\rho g d^2}{18\mu} \quad (21)$$

$$\text{for } Re>100, \quad V = \sqrt{\frac{8}{3} \frac{\Delta\rho g d}{\rho_f}} \quad (22)$$

Notice that for very small particles the terminal speed grows with d^2 , whereas for larger ones it is with $d^{1/2}$. A plot of $V(d)$ is shown in Fig. 5 for the typical case of sedimentation of condense particles in a gas, i.e. for $\Delta\rho=10^3 \text{ kg/m}^3$, $\rho_f=1 \text{ kg/m}^3$, $\nu=10^{-5} \text{ m}^2/\text{s}$, $g=10 \text{ m/s}^2$ (Stokes flow applies to $d<0.1 \text{ mm}$, and constant c_D to $d>2 \text{ mm}$, with a transition gap in between).

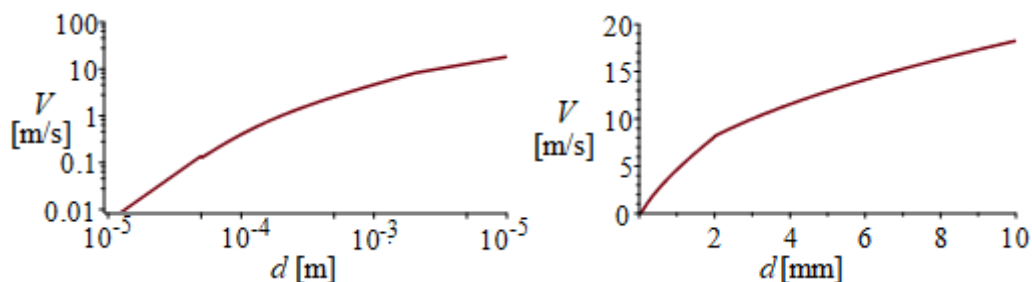


Fig. 5. Typical sedimentation speed, V , vs. particle diameter, d , for condensed particles falling in air.

Notice that a falling sphere (or any other shape) may depart from the vertical trajectory due to fluid-object instabilities (at $Re > 10$, eddies form and detach irregularly, creating transversal forces besides vertical drag); that is why leaves do not fall vertically from a tree.

Settling of particles is hindered in concentrated mixtures, and to account for that an empirical factor is introduced such that $V_{\text{crowded}} = fV_{\text{free}}$ with $f = 10^{-1.82(1-\varepsilon)}/\varepsilon^2$ and $\varepsilon = V_P/V$ the volume ratio of the particles in the mixture. Settling of particles is also hindered in small containers and similarly $V_{\text{small}} = fV_{\text{free}}$ with $f = 1/1 + 2.1(d/D_{\text{tank}})$.

Stokes sedimentation speed (21) may also be used to compute the viscosity of a fluid by measuring the sedimentation speed of calibrated particles in the slow regime:

$$\text{for } Re < 10, \quad \mu = \frac{\Delta\rho g d^2}{18V} \quad (23)$$

Finally, notice that the above modelling of sedimentation only applies to particle size $d > 10^{-5}$ m because (19) does not include the random molecular forces that originate the Brownian motion (see below). Smaller particles do not fall but hover around their equilibrium position. A good estimation of this size threshold can be obtained by a balance of the tendency to fall, measured by the sedimentation speed (21), with the tendency to jiggle around, measured by the speed of diffusion (18) of fluid particles through a layer of a similar size to that of the sedimenting particles, what yields:

$$V = \frac{\Delta\rho g d^2}{18\mu} = \frac{D_i}{d} \Rightarrow d = \left(\frac{18\mu D_i}{\Delta\rho g} \right)^{1/3} \xrightarrow{\text{in air}} \left(\frac{18 \cdot 10^{-5} \cdot 10^{-5}}{10^3 \cdot 9.8} \right)^{1/3} = 6 \cdot 10^{-5} \text{ m} \quad (24)$$

i.e. particles much smaller than this size will hover in the air (e.g. cloud droplets of $d = 2 \cdot 10^{-5}$ m), whereas much larger particles will sink (e.g. rain droplets of $d = 2 \cdot 10^{-3}$ m).

SIZE MEASUREMENT

Particles in the size range 10^{-9} m $< d < 10^{-6}$ m are cumbersome to measure because optical microscopy becomes difficult below light wavelengths (10^{-6} m), and no longer applies below 10^{-7} m, and electronic microscopy only applies to non-living systems because of radiation dose. Living particles in that range are however most interesting to study, since it is there that the difference between inert systems and self-organised system appears. Nephelometry (from Gr. νεφέλη, cloud) uses a light beam and a detector at right angle, to measure particle size and concentration, but smaller sizes can be measured by dynamic light scattering ([DLS](#)).

Settling and diffusion processes may be applied to size and molar mass determination, as well as computing other parameters as Avogadro's number (7), viscosity of the medium (12). or diffusion coefficients, as exemplified now. Equating the molar flux due to diffusion of component i , $j_{i,\text{dif}} = -D_i \nabla c_i$, to the molar flux due to sedimentation $j_{i,\text{sed}} = V c_i$,

$$j_i = Vc_i = D_i \nabla c_i \longrightarrow V = D_i \frac{d \ln(c_i)}{dz} = D_i \frac{d \ln(x_i)}{dz} \quad (25)$$

and substituting the left-hand-side with (10) and right-hand-side with (5):

$$V = \frac{\Delta \rho g d^2}{18 \mu} = D_i \frac{N_A \Delta \rho \frac{\pi d^3}{6} g}{RT} \Rightarrow D_i = \frac{kT}{3 \pi \mu d} \quad (26)$$

known as [Stokes-Einstein equation](#). It shows that D_i is larger for smaller particles (e.g. H_2 diffuses the best).

Example 3. Find the size of human-hemoglobine molecules knowing that its diffusion coefficient in water is $D_i = 63 \cdot 10^{-12} \text{ m}^2/\text{s}$.

Solution. From (26):

$$d = \frac{kT}{3 \pi \mu D_i} = \frac{1.38 \cdot 10^{-23} \cdot 293}{3 \pi 10^{-3} \cdot 63 \cdot 10^{-12}} = 7 \cdot 10^{-9} \text{ m}$$

what compares very well with the most accurate value of $5 \cdot 10^{-9} \text{ m}$.

Example 4. Find the molar mass of human-hemoglobin molecules knowing that its diffusion coefficient in water is $D_i = 63 \cdot 10^{-12} \text{ m}^2/\text{s}$, the sedimentation speed in a centrifuge with $g = 10^5 g_0$ is $V = 0.44 \cdot 10^{-6} \text{ m/s}$, and its density 1330 kg/m^3 .

Solution. From (26):

$$V = D_i \frac{N_A \Delta \rho \frac{\pi d^3}{6} g}{RT} = D_i \frac{M \frac{\Delta \rho}{\rho} g}{RT} \Rightarrow M = \frac{VRT}{\frac{\Delta \rho}{\rho} g D_i} = \frac{0.44 \cdot 10^{-6} \cdot 8.3 \cdot 293}{\frac{330}{1000} \cdot 9.8 \cdot 10^5 \cdot 63 \cdot 10^{-12}} = 50 \text{ kg/mol}$$

what compares well with the most accurate value of 65 kg/mol (another method is applied in P-7.11).

ACCELERATION

The equation of motion for a settling particle is:

$$\text{for } Re < 10, \quad m \ddot{z} = -m \frac{\Delta \rho}{\rho_P} g + 3 \pi \mu d \dot{z} + F(t) \quad (27)$$

$$\text{for } Re > 100, \quad m \ddot{z} = -m \frac{\Delta \rho}{\rho_P} g + c_D \frac{\pi d^2}{4} \frac{1}{2} \rho_f \dot{z}^2 + F(t) \quad (28)$$

where the first force term is the net weight (weight minus Archimedean push), that is the driving one; the second term is the fluid drag, and the third one is the random force causing Brownian motion and diffusion. The terminal velocity was obtained by equating the two first forces (net weight to drag). The time it takes to reach this terminal velocity (or equivalently the distance travelled), can be estimated by comparison of the acceleration (left hand side) with the driving term (the net weight, or with the steady drag, since they are equal); thence:

$$\text{for } Re < 10, \quad \Delta t_{acc} = \frac{V}{\ddot{z}} = \frac{\frac{\Delta \rho g d^2}{18\mu}}{\frac{\Delta \rho}{\rho_p} g} = \frac{\rho_p d^2}{18\mu} \quad (29)$$

$$\text{for } Re < 10, \quad z_{acc} = \frac{1}{2} \ddot{z} \Delta t_{acc}^2 = \frac{1}{2} \frac{\Delta \rho}{\rho_p} g \left(\frac{\rho_p d^2}{18\mu} \right)^2 = \frac{\rho_p \Delta \rho g d^4}{648\mu^2} \quad (30)$$

$$\text{for } Re > 100, \quad \Delta t_{acc} = \frac{V}{\ddot{z}} = \frac{\sqrt{\frac{4}{3} \frac{\Delta \rho}{\rho_f} \frac{c_D}{g d}}}{\frac{\Delta \rho}{\rho_p} g} = \sqrt{\frac{4}{3} \frac{\rho_p^2 g}{\rho_f \Delta \rho} \frac{d}{c_D}} \quad (31)$$

$$\text{for } Re > 100, \quad z_{acc} = \frac{1}{2} \ddot{z} \Delta t_{acc}^2 = \frac{1}{2} \frac{\Delta \rho}{\rho_p} g \frac{4}{3} \frac{\rho_p^2}{\rho_f \Delta \rho} \frac{d}{g c_D} = \frac{2 \rho_p d}{3 \rho_f c_D} \quad (32)$$

Some values of the acceleration distance on settling, Δz_{acc} , are presented on Table 2 at the end.

COALESCENCE AND RAIN

Settling of small particles is a very slow process and many times the interest is in precipitation (quick settling), so one may wonder how can cloud-drops manage to get 1 million times more bulky (100 times larger in diameter), to form rain-drops and fall. Condensation (i.e. vapour molecules aggregation to a condense phase), is only efficient in producing small drops that do not fall (1..10 μm); further growth occurs by coalescence, which is simply the merging of water drops or ice flakes that happen to collide (the merging is most effective when an electric field is present). Coalescence takes time, but in the tropics, a cloud can form, grow, and produce rain in as little as 30 minutes.

Precipitation (in the atmosphere or in the lab) first requires that the substance is present in the mixture (e.g. water-vapour molecules in the air), then it requires that the mixture is supersaturated (i.e. actual vapour pressure greater than saturation vapour pressure; notice that the saturation vapour pressure is defined over a flat surface), then it requires the presence of nucleation sites (usually heterogeneous, since homogeneous nuclei are unstable if smaller than a critical size), then nuclei accretion by vapour deposition (condensation) stimulated by large concentration gradients (e.g. due to vertical adiabatic expansion or cold and warm fronts mixing), then growth by coalescence (mainly for liquid drops), and finally sedimentation in a force field. Clouds in the atmosphere do not usually form locally (less than 15 % are born in a 500 km spot), but are brought by the wind.

Precipitation in middle latitudes usually begins as snow at altitudes above 3 km, but the form of the precipitation reaching the ground depends on the temperature profile of the atmosphere. If the temperature near the ground is warm enough, the snow has time to melt and reaches the ground as rain. A warm layer aloft and a subfreezing layer at the surface may produce sleet (ice pellets) or freezing rain (rain that freezes immediately upon contact with surface objects). Hail occurs when alternating strong updrafts and downdrafts cause ice crystals to pass repeatedly through layers that contain supercooled water. Table 1 introduces some precipitation types.

Table 1. Types of precipitation.

State	Size	Name	Description
liquid	0.005..0.05 mm	mist	smallest size noticed on the skin, 1 km visibility, stratus clouds
liquid	0.05..0.5 mm	drizzle	very light continuous generalised rain from stratus clouds
liquid	0.5..5 mm	rain	irregular rain from nimbostratus or cumulonimbus
solid	0.5..5 mm	sleet	soft light snow, dangerous for travel
solid	1..10 mm	glaze	glossy semitransparent coating on solid objects
solid	1..10 mm	rime	frosty coating on solid objects due to vapour supercooling
solid	1..10 mm	snow	frozen precipitation in soft flakes of plate or needle crystals
solid	1..100 mm	hail	ice lumps from cumulonimbus clouds with strong rising currents

Raindrop size distribution depends on rainfall rate, R , being usually modelled by an exponential function (known as Marshall-Palmer drop distribution). The probability to find a drop with size-range $[D, D+dD]$ is:

$$dp(D)=A\exp(-AD)dD \quad (33)$$

with $A=a(R/R_0)^b$ and the usual values $a=172 \text{ m}^{-1}$, $b=-0.21$ ($R_0=1 \text{ m/s}$ is just the unit to make dimensionless the power factor). The cumulative probability, i.e. the probability to find a drop with size less than D , is $P(D)=1-\exp(-AD)$. The absolute number of raindrops per unit volume, $n(D)$, with size-range $[D, D+dD]$ is similarly $dn(D)=n_0\exp(-AD)dD$, with $n_0=8 \cdot 10^{-6} \text{ m}^{-4}$, with a total number of n_0/A of drops per unit volume. A typical rainfall rate is $R=20 \cdot 10^{-6} \text{ m/s}=20 \cdot 10^{-6} \text{ m}^3/(\text{m}^2 \cdot \text{s})=70 \text{ mm/h}$ (the range $10 \cdot 10^{-6} \dots 50 \cdot 10^{-6} \text{ m/s}$ already encompass most cases); rainfall rates follow a gamma probability distribution function, $dp(R)=r(rR)^2\exp(-rR)dR/2$, with $r=10 \cdot 10^{-6} \text{ m/s}$ as a typical value. Notice that R and $n(D)$ are related through the settling speed, $R=\int_0^\infty n(D)dD V_{set}(D) \pi D^3 / 6$. For the typical rainfall rate of $R=20 \cdot 10^{-6} \text{ m/s}$, the total number of drops is around 5000 drop/m^3 (grows with R), with a total volume of $3 \cdot 10^{-6}$ (i.e. 3 ppm of liquid volume). Notice also that there is much more water in the gas phase than in the liquid phase: per cubic meter, 3 g within the liquid raindrops, and some 15 g within the humid air around, corresponding to a saturation humidity ratio at $20 \text{ }^\circ\text{C}$ of $w=15 \text{ g/kg}$).

The term coalescence is usually restricted to liquid particles, using preferably the term flocculation for solid particles, although they are both clustering processes much influenced by electrostatic forces. Flocculation is advantageously used in many physicochemical processes to separate materials in suspension, as in water-treatment plants. There are some liquids that coalesce easily, like fresh water, brines of $<8 \text{ g/kg}$, oils and sulfuric acid, whereas there are other liquids that do it with difficulty: brines with $>10 \text{ g/kg}$, aqueous alcohol solutions, benzene, and nitric acid.

SUMMARY OF DISPERSE SYSTEMS CHARACTERISTICS

Table 2 gives a summary of the characteristics of disperse systems that have been previously analysed.

Table 2. Type of mixture and settling characteristics according to particle size.

Size d	$L_{1/2}$	Type	Settling	V_{sed}	Δz_{acc}	V_{sed}^*	Comment
10^{-10} m	10^6 m	Solution	No	0	0	0	atoms, molecules
10^{-9} m	10^3 m	Solution	No	0	0	0	large molecules
10^{-8} m	1 m	Colloid	No	0	0	0	polymers
10^{-7} m	10^{-3} m	Colloid	No	$0.5 \text{ } \mu\text{m/s}$	0	0	soot, proteins
10^{-6} m	10^{-6} m	Colloid	Very slow	$50 \text{ } \mu\text{m/s}$	0	$0.5 \text{ } \mu\text{m/s}$	fog, smoke, bacteria

10^{-5} m	10^{-9} m	Suspension	Slow	5 mm/s	0	50 μ m/s	dust, red blood cells
10^{-4} m	10^{-9} m	Suspension	Fast	0.5 m/s	20 μ m	5 mm/s	finest rain, sand dust
10^{-3} m	10^{-9} m	Heterogen.	Very fast	5 m/s	1 m	0.5 m/s	raindrops, sand

*Settling speed V_{sed} and acceleration span Δz_{acc} in previous columns apply to settling of condensed particles in air, with $\Delta\rho \sim 10^3 \text{ kg/m}^3$, but V_{sed} in this column applies to settling speed of condensed particles in water with $\Delta\rho \sim 10^3 \text{ kg/m}^3$ and to rising speed of gas particles in water.

Larger heterogeneous systems may have much larger terminal velocities; thus, heavy rain with 5 mm drops (larger drops fracture while falling) typically fall at 9..10 m/s (whereas snowflakes of the same size fall at 1 m/s), typical hailstones of 10 mm fall at 15 m/s, and huge hailstones of 0.1 m fall at 50 m/s (an iron ball of the same size falls at 200 m/s).

A person falling in air may reach 50..70 m/s before its parachute deploys, falling at 5 m/s afterwards. Notice that in the equations for terminal speed (10-11) bulk spheres were assumed; the effect of a different geometry may be incorporated in (11) by changing appropriately the characteristic length, d , the drag coefficient c_D , and the effect of the particle not being bulky but with holes inside for instance, may be incorporated in (11) by changing appropriately the density difference with the medium, $\Delta\rho$ (e.g. a ping-pong ball of 40 mm falls at 9 m/s). Falling speed in air may be supersonic ($>340 \text{ m/s}$) for solid objects with $d/c_D > 1$ (from (11) with $\Delta\rho = 10^4 \text{ kg/m}^3$), i.e. for metal balls larger than 0,3 m, and for smaller-diameter metal spikes. The terminal velocity for a plane falling in air may be very high because of the large density ratio and low drag coefficient, whereas the terminal velocity for a sinking ship is just some 10 m/s according to (11).

In practical condense-fuel combustion, the size of the particles (liquid or solid) ranges from 5 μ m to 50 μ m, and they would settle at 0.01 m/s, but this effect can be neglected even when compared with room-temperature premixed deflagration speeds ($\sim 0.5 \text{ m/s}$). Isolated fuel particles of this size burn with a spherical flame of a few millimetres in diameter, whose rising speed in air by buoyancy ($< 0.1 \text{ m/s}$) may also be neglected (however, those small sizes are not convenient for experimentation, and a microgravity environment helps a lot).

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