Physics 850: Soft Condensed Matter Physics, Fall04
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Lecture 7: Dynamics of individual particles in solvent – the Langevin Equation

Dynamics of particle motion: Langevin eqn

Equilibrium configurations of energies are correctly described using stat mech with no mention of the motion of solvent (e.g. H_2O) molecules. Dynamics of fluctuations or response to external forces requires something more...

\[ \frac{m \, dv}{dt} = -b \, v + \vec{f}(t) \]  (+ external force)

- viscous drag, with solvent molecules
- rapid fluctuations (collisions)
- from averaged response of solvent (flow)

Example

Spherical particle, radius \( R \), mass \( m \)

\[ b = 6 \pi \eta R \]  (friction coefficient)

not \( R^2 \)

Viscosity represents dissipation.

Units: Pa·s or dyne·cm⁻²·s

* for a “Newtonian” fluid (e.g. simple liquid), \( \eta \) = constant

For “non-Newtonian” fluid (e.g. polymer solution), \( \eta \) depends on shear rate and may differ for shear and extensional flow
What is viscosity of a simple liquid? (from Witten's Structured Fluids)

Upon being sheared, a liquid's structure changes:

\[ \text{shear} \]

\[ \text{e.g. now too close together along } \rightarrow \text{direction} \]

Time scale for fluid response (assume T is well above glass transition, T_c)

\[ t^* \approx \frac{a}{\sqrt{\nu_a^2}} \approx \text{typical time for molecule to move its own distance} \]

\[ \frac{k_B T}{m} \approx 4 \times 10^{-4} \text{ Nm} \]

Note: \( k_B T = 4 \sigma N \cdot \text{mm} \) at room temp

\[ v_a = \frac{24 \times 10^{-3} \text{ m/yr}}{6 \times 10^{-10}} \]

\[ = \frac{15 \times 10^{-11}}{2 \times 10^{-13}} \approx 10^{-12} \text{ s} \]

* Energy scale: modulus \( \frac{\text{energy}}{\text{volume}} 
- \text{energy must be } \approx k_B T \text{ for liquid if it's } \gg k_B T \text{ - solid if it's } \ll k_B T \text{ - gas} 

\[ \text{so modulus } \approx \frac{k_B T}{a^2} = \frac{4 \times 10^{-4} \text{ Nm}}{(2 \times 10^{-10})^3 \text{ m}^3} = 5 \times 10^8 \text{ Nm}^{-2} \]  

\[ \eta [\text{Pa} \cdot \text{s}] = 5 \times 10^8 \text{ Nm}^{-2} \cdot 10^{-5} = 10^{-3} \text{ Pa} \cdot \text{s} \text{ (order of magnitude estimate only!)} \]

Result: this is the value for H_2O.
Shear viscosity and surface tension (w/vacuum) of various Liquids at 20°C
(http://www.science.uwaterloo.ca/~cchieh/cact/c123/liquid.html)

<table>
<thead>
<tr>
<th>Common liquid</th>
<th>Viscosity /cP</th>
<th>Surface tension /N m⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethyl ether</td>
<td>0.233</td>
<td>0.0728</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.58</td>
<td>0.0271</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.652</td>
<td>0.0289</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>0.969</td>
<td>0.0270</td>
</tr>
<tr>
<td>Water</td>
<td>1.002</td>
<td>0.0728</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.200</td>
<td>0.0228</td>
</tr>
<tr>
<td>Mercury</td>
<td>1.554</td>
<td>0.436</td>
</tr>
<tr>
<td>Olive oil</td>
<td>84</td>
<td>-</td>
</tr>
<tr>
<td>Castor oil</td>
<td>986</td>
<td>-</td>
</tr>
<tr>
<td>Glycerol</td>
<td>1490</td>
<td>0.0634</td>
</tr>
<tr>
<td>Glasses</td>
<td>very large</td>
<td>(&gt;10¹³)</td>
</tr>
<tr>
<td>Gallium</td>
<td>1.9</td>
<td>(at 53°C, ~ 20° above m.p.) (from CRC Handbook)</td>
</tr>
<tr>
<td>H₂ gas</td>
<td>0.009</td>
<td>(at 1 atmo pressure, from CRC)</td>
</tr>
</tbody>
</table>

Poise, P = cgs unit (dyne•s/cm²)
1 cP (centi-Poise) = 0.01 P
1 mPa•s = 1 cP

Witten’s argument does not apply because 20°C is the m.p., so energy scale can be >> k_B T. (glycerol does not actually freeze at this T, but that is a kinetic matter)

Approx. exponential change (note log scale)
Working with the Langevin equation:
(see e.g. Pathria § 13.4)

\[ m \frac{d \mathbf{v}}{dt} = -b \mathbf{v} + \mathbf{f}(t) \]

\[ \text{faster than } 10^{-12} \text{ because collisions very rapidly fluctuate} \]
\[ \text{very rapidly fluctuating = not correlated} \]
\[ \text{(it's often assumed } \mathbf{f}(t) \mathbf{f}(t+a) \propto \delta(t)) \]

This fluctuates because of \( \mathbf{f} \)

Ensemble - average of \( \mathbf{v} \)

\[ m \langle \frac{d \mathbf{v}}{dt} \rangle = -b \langle \mathbf{v} \rangle + \langle \mathbf{f}(t) \rangle \]

\[ \rightarrow \text{ Solution: } \langle \mathbf{v}(t) \rangle = \mathbf{v}(0) e^{\frac{-t}{\tau}} \]

\[ \tau = \frac{m}{b} = \text{viscous relaxation time} \]

Example:

a) 1-mm sphere in water
\[ \tau = \frac{\frac{4}{3} \pi (10^{-3})^3 \times 10^{-14} \times 10^3}{6 \pi \eta 10^{-6} \times 10^{-9}} \approx 10^7 \]

b) Spherical submarine, \( R = 1 \text{m} \)
\[ \tau \propto \frac{R^3}{a^2} = \frac{R^2}{a} \rightarrow \tau \approx 10^5 \]

Temporal correlation of \( \mathbf{v} \):

\[ \langle \mathbf{v}(t), \mathbf{v}(t+t') \rangle \text{ = function of } t \equiv C_v(t) \]

Use the above result: \( \langle \mathbf{v}(t), \mathbf{v}(t+t') \rangle = \mathbf{v}(t) e^{\frac{-t}{\tau}} \)

\[ C_v(t) = \langle \mathbf{v}(t)^2 e^{-t/\tau} \rangle \]

\[ C_v(t) = \frac{3 k_B T}{m} \quad \text{e}^{-t/\tau} \]

A particle forgets its velocity over a time of \( \tau \)

(\( \rightarrow \) proper accounting for heat dissipation gives \( \mathbf{C}_v \mathbf{e}^{-t/\tau} \), but the \( t^{-3} \) at longer time. Has no effect on motion for \( t \gg \tau \), which is our focus)
Response to external forces: Terminal vel.

\[ \frac{dV}{dt} = -bv + F_0 \]

\[ \langle V(t) \rangle = \frac{F_0}{b} (1 - e^{-bt}) \quad \text{if } V(0) = 0 \]

[Graph showing terminal velocity]

Terminal velocity \( \frac{F_0}{b} \) is reached when \( t \geq \frac{1}{b} \).

Example: Sedimentation of latex spheres in water

- Sphere radius \( R \), density \( \rho \), viscosity \( \eta \), particle mass \( m_\text{particle} \), and density \( \rho_\text{water} \)
- Initial particle mass \( m_\text{particle} \), volume \( V_\text{particle} \)

\[ F_0 = g (m_\text{particle} - m_\text{water}) = g \cdot \frac{4}{3} \pi R^3 \Delta \rho \quad \Delta \rho = 0.05 \]

\[ U_\text{sed} = g \cdot \frac{4}{3} \pi R^3 \Delta \rho = \frac{2 \cdot g \cdot \Delta \rho \cdot R^2}{6 \pi \eta R} \]

\[ U_\text{sed} \approx 0.1 \text{ mm/s} \]

\[ \text{Does the sphere sit on the bottom? No - Brownian motion keeps it suspended over a height.} \]

\[ \text{Known as 'gravitational length', } l_g \]

\[ (m_\text{particle} - m_\text{water}) g l_g = k_B T \rightarrow l_g \approx 8 \text{ mm} \]
Mean-square displacement from Langevin eqn.

\[ \langle \mathbf{r}, \frac{d\mathbf{v}}{dt} \rangle = -\frac{1}{m} \langle \mathbf{v}, \frac{d\mathbf{v}}{dt} \rangle + \frac{\mathbf{f}_T}{m} \]

\[ = 0 \quad \text{because } \frac{d\mathbf{v}}{dt} \text{ not correlated.} \]

\[ \frac{d}{dt} \langle r^2 \rangle = -\frac{b}{2m} \frac{d}{dt} \langle r^2 \rangle \]

So

\[ \frac{1}{2} \frac{d^2}{dt^2} \langle r^2 \rangle - \langle v^2 \rangle = -\frac{b}{2m} \frac{d}{dt} \langle r^2 \rangle \]

or

\[ \frac{d^2}{dt^2} \langle r^2 \rangle + \frac{1}{\tau} \frac{d}{dt} \langle r^2 \rangle = 2 \langle v^2 \rangle \]

Solution, with \( \frac{d}{dt} \langle r^2 \rangle \bigg|_{v_0} = 0 \)

\[ \langle r^2(t) \rangle - \langle r^2(0) \rangle = 6kT \frac{T}{m} \left[ t - \tau (1 - e^{-\frac{t}{\tau}}) \right] \]

Limits: \( \frac{t}{\tau} \ll 1 \) then

\[ \langle r^2(t) - r^2(0) \rangle = 6kT \frac{T}{m} \frac{t}{\tau} \]

\( \frac{t}{\tau} \gg 1 \) \( \Rightarrow \) \[ \langle r^2(t) - r^2(0) \rangle = \frac{6kT}{b} t \]

\[ \mathbf{Ballistic \ motion} \]

\[ \mathbf{Diffusive \ motion}; \text{ mean square displacement}, \quad \langle r^2(t) \rangle = 6D t \]

\[ D = \frac{k_BT}{b} \]
Measuring Diffusion using Video Microscopy

Small offset here from centroid measurement resolution,
\[ \delta \sim (0.015 \, \mu m)^2. \]

Data for an isolated sphere,
\[ R = 0.498 \, \mu m \]

Slope = \( 4D \) (in two dimensions) \( \rightarrow D = 0.46 \pm 0.01 \, \mu m^2/s, \)
in agreement with Stokes-Einstein value.

<< Rayleigh limit! 0.001 \, \mu m precision in center of mass of a particle of known shape is feasible
Fluctuation-Dissipation Theorem

\[ \langle r^2(t) \rangle = 6D t, \text{ where } D = \frac{k_B T}{b} \]

A general result: dissipation leads to fluctuation. But larger dissipation \( \Rightarrow \) smaller fluct.

In more detail:

\[ \frac{6k_B T}{b} = \int_{-\infty}^{\infty} \vec{V}(t) \cdot \vec{v}(t) \, dt \]

Another example:

\[ \frac{6k_B T}{R} = \int_{-\infty}^{\infty} \langle I(t) \cdot I(t) \rangle \, dt \]

Kubo's theorem

resistance (dissipation)

current (fluctuations)

electronic

\( b \rightarrow R \)

\( m \rightarrow L \)

\( r \rightarrow Q \)

\( f \rightarrow V \text{ (voltage)} \)

\( V \rightarrow I \)