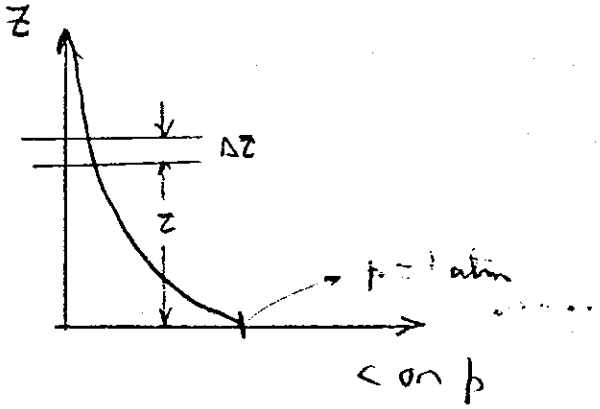
Diffusion in a Force Field

The value of Avogadro's number was first measured directly in 1909 by Perrin.* For these experiments, Perrin was awarded the Nobel prize in physics in 1921. The interpretation of these experiments is based on the theory of sedimentation equilibrium. Using monodisperse colloidal particles of known size dispersed in a liquid, Perrin measured the equilibrium concentration profile in a gravitational force field.

Knowning the particle size, Perrin could deduce Avogadro's number. Today we accurately know the value of Avogadro's number and we can use the results of a similar experiment to deduce the size of colloidal particles in an unknown.

Sedimentation Equilibrium (gases)

Suppose I have a column of gas which is very tall. Like the atmosphere on our planet, the gravitational force acting on the gas molecules causes the pressure of the gas to be higher at the bottom of the column than at the top.



Selecting a thin slice of gas, thickness Δz, and performing a force balance on it yields:

$$p(z)A - p(z+\Delta z)A = c(z)A\Delta z M F_g$$

where F_g = g = grav. force on unit mass of gas
p = gas pressure
A = area of column
c = gas concentration (moles/vol)
M = molecular weight of gas (g/mole)
g = acceleration of gravity

Dividing by $A\Delta z$ and taking the limit as $\Delta z \rightarrow 0$ yields

$$dp/dz = -MF_g c \qquad (1)$$

For an ideal gas $$p = cRT \qquad (2)$$

(2) into (1): $$dp/dz = -MF_g p/RT \qquad (3)$$

If we now assume that the gas is uniform in temperature:

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*Jean Baptiste Perrin (1870-1942): Fr. physicist.

$$T \neq T(z)$$

and ignore changes in the gravitational acceleration with elevation, then (3) can be easily integrated:

$$p(z) = p_0 \exp(-MF_g z/RT)$$

or

$$c(z) = c_0 \exp(-MF_g z/RT) \qquad (4)$$

where the subscript 0 denotes the value at z=0. It turns out that (4) does not accurately predict the pressure profile in the earth's atmosphere because there are significant temperature variations with elevation due to radiation, wind currents, etc. In a laboratory experiment, we can avoid these effects and thereby achieve thermal equilibrium in which the temperature of the system is uniform.

Generalized to Nonuniform Force Fields

Suppose the gravitational field was not constant:

$$g = g(z)$$

The solution for the concentration profile due to sedimentation equilibrium turns out to be:

$$c(z) = c_0 \exp[-M\Phi_g(z)/RT] \qquad (5)$$

where

$$\Phi_g(z) = \int_0^z F_g(z')\,dz'$$

is the gravitational potential energy per unit mass. This represents the work required to raise a unit mass from z=0 to z=z.

If

$$g=\text{const}$$

then

$$\Phi_g = F_g z$$

and (5) reduces to (4).

Actually (5) applies to any force field. There is nothing in its derivation which restricts this derivation to gravitational forces. (5) also applies to electrostatic or magnetic forces, provided we use the proper expression for the potential energy associated with the force. These forces might have different directions at different positions as well as different magnitude.

Thus, more generally, if the gas molecules feel a net force

$$\underline{\mathbf{F}}(\underline{\mathbf{x}}) = \text{net force/mass (vector)}$$

$\underline{x}$ = position vector (x,y,z)

then the concentration of gas molecules at equilibrium will be given by:

$$c(\underline{x}) = c_0 \exp[-M\Phi(\underline{x})/RT], \tag{6}$$

where $\Phi(\underline{x}) = -\int_C \underline{F}\cdot d\underline{x}$ = potential energy/mass

is the net potential energy/mass associated with the net force. $\int_C$ denotes a contour integral: the contour goes from the reference state to the point $\underline{x}$. For conservative force fields like gravity and electrostatic forces, this contour integral is independent of the path: it depends only on the initial and final points -- not on the shape of the path connecting them.

This expression for the potential can be differentiated to give:

$$\underline{F} = -\nabla\Phi$$

Generalized to Any Ideal Mixture

Although we have derived Boltzmann's equation for an ideal gas, it turns out it also applies for any ideal solution. Recall from thermodynamics that the criteria for phase equilibrium is the equality of chemical potential among all phases:

μ_i in Phase 1 = μ_i in Phase 2

for each component i. Of course, it is understood that at equilibrium, the chemical potential is uniform throughout phase 1:

μ_i: [J energy/mole

$$\nabla\mu_i = \underline{0} \text{ throughout Phase 1 or 2} \tag{7}$$

When the solute i interacts with the rest of the universe outside our system, this criteria has to be modified (e.g. Our gas molecules inside the column of air interact with the earth outside the column -- this is gravity.) When the solute experiences an force from outside the system, then (7) becomes:

$$\nabla(\mu_i + M_i\Phi_i) = \underline{0}$$

or

$$d\mu_i + M_i d\Phi_i = 0 \tag{8}$$

where μ_i = chemical potential of component i

M_i = mol. wgt. of i

Φ_i = potential energy/mass of i

For an ***ideal solution***, the chemical potential is calculated from:

$$d\mu_i = RT\, d\ln c_i \qquad (9)$$

Subsituting (9) into (8) and integrating yields (6). Let me make one simplification: divide numerator and denominator of the exponent by Avogadro's number. Now define the new numerator as

$$\phi \equiv (M/N_A)\Phi_i$$

which is the potential energy per solute molecule. Likewise, define the new denomenator as

$$k \equiv R/N_A$$

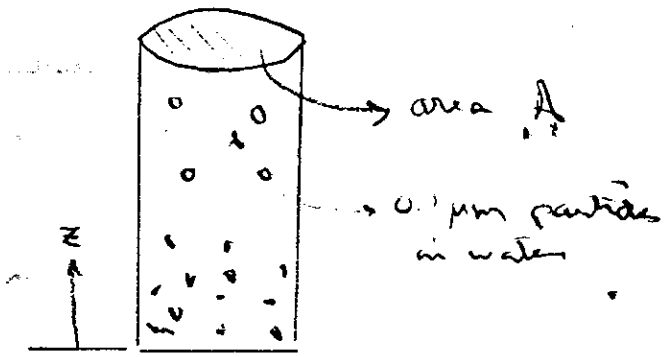
which we call ***Boltzmann's constant.*** In terms of our new variables, (6) becomes:

$$c_i(\underline{x}) = c_0 \exp[-\phi_i(\underline{x})/kT] \qquad (10)$$

which is called ***Boltzmann's equation.***

Sedimentation Equilibrium of a Hydrosol

Now we have the theoretical basis for interpreting the experiments of Perrin. Suppose I disperse colloidal particles in water. Perrin used gamboge.* Say the particles are all 0.1μm in diameter, for example. According to Boltzmann's law, if I wait long enough, the particles will distribute themselves nonuniformly with greater concentration at the bottom of the container than at the top.



The net force on one colloidal particle immersed in water is its weight in air minus the weight of water displaced by it. Assuming the particles have spherical shape and all have the same size, then:

$$f_g = \frac{4}{3}\pi a^3 (\rho_p - \rho_f) g$$

is the net gravitational force felt by any single particle. This is independent of where the particle is located (as long as it's

*A gum resin obtained from a tropical Asian tree used as a yellow pigment.

submerged), so the gravitational potential energy of one particle is just this force times z:

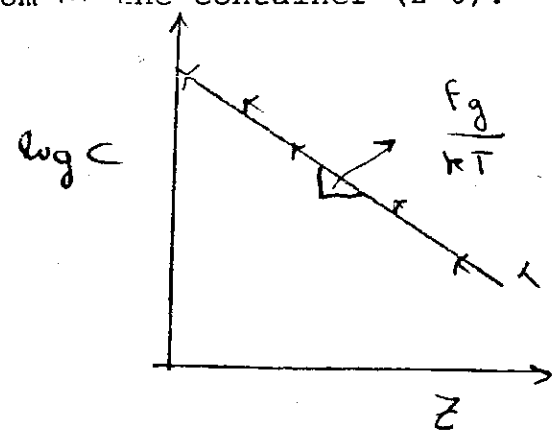
$$\phi = f_g z$$

and Boltzmann's equation requires:

$$c(z) = c_0 \exp(-f_g z/kT)$$

where c_0 is the value of c at the bottom of the container (z=0).

Plotted on semi-log coordinates, this equation is a straight line whose slope is f_g/kT. Perrin measured the concentration profile and determined this quantity for particles of known size and thus known f_g. He could deduce k and so could infer the value of Avogadro's number:



$$N_A = R/k$$

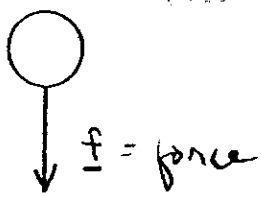
On the other hand, if k is known, then we can deduce f_g and thus the size of the particles.

Rate of Sedimentation

Now let's try to estimate how long it takes to reach this equilibrium state. Does it take seconds? days? years? From Fick's law of diffusion:

$$\{\text{flux due to B.M.}\} = -D\nabla c$$

Now we have a second mechanism for motion. In addition to Brownian motion, a colloidal particle also experiences the force field, e.g., gravity. As a result of this applied force, the particle begins to move. In a viscous fluid like water, the particle will achieve a terminal velocity which is proportional to the force:



$$\underline{v}_p = \underline{f}/B \qquad v_{TZ} = f/\zeta$$

where is called the ***friction coefficient*** of the particle. For small spherical particles of radius a, the mobility is given by ***Stokes law***:

$$B = 6\pi\mu a$$

To get the flux due to migration in the force field, we multiply the terminal velocity of the particles by their concentration at that location:

$$\{\text{flux due to force}\} = (\underline{f}/B)c$$

Adding these two contributions to the flux, we have

$$\underline{J} = -D\nabla c + (\underline{f}/B)c$$

or

$$\underline{J} = -D\nabla c - c(\nabla\phi/B)$$

At equilibrium the flux must vanish everywhere, leaving

$$dc/c = -(1/BD)d\phi$$

Integration gives:

$$c = c_0 \exp(-\phi/BD)$$

where c_0 is the particle concentration at the location where $\phi=0$ (i.e. at the reference state).

Thus result looks a lot like Boltzmann's equation, although the two equations were derived using very different principles. Clearly the concentration profile should be the same, regardless of how we calculate it. Equating the exponents of the two expressions

$$D = kT/B$$

which is called the ***Nernst-Einstein equation.*** For spherical particles, we can substitute for the friction coefficient:

$$D = kT/6\pi\mu a$$

which is called the ***Stokes-Einstein equation.*** Thus the particle size can also be inferred from measurments of the diffusion coefficients of the particles.

Electrostatics

Another powerful technique for studying colloidal dispersions is light scattering. Light is electromagnetic radiation. When light passes through a dielectric material, the atoms of that material feel a rapidly fluctuating electric and magnetic fields. To understand light scattering, you must understand how atoms respond to fluctuating electric fields.