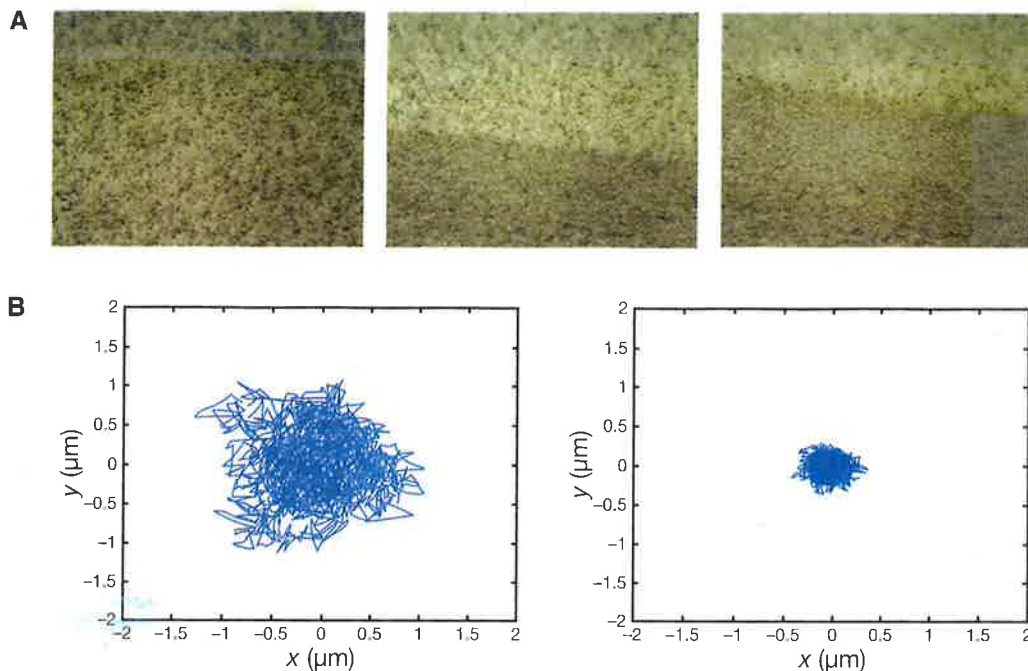


## Lecture 8. Brownian motion. Thermal fluctuations - Diffusion

The building blocks of soft matter are  $\sim 10\text{nm} - 10\mu\text{m}$  in size. These components are "suspended" in a fluid.

At these length scales thermal energy is comparable to energy of interactions between particles, surface interactions, elastic energy, thus thermal fluctuations can drive macroscopic motion that is the result of microscopic stochastic fluctuations. By analyzing brownian motion we can infer macroscopic material properties from microscopic fluctuations.

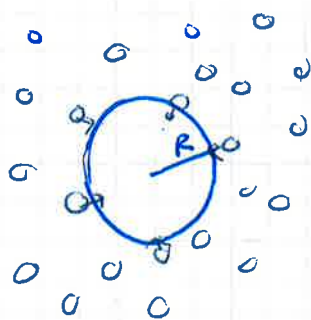


**FIGURE 1** Microscopic view of the process of letting vinegar mix with milk on a microscope slide. (A) Left: Milk only; all the fat globules are wiggling. Middle: A front of vinegar has started moving in from the bottom, leaving behind an area that appears stationary. The top area with milk only is still wiggling. Right: The vinegar has moved almost all the way through and the entire bottom area is stationary.

(B) Left: Motion of an individual fat globule in (A) before the mixture solidifies. The line tracks the center of the fat globule, showing that it wiggles around over a wide area in a random fashion. Right: Motion of a fat globule after the mixture solidifies. The globule still jiggles randomly but is much more strongly confined in space.

From:  
Science and  
Cooking.  
Brenner,  
Sörensen and  
Veitj.

### Longer in equation for Brownian motion



We'll consider the motion of a spherical particle of radius  $R$  and mass  $M$  in a stationary fluid without convection.

We will ignore external forces ~~to~~, e.g. gravity.

The forces this particle experiences are

$\vec{F}_{\text{drag}}$  due to the fluid

$\vec{F}_{\text{collisions}}$  due to random collisions with fluid molecules. Timescale of these collisions is very fast

Since we consider we are in a regime where we have Brownian motion, particle should be small  $\rightarrow M$  is small  $\rightarrow$  no inertia, we are at  $Re \ll 1$ .

We previously saw that for a sphere with radius  $R$  and velocity  $\underline{v}$  the Stokes drag is:

$$\vec{F}_{\text{drag}} = -6\pi\eta R \underline{v}$$

We can thus write the equation of motion for a particle in a fluid with mass  $M$  as:

$$M \frac{dv}{dt} = F_{\text{drag}} + F_{\text{collisions}}$$

↑  
Stokes drag  
 $-6\pi\eta Rv$

↑  
rapidly fluctuating force  
due to molecular collisions



Stochastic force  
due to collisions  
fluctuates rapidly  
averages to zero

$$\Rightarrow \frac{dv}{dt} = -\Gamma v + \frac{F_{\text{collisions}}}{M} \quad \text{where we defined } \Gamma = \frac{6\pi\eta R}{M} \text{ the relaxation rate}$$

If we ignore the stochastic force from the collisions we are left with one equation that describes the relaxation of the velocity due to linear Stokes drag.

$$\frac{dv}{dt} = -\Gamma v \Rightarrow v(t) = v_0 e^{-\Gamma t}$$

where the timescale of relaxation is:

$$\tau = \Gamma^{-1} = \frac{M}{6\pi\eta R} = \frac{4/3\pi R^3 \rho_p}{6\pi\eta \rho_f R} = \frac{2}{9} \frac{R^2}{\nu} \frac{\rho_p}{\rho_f}$$

where  $\rho_p \equiv$  density of particles  
 $\rho_f \equiv$  density of fluid  
 $\nu \equiv$  kinematic viscosity

$\frac{R^2}{\nu}$  sets relaxation rate

We can estimate this relaxation timescale for a  $1 \mu\text{m}$  particle in water:

$$\nu = 1 \times 10^{-6} \frac{\text{m}^2}{\text{s}}$$

$$\tau = \frac{2}{9} \left( \frac{10^{-12}}{10^{-6}} \right) \frac{\rho_p}{\rho_f} \sim 10^{-6} \text{ s}$$

this is many orders of magnitude longer than the timescale on which the particle receives kicks from the fluid molecules

→ it's much too short to ever discuss the relaxation.

With this we can see we have a separation of timescales between relaxation and collision time. This holds also for smaller particles so it's accurate to think of the  $F_{\text{collisions}}$  as 'rapidly fluctuating and averaging to zero'.

The equation we found is known as the Langevin equation, which models Brownian motion:

$$\frac{dv}{dt} = -\Gamma v + L(t)$$

where  $\Gamma = \frac{6\pi\eta R}{M}$  relaxation rate

$L(t)$  fast fluctuating stochastic term  
of average zero:  $\overline{L(t)} = 0$

We take  $F_{\text{collisions}}$  to be Gaussian distributed, moreover since the fluctuations of these forces occur on the timescales of molecular collisions ( $\sim 10^{-12}$  s) we take them to be uncorrelated in time:

$$\langle L(t) L(t') \rangle = 2\gamma \delta(t-t') \quad \text{where } \gamma \text{ is the parameter of force strength}$$

Fluctuating forces  
are uncorrelated in  
time

$\delta(t)$  is delta function.

### Mean square variations of velocity and position: Diffusion

The Langevin equations can be solved by the variation of constants method. We first note that the solution to the homogeneous equation

$$\frac{dv}{dt} + \Gamma v = 0 \text{ is given by: } v(t) = v^* e^{-\Gamma t} \text{ where } v^* \text{ is an integration constant}$$

Now we consider this integration constant to be time dependent and write an ansatz for the original equation:

$v(t) = v^*(t) e^{-\Gamma t}$  and substituting in the Langevin equation we get:

$$\frac{dv^*}{dt} e^{-\Gamma t} + e^{-\Gamma t} (-\Gamma) v^* = -\Gamma (v^* e^{-\Gamma t}) + L(t)$$

$$\Rightarrow \frac{dv^*}{dt} = e^{\Gamma t} L(t) \Rightarrow v^*(t) = \int_0^t e^{\Gamma t'} L(t') dt' ; \text{ Remembering: } v(t) = v^* e^{-\Gamma t}$$

So we have that the solution to the Langevin equation is:

$$v(t) = v_0 e^{-\Gamma t} + \int_0^t e^{-\Gamma(t-t_1)} L(t_1) dt_1$$

From this result we can analyze the mean square fluctuations of the velocity:

$$\langle (\Delta v(t))^2 \rangle = \langle v(t)^2 \rangle - \langle v(t) \rangle^2$$

Now since  $\langle L(t) \rangle = 0$ , stochastic force  $\Rightarrow \langle v(t) \rangle = v_0 e^{-\Gamma t}$

$$\langle v(t)^2 \rangle = (v_0 e^{-\Gamma t})^2 + \left\langle \left( \int_0^t e^{-\Gamma(t-t_1)} L(t_1) dt_1 \right)^2 \right\rangle$$

$$= v_0^2 e^{-2\Gamma t} + \int_0^t dt_1 \int_0^t dt_2 e^{-\Gamma(t-t_1) - \Gamma(t-t_2)} \langle L(t_1) L(t_2) \rangle$$

When squaring  $v(t)$  the cross term vanishes since  $\langle L(t) \rangle = 0$

$$\approx v_0^2 e^{-2\Gamma t} + \int_0^t dt_1 e^{-2\Gamma(t-t_1)} 2\gamma = \frac{\gamma}{\Gamma} (1 - e^{-2\Gamma t}) + v_0^2 e^{-2\Gamma t}$$

$\therefore$  the mean square fluctuations of the velocity are given by:

$$\langle (\Delta v(t))^2 \rangle = \frac{\gamma}{\Gamma} (1 - e^{-2\Gamma t}) \quad \text{mean square velocity fluctuations}$$

At short timescales  $t \ll \Gamma^{-1}$  we can expand  $e^{-2\Gamma t} \sim 1 - 2\Gamma t + \mathcal{O}(t^2)$

$\Rightarrow \langle (\Delta v(t))^2 \rangle \approx 2\gamma t$  velocity fluctuations grow linearly in time

At long timescales  $t \gg \Gamma^{-1}$  we have that  $e^{-2\Gamma t} \rightarrow 0$

$\Rightarrow \langle (\Delta v(t))^2 \rangle \approx \frac{\gamma}{\Gamma}$  there is a stationary velocity distribution.

A similar analysis can be done to calculate the mean square displacement, since the displacement is the time integral of the velocity. here we will just quote the long time result where:

$$\langle (\Delta x(t))^2 \rangle \approx \frac{2\gamma}{\Gamma^2} t \quad \text{for } t \gg \Gamma^{-1}$$

And if we identify  $D = \frac{\gamma}{\Gamma^2}$  we get the familiar equation for the mean squared displacement of a particle undergoing brownian motion:

$$\langle (\Delta x(t))^2 \rangle = 2Dt$$

mean square displacement is proportional to time,

The diffusion coefficient gives the "strength" of the diffusion.

So far our results are quite general and apply to non-thermodynamic systems as well. Intuitively in a thermal system, the strength of the random molecular kicks should increase with temperature.

since the surrounding molecules act as a heat bath for the Brownian particle, the average thermal kinetic energy associated with each velocity component of the Brownian particle is  $\frac{1}{2} k_B T$ :

$$\frac{1}{2} M \langle v^2 \rangle = \frac{1}{2} k_B T$$

If we now take into account that the fluctuating forces in the Langevin equation come from fluid molecules in thermal equilibrium we should require:

$$\frac{1}{2} M \langle v^2(t) \rangle \xrightarrow{t \rightarrow \infty} \frac{1}{2} k_B T$$

mean square velocity fluctuations should approach the proper thermal average value

and we have seen that for  $t \gg \tau^{-1}$

$$\langle (\Delta v(t))^2 \rangle \approx \frac{\gamma}{\Gamma}$$

Combining these 2 results we get that:

$$\gamma = \frac{k_B T}{M} \Gamma$$

noise strength increases linearly with temperature.

Higher  $T \Rightarrow$  higher fluctuating force

substituting this in our expression for the diffusion coefficient we have:

$$D = \frac{k_B T}{M} \frac{\Gamma}{\Gamma^2} = \frac{k_B T}{M \Gamma} \quad \text{and remembering } \Gamma = \frac{6\pi\eta R}{M} \quad \text{we get:}$$

$$D = \frac{k_B T}{6\pi\eta R} \quad \text{Stokes-Einstein equation}$$

Example of a fluctuation-dissipation relation.

in this case fluctuations  $\rightarrow$  diffusion

transport coefficient  $\rightarrow$  viscosity of fluid

Now we can understand the origin of this equation intuitively from the definition of the diffusion coefficient from

$$\langle (\Delta x(t))^2 \rangle = 2Dt \quad \text{we see that } [D] = \frac{l^2}{t}$$

Then the diffusion coefficient for a random walk in 1D has to be:

$$D \approx \frac{l^2}{\tau}, \quad \text{particle moves } l, \text{ every } \tau$$

For a Brownian particle in a fluid the correlation time of the velocity is  $\tau = \Gamma^{-1}$  so the particle changes direction after  $t \sim \tau$ . How far does the particle move before changing direction?

$$l_c^2 \simeq \langle v^2 \tau^2 \rangle = \frac{k_B T}{M} \tau^2$$

So our diffusion coefficient should scale as:

$$D \simeq \left( \frac{l_c^2}{\tau} \right) = \frac{k_B T \tau}{M} = \frac{k_B T}{\Gamma M} = \frac{k_B T}{6\pi\eta r}$$

In this case we get lucky and get the exact answer! This is not always the case but it's always possible to estimate the order of magnitude of the diffusion coefficient from the underlying physics.

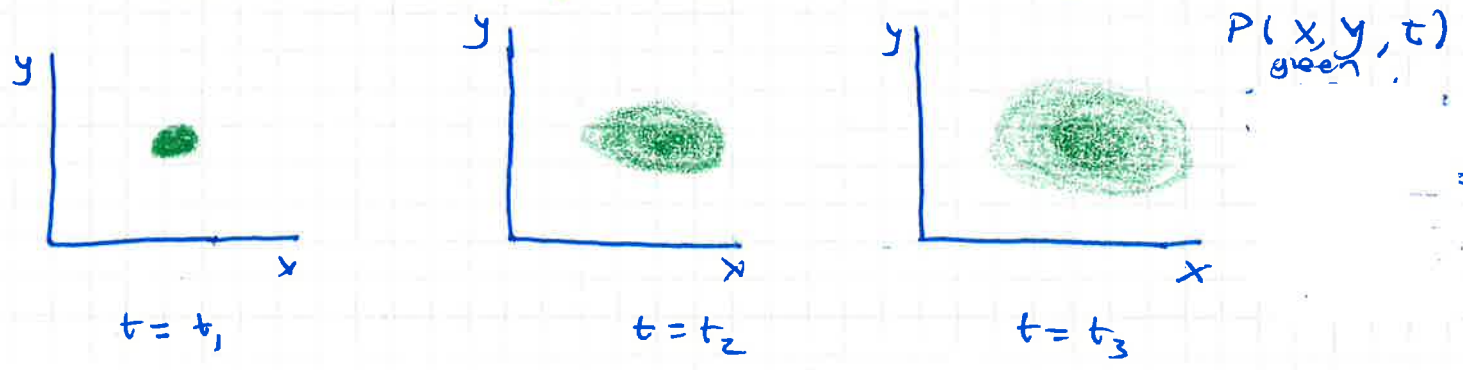
### The Fokker-Planck equation

There is an equivalent description for Brown to the Langevin equation, for Brownian motion, in terms of a Fokker-Planck equation for a probability distribution.

This formulation provides a more natural language to interpret experimental data since it's easy to measure probability distributions.

We will use the probability density  $P(x, t)$  for the process  $x(t)$ . In particle terms  $p(x, t)dx$  for an ensemble of particles gives the probability that any one particle will be found within  $dx$  about  $x$  at time  $t$ .

In this view we can think of  $X$  as a <sup>forming</sup> phase space, i.e. the set of all possible configurations the system can occupy, and  $P$  being the probability of an ensemble of system.



Each point in the phase space corresponds to one possible realization of the system. ~~The set of all~~ <sup>The ensemble of all possible realizations</sup> forms a cloud of points in space and  $p(x, t)$  represents the density of these points, i.e. how densely the ensemble is distributed around each region of  $x$ .

It is possible to show that the Langevin equation with delta correlated noise of strength  $2\gamma$   $\langle L(t)L(t') \rangle = 2\gamma \delta(t-t')$  is equivalent to the F-P equation for the dynamical evolution of  $P$ .

$$\frac{dx}{dt} = a(x) + bL(t) \quad \text{Langevin}$$

$\Leftrightarrow$

$$\frac{\partial P}{\partial t} = - \underbrace{\frac{\partial}{\partial x} [a(x)P]}_{\text{Drift: Deterministic flow}} + \underbrace{\gamma \frac{\partial^2}{\partial x^2} [b^2 P]}_{\text{Diffusion: Random spreading}} \quad \text{Fokker-Planck}$$

Drift: Deterministic flow      Diffusion: Random spreading

We can use this equivalence to find the F-P equation equivalent ~~back~~ to the Langevin equation  $\frac{dv}{dt} = -\Gamma v + L(t)$ . In this case  $v$  plays the role of  $x$ ,  $a(x) = -\Gamma v$  and  $b = 1$ . So:

$$\frac{\partial P(v, t)}{\partial t} = \frac{\partial}{\partial v} \left( \Gamma v + \gamma \frac{\partial}{\partial v} \right) P(v, t)$$

The Fokker-Planck equation for the position of a Brownian particle in an external potential. For studying diffusion the probability density  $P(v, t)$  is not so relevant since we're often more interested in the effects of diffusion in position space.

From our original Langevin equation we have:

$$\frac{dv}{dt} = -\Gamma v + L(t) \quad \text{if we coarse grain over times much larger than } \tau = \Gamma^{-1}$$

we can ignore the ~~local~~ fluctuations, describe diffusion of the ~~traces~~ by a simplified Langevin equation.

Since the relaxation ~~rate~~ rate  $\Gamma = \frac{6\pi\eta R}{M}$  is large for small particles we can ignore the derivative term and get:

$$\Gamma v = L(t) \Rightarrow \frac{dx}{dt} = \Gamma^{-1} L(t)$$

From this Langevin equation we can write a F-P equation for  $P(x, t)$ . Using our equivalence formula we get:

$$\frac{\partial P(x, t)}{\partial t} = \frac{\partial}{\partial x} \left( \frac{U'}{\Gamma M} P(x, t) \right) + D \frac{\partial^2 P(x, t)}{\partial x^2}$$

Fokker-Planck equation describing the diffuse spread and drift of a probability density  $P(x, t)$  under the influence of a potential  $U$  and random noise forces.

where the presence of a potential  $U$  translates into  $a(x) = \frac{-U'}{\Gamma M}$ , while  $b = \Gamma^{-1}$  and we also made use of  $\frac{\gamma}{\Gamma^2} = D$ .

We can check for self-consistency by noting that the thermal equilibrium distribution should be a stationary solution of the F-P equation for  $P(x, t)$ :

Indeed substituting  $P_{eq}(x) \sim e^{-U(x)/k_B T}$  in the F-P equation yields:

$$\left( \frac{U'}{\Gamma M} + D \frac{\partial}{\partial x} \right) e^{-U/k_B T} = 0 \quad \Leftrightarrow \quad D = \frac{k_B T}{\Gamma M} = \frac{k_B T}{6\pi\eta R}$$

We recover the Stokes-Einstein equation.

$$\Rightarrow \frac{\gamma}{\Gamma M} e^{-U/k_B T} = -D e^{-U/k_B T} \left( \frac{-U'}{k_B T} \right)$$

In the absence of a potential the F-P equation for  $P(x, t)$  reduces to the diffusion equation:

$$\frac{\partial P(x, t)}{\partial t} = D \frac{\partial^2 P(x, t)}{\partial x^2}$$

If we assume that at  $t=0$  the particle is at  $x=0 \Rightarrow P(x, t=0) = \delta(x)$ . The solution with this initial condition is:

$$P(x, t) = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt}$$

(remember: for a gaussian w/ zero mean and variance  $\sigma^2$ )

$$P(x, t) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-x^2/2\sigma^2}$$

and  $\langle x^2 \rangle = \sigma^2$

From the exponent we can see that diffusion spreading spreads with a width growing as  $\sqrt{t}$

Since the solution reduces to the delta function initial condition as  $t \rightarrow 0$ , we can write the solution of the diffusion eq. for any general initial distribution  $P(X, t=0) = P_0(X)$  as:

$$P(X, t) = \int_{-\infty}^{\infty} dx_1 \frac{1}{\sqrt{4\pi Dt}} e^{-|X-x_1|^2/4Dt} P_0(X_1)$$

This expression illustrates that if the initial distribution is non-zero in the localized region centered around  $X_0$ , at long times the probability distribution approaches a gaussian centered around  $X_0$ . This expression also implies that equation (\*) is the Green's function for the diffusion equation.

### Effect of particle size on diffusion and dispersion of Brownian particles

We can now return to thinking about our ~~particle~~ Brownian particle of radius  $R$  in a fluid and explore the implications of its size on diffusion and dispersion.



First we can look at the time it'd take diffusion to move a Brownian particle by twice its radius (i.e. displace it by one particle length).

$$\langle \Delta x^2 \rangle = 2Dt = \frac{2k_B T}{6\pi\eta R} t \quad \text{we want } \langle \Delta x^2 \rangle = (2R)^2$$

$$\Rightarrow 4R^2 = \frac{2k_B T}{6\pi\eta R} t \quad \Rightarrow t = \frac{(2)(6\pi\eta R^3)}{k_B T} \quad \begin{array}{l} \text{at room temperature } k_B T \approx 4 \times 10^{-21} \text{ J} \\ \text{for water } 6\pi\eta \approx 2 \times 10^{-2} \text{ kg/ms} \end{array}$$

$$\Rightarrow t = \frac{(2)(2 \times 10^{-2})}{4 \times 10^{-21}} R^3 = 10^{19} R^3 \text{ (s/m}^3\text{)} \\ = 10 R^3 \text{ (s/}\mu\text{m}^3\text{)} \quad \text{time scales as } R^3.$$

If  $R = 1 \mu\text{m}$   $t = 10\text{s}$  which is a reasonable time for observation in a microscope.  
for larger particles we'd wait a looong time  
for particles 10 times smaller, they'd diffuse their length in  $\sim 10\text{ms}$  too fast.

Having particles  $\sim 1 \mu\text{m}$  in size allows us to observe their dynamics.

For a Brownian particle in the presence of gravity, the gravitational potential is:

$$U = M_{\text{eff}} g h \quad \text{where } M_{\text{eff}} \text{ is the effective mass due to buoyancy (Remember Archimedes principle)} \\ h \text{ is the height}$$

The equilibrium distribution gives the usual exponential law:

$$P_{\text{eq}} \sim e^{-M_{\text{eff}} g h / k_B T}$$

Similarly for what we did with diffusion we will determine the particle radius  $R$ , at which thermal fluctuations lift the particle by a distance in the order of its radius.

In other words we need to find the value of  $R$  for which the exponent is  $\sim 1$  for  $h=R$

(Choosing the exponent  $\sim 1$  means  $P(h) \sim e^{-1} \sim 0.37$ , so particle has a reasonable probability of being there)

Now  $M_{\text{eff}} = V \Delta \rho = \frac{4}{3} \pi R^3 \Delta \rho$  where  $\Delta \rho$  is the difference in density between fluid and particle.

So the condition for the exponent being  $\sim 1$ :

$$\frac{-M_{\text{eff}} g h}{k_B T} \sim 1 \Rightarrow \frac{\frac{4}{3} \pi R^3 \Delta \rho g R}{k_B T} \sim 1 \Rightarrow R \sim \left( \frac{3 k_B T}{4 \pi \Delta \rho g} \right)^{1/4}$$

considering  $k_B T \approx 4 \times 10^{-21} \text{ J}$

$$g = 10 \text{ m/s}^2$$

$\Delta \rho = 50 \text{ kg/m}^3$  (e.g. polystyrene particles  $\rho_p = 1050 \text{ kg/m}^3$   
in water  $\rho_w = 1000 \text{ kg/m}^3$ )

We get:

$$R \sim \left[ \frac{3 (4 \times 10^{-21})}{4 \pi (50) (10)} \right]^{1/4} \approx \left( \frac{10^{-21}}{5 \times 10^2} \right)^{1/4} \approx 10^{-24/4} \text{ m} \approx 1 \mu\text{m}$$

Because of the rapid crossover due to  $e^{-4}$  ~~settling timescale~~ for particles larger than  $\sim 1 \mu\text{m}$  thermal fluctuations are unable to lift them appreciably, so they settle. On the other hand smaller particles will be strongly affected by thermal fluctuations & much less so by gravity so they disperse through the container.

For both diffusion and dispersion the crossover lengthscale is  $\sim 1 \mu\text{m}$ .

A micron is about the ~~pro~~ crossover lengthscale distinguishing:

Granular media  
(particles not affected  
by Brownian motion)  
e.g. piles of sand,  
avalanches.

and

Dispersions  
(particles that can be  
viewed as a statistical-physical  
system. (Affected by  
Brownian motion)  
e.g. colloidal systems