

Soft Condensed Matter

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Abstract

Abstract of this course

1 Element of fluid dynamics

This section devotes itself to the basics of fluid dynamics,

1.1 Fluid Dynamics equations

1.1.1 Mass flux and continuity equation

1. Rate of change in mass in volume integral of change in density.
2. Conservation of mass states that the rate of change is equal to the net flux of mass flowing, followed by a divergence theorem to change the surface integral to a volume integral.
3. Combining the rate of change in mass and conservation of mass, as both are volume integral:

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v})$$

4. For incompressible fluid, ρ is constant, and the continuity equation simplify to $\nabla \cdot \mathbf{v} = 0$.

1.1.2 Momentum Flux and the equation of motion

1. Rate of change in total momentum $P_i(V, t)$

$$\frac{\partial P_i(V, t)}{\partial t} = \frac{\partial}{\partial t} \int_V d^3r \rho v_i = \int_V \left(\frac{\partial}{\partial t} \rho \right) v_i + \rho \frac{\partial}{\partial t} v_i$$

2. The change in momentum is the sum of the forces, which take into account 4 contributions, **Convention of momentum, Pressure Forces, Viscous Forces, Body Forces**.
3. Overall stress tensor

$$\sigma_{ij} = \sigma'_{ij} - p\delta_{ij}$$

where the two items are contributions for viscous pressure and pressure forces

- 4.

1.2 Navier-Stokes equation

1. The complete Navier-Stokes equation

$$\rho[\partial_t \mathbf{v} + (\mathbf{v} \cdot \nabla) \mathbf{v}] = -\nabla p + \eta \nabla^2 \mathbf{v} + \rho \mathbf{g}$$

2. Left-hand side relates to inertial force densities
3. Right-hand side encompasses intrinsic viscosity and applied force densities (pressure gradient and gravity)
4. Conservative external forces, including gravity, the external force term is absorbed into the pressure term.

1.3 Material Derivative

1. Concept of streamline
2. Lagrangian rate of

$$\frac{Df}{Dt} = \frac{\partial f}{\partial t} = (\mathbf{v} \cdot \nabla)f$$

3. In particular, the acceleration of fluid elements is:

$$\frac{D\mathbf{v}}{Dt} = \frac{\partial \mathbf{v}}{\partial t} = (\mathbf{v} \cdot \nabla)\mathbf{v}$$

- 4.

1.4 Reynold Number and Stokes Flow

When discussing fluids of limited of low flow velocities, or small sizes. Reynolds number is inversely proportional to the viscosity.

1. Reynold number

$$Re = \frac{\rho v_0 L_0}{\eta}$$

Take note that Reynold's number is inversely proportional to viscosity.

2. Low Reynolds number $Re \ll 1$, the viscous term dominates over inertia, non-linear Navier-Stokes equation is reduced to the linear Stokes equation:

$$0 = -\nabla p + \eta \nabla^2 \mathbf{v}$$

3. If an external force is applied, for instance, an oscillating boundary, the time derivative is given by the external force and is not negligible, which gives time-dependent Navier Stokes Equation

$$\rho \partial_t \mathbf{v} = -\nabla p + \eta \nabla^2 \mathbf{v}$$

1.5 Properties of Stokes flow and locomotion of microorganism and nanomachines

1. Since time doesn't enter explicitly the Stokes equation, and it is linear, the flow pattern is unchanged when the pressure is increased, only the flow velocity is changed.
2. If reverse spacial direction, the pressure gradient changes sign while the Laplacian keeps its sign, the flow velocity changes sign, therefore Stoke equation is unchanged under reversal of spatial coordinates.
3. Kinetic reversibility properties of Stokes flow implies that a microorganism attempts

4. This observation has interesting consequences for locomotion on small scales as is applicable to microorganisms or artificial nanomachines. Indeed, the kinematic reversibility property of Stokes flows implies that a microorganism that attempts to swim through a reversible sequence of changes of shape, returning to its original shape by going through the sequence in reverse, will not translate, since any motion that it undergoes in the first half of the cycle will be reversed in the second part of the swimming cycle. This is known as the Scallop theorem (originally by Edward Purcell). A scallop swims to a good approximation by opening and closing a single hinge. At low Reynolds numbers, the forward movement upon opening would be exactly canceled by the motion during the reverse stroke and thus the scallop would remain stationary. A real scallop is able to avoid this problem by closing the hinge very rapidly, escaping the low Reynolds number regime. This is made possible by its size such an escape becomes increasingly difficult for smaller-scale objects such as microorganisms and artificial nanorobots.

5. Different strategies to break time-reversal symmetry to the operator with a circular motion using rotary molecular motors. Example like E.coli

1.6 Vorticity

1.7 Fluid in mechanical equilibrium

1. Viscous Fluid in mechanical equilibrium has to be at rest, $\mathbf{v} = 0$ relative to containing.
2. Navier-Stokes equation reduce to:

$$0 = -\nabla p - \rho g \mathbf{e}_z$$

3. Incompressible fluid, integrate this equation to yield:

$$p(z) = p^* - \rho g z$$

where p^* is constant of integration, which represents the pressure at $z = 0$ and the z dependent contribution to the pressure is given as the hydrostatic pressure:

$$p_{hs} = -\rho g z$$

We can therefore regroup the effects of gravity into the pressure term and write the total pressure as:

$$p_{tot} = p + p_{hs}$$

4.

1.8 Couette Flow

Couette flow is a flow induced in a liquid through the movement of one or more walls. No pressure gradient. **Example: Planar geometry**

Bottom plate at $z = 0$ and top plate $z = h$, the liquid is moving with speed v_0 while stationary at the bottom. Use Stokes equations, together with boundary condition

$$\eta \partial_z^2 v_x(z) = 0$$

Use viscous stress tensor σ' to determine the horizontal force where $F_z = \sigma'_{xz} A = \eta \frac{v_0 A}{h}$

1.9 Oscillatory flow

1. The equation for the motion for the flow field is given by the time-dependent Stokes equation
2. Wave solution:

$$v_x = v_0 e^{i\omega t} e^{(-1+i)z/\sigma}$$

where the parameter σ gives the decay length of the wave in the fluid.

3. Force per area is given by:

$$FA = \eta \partial_z v_x(z=0) = (-1+i) \frac{\eta v}{\sigma}$$

1.10 Diffusion of momentum

1. Equation of flow field is a diffusion equation for the transverse flow with a diffusion coefficient equal to $\eta/\rho = \nu$, the kinetic viscosity.
2. Transverse momentum diffuses in the z -direction away from its source at the moving plate.

1.11 Stokes drag force

Consider A spherical body of radius a moving with a velocity \mathbf{v} through a fluid with is overall stationary. It creates a temporary disturbance in the flow field which disappears after body passes a fixed observation point. The drag force that the sphere experiences due to the motion of the underlying fluid is $\mathbf{F} = 6\pi\eta a\mathbf{v}$

1.11.1 Scaling argument

In the low Reynolds number regime, assuming stationary flow and neglecting the pressure gradient term, we have the Navier Stokes equation:

$$\nabla^2 v_T = 0$$

1.11.2 Full analysis

**No examinable

1.12 Hydrodynamic interaction between colloidal particles

As a consequence of the moving colloid. The flow velocity at a distance r decays as $1/r$. Through this velocity field, one colloid can exert drag force on another. Such hydrodynamic interaction is **long ranged and decay slowly as the inverse of the particle separation**. This interaction can be expressed by extending Stokes's relation to multiple particle:

$$\mathbf{v} = H\mathbf{F}$$

Here H is the mobility matrix

1.13 Poiseuille flow

Pressure driven steady states flow through small channels. (Recall that both Couette flow consider system in absence of pressure) **Example: Parallel Plate Channel**

Fluid flows in x-direction, symmetry in both y and z direction:

$$\partial_z^2 v_x(z) = -\frac{\Delta p}{\eta L}$$

Given B.C. At $z = 0$ and h

$$\begin{aligned} v_x(z = 0) &= 0 \\ v_x(z = h) &= 0 \end{aligned}$$

Solution is a parabolic

$$v_x(z) = \frac{\Delta p}{2\eta L}(h - z)z$$

Overall flow is characterized by the volumetric flow rate, Q

$$Q = \int_c dy dz v_x(y, z)$$

The flow rate through a section of width x , meaning

$$Q = \int_0^\omega dy \int_0^h dz \frac{\Delta p}{2\eta L}(h - z)z = \frac{h^3\omega}{12\eta L}\Delta p$$

Example: Channel with circular cross-section

$$(x, y, z) = (x, r \cos(\psi), r \sin(\psi))$$

$$\vec{e}_x = \vec{e}_x$$

$$\vec{e}_r = \cos \psi \vec{e}_y + \sin \psi \vec{e}_z$$

$$\vec{e}_\psi = -\sin \psi \vec{e}_y + \cos \psi \vec{e}_z$$

Volumetric flow rate:

$$Q = \int_0^{2\pi} d\psi \int_0^a dr r \frac{\Delta p}{4\eta L} (a^2 - r^2) = \frac{\pi a^4}{8\eta L} \Delta p$$

1.13.1 Hydraulic resistance and Compliance

Definition Hydraulic resistance:

$$\Delta p = R_{hydr} Q$$

The flow rate, Q in a straight channel at a steady state is proportional to the pressure difference at its ends Δp . This relationship holds for any channel geometry and is known as the Hagen-Poiseuille law. Compare Fluid to Circuits,

Summary		
	Ohm's Law	Hagen-Poiseuille's Law
Current	Electric current I	Volumetric flow rate Q
Transported quantity	Charge q	Fluid volume ν
Driving force	Potential Difference ΔV	Pressure difference Δp
Resistance	Electric resistance	Hydraulic resistance $R_{hydr} = \frac{\Delta p}{Q}$
Capacitance	$C = \frac{dq}{dv}$	Hydraulic Capacitance $C_{hydr} = \frac{d\nu}{dp}$

2 Viscoelasticity**2.1 Basic Concept of Elasticity****2.1.1 Strain**

1. Definition of strain tensor

$$\epsilon_{ik} = \frac{1}{2}(\partial_k u_i + \partial_i u_k)$$

Strain tensor is symmetric and diagonalisable

2.1.2 Stress

1. Stress is defined as force $d\mathbf{f}$ per unit area dS transmitted across the surface element dS :

$$dF_i = \sigma_{ik} dS_k$$

2. For example, σ_{xy} is the force per unit area in the x direction transmitted across the plane into the normal vector in the y -direction.

2.2 Linear elasticity and Hooke's Law

2.2.1 Hooke's Law

1. For small strains, there is a linear relationship between stress and strain as stated in the Hooke's law.

$$\sigma_{ij} = C_{ijkl}\epsilon_{kl}$$

where C_{ijkl} is the stiffness tensor.

2. Stiffness tensor has element, given that it is symmetric, it has 21 independent elements, of which 3 are related to the orientation of body in space. Therefore, 18 independent tensor element need to be considered.
3. Consider an **isotropic linear** elastic medium. For such material, all directions be have the same way and no specific internal directions; as such the **The right handside of the equation can only have elements proportional to the strain tensor itself, or the only scalar combination $\sum_k \epsilon_{kk}$ of the matrix element of the strain tensor, as any other combination of matrix elements of the strain tensor would not result in behavior which is identical in all spatial directions**

2.2.2 Poisson's ratio

1. When a stress σ_{xx} is applied for instance , along x axis, it stretches along this direction by strain ϵ_{xx} . Stress and strains are linearly proportional:

$$\sigma_{xx} = E\epsilon_{xx}$$

where E is the Young's modulus, which has unit of **pressure**.

2. Material also contract in the other directions, $\epsilon_{yy} = \epsilon_{zz} < 0$. We define Poisson's ration as:

$$\nu = -\frac{\epsilon_{yy}}{\epsilon_{zz}}$$

3. The resultant strain tensor is:
$$\begin{pmatrix} \epsilon_{xx} & 0 & 0 \\ 0 & -\nu\epsilon_{xx} & 0 \\ 0 & 0 & -\nu\epsilon_{xx} \end{pmatrix}$$

4. and strains due to σ_{xx} is given as:

$$E\epsilon_{xx} = \sigma_{xx} \tag{1}$$

$$E\epsilon_{yy} = -\nu\sigma_{xx} \tag{2}$$

$$E\epsilon_{zz} = -\nu\sigma_{xx} \tag{3}$$

5. Moreover, the linear system can be solved for σ_{ii} :

$$\sigma_{xx} = \frac{E}{(1+\nu)(1-2\nu)}[(1-\nu)\epsilon_{xx} + \nu\epsilon_{yy} + \nu\epsilon_{zz}]$$

2.2.3 Bulk Modulus

1. Bulk modulus measures the contraction of body under isotropic pressure:

$$-p = \sigma_{xx} + \sigma_{yy} + \sigma_{zz}$$

2. Bulk Modulus is defined as:

$$p = -B\frac{\Delta V}{V}$$

where $\frac{\Delta V}{V} = \text{Tr}\{\epsilon\} = -3p(1-2\nu)/E$

3. we get:

$$B = \frac{E}{3(1-2\nu)}$$

2.2.4 Shear deformation

2.2.5 Physical Constrains

1. Bulk Modulus cannot be negative, otherwise would expand
2. This also means that $\nu < 1/2$.
3. For a perfectly incompressible material, $\nu = 0$
4. While most materials have $\nu > 0$, there are materials that have negative ν
5. Shear Modulus G and Young's Modulus E are positive

2.3 Viscoelasticity

Newtonian liquids Do not have shear modulus but resist flow through their viscosity, which is assumed to be constant and independent of the flow rate.

Hookean Solids Respond immediately to a stress and change their shape and do not dissipate energy

2.4 Linear viscoelastic materials and experiments

Linear means that a system whose response is linearly proportional to the applied stresses. **shear modulus independent of strain.**

Creep experiment Stress σ_0 is applied, response strain ϵ is measured.

Stress relaxation experiment Rapid strain ϵ_0 is applied and maintained, and the decay of stress $\sigma(t)$ is measured. Decay is governed by relaxation modulus $G(t)$, with $\sigma(t) = G(t)\epsilon_0$

2.5 Time translation invariance

In this section, we add incremental stresses accumulated as a function of history of material and see how is strain σ behaves.

1. Each of these strain increment will trigger time-dependent increment in stress $d\sigma(t) = G(t - t')d\epsilon(t')$ Overall stress is linear superposition of all the contribution of $d\sigma(t)$:

$$\sigma(t) = \int d\sigma(t) = \int G(t - t')d\epsilon(t') = \int_{-\infty}^t G(t - t') \frac{d\epsilon(t')}{dt'} dt'$$

This is a 'retarded' linear response.

2. In the case of complex viscoelastic fluids, we have constant shear rate $\dot{\epsilon}$, therefore:

$$\sigma(t) = \dot{\epsilon} \int_{-\infty}^t G(t - t') dt' = \int_0^{\infty} G(\tau) d\tau$$

From here we get viscosity

$$\eta = \int_0^{\infty} G(\tau) d\tau$$

2.6 Complex modulus

In this section ,we consider response of a stress in response to an applied oscillating strain:

$$\epsilon(t) = \epsilon_0 e^{i\omega t}$$

1. Substitute this into previous expression for σ .
2. We have:

$$\sigma(t) = G^*(\omega)\epsilon_0 e^{i\omega t}$$

where

$$G^*(\omega) = i\omega \int_0^\infty G(\tau) e^{-i\omega\tau} d\tau$$

3. Ideal solid $G(\tau) = G_0$ and $G^*(\omega) = G_0$
4. Newtonian fluid $G(\tau) = \delta(\tau)\eta$ and $G^*(\omega) = i\omega\eta$
5. General visco-elastic material, we have $G^*(\omega) = G' + iG''$, where G' describes in-phase response from elastic contribution and G'' is the out of phase response from the viscous dissipative contribution.

2.7 Simple model of viscoelastic material

In this section, we discuss some models of viscoelastic material such as Maxwell fluid.

2.7.1 Maxwell fluid

Maxwell fluid has a relaxation time scale τ :

$$G(t) = G_0 e^{-t/\tau}$$

2.7.2 Kelvin-Voigt solid

2.7.3 Zener standard linear solid

2.8 Stochastic forces and Brownian Motion

2.9 Langevin equation

Definition Langevin Equation:

$$m \frac{d\mathbf{v}}{dt} = -\gamma \mathbf{v} + \mathcal{E}(t)$$

\mathcal{E} is the random force field which described the molecular collisions.

γ is the drag coefficient, if we approxiamte the particle as a spherical object, then $\gamma = 6\pi\eta r$

1. In this section, we considered the Langevin equation, its solution and its relationship to the diffusion equation. We then considered the over-damped limit of the equation in a system with potential energy, ‘Confined Brownian Motion’.
2. The probability density function is an equivalent approach to the Langevin equation.
3. We also find the mean square value of displacement and velocity and compare them with the equipartition theorem in thermal dynamics.
4. The motion of a thermally exited particle subjected to a stocahstic force can be described by two equivalent approaches:

2.9.1 White noise

In an isotropic fluid, molecular collisions with the solvent do not have a preferential direction. Thus, we have $\langle \vec{\xi}(t) \rangle = 0$. Moreover, due to the random uncorrelated nature of the noise force field, $\vec{\xi}(t)$ and

$\vec{\xi}(t')$ must be uncorrelated when $t \neq t'$, i.e. $\langle \vec{\xi}(t) \cdot \vec{\xi}(t') \rangle = \langle \vec{\xi}(t) \rangle \langle \vec{\xi}(t') \rangle = 0$ for $t \neq t'$. The properties of $\vec{\xi}$ can therefore be summarised as:

$$\begin{aligned}\langle \vec{\xi}(t) \rangle &= 0 \\ \langle \vec{\xi}(t) \cdot \vec{\xi}(t') \rangle &= c\delta(t - t')\end{aligned}$$

This is the definition of white noise. The value of the constant c will be discussed

2.10 Free system

2.10.1 Solution of Langevin equation and fluctuation-dissipation theorem

In this section, we obtained the solution for velocity for the Langevin equation before investigating the mean square velocity in the long time limit, which we find, by considering the partition theorem, the constant term in the mean square random force field. We find the solution by substitution: $\vec{v}(t) = \vec{w}(t)e^{-\frac{\gamma}{m}t}$

$$\langle \vec{v}(t) \rangle = \vec{v}_0 e^{-\frac{\gamma}{m}t} + \int_0^t e^{-\frac{\gamma}{m}(t-t')} \underbrace{\frac{\langle \vec{\xi}(t') \rangle}{m}}_{=0} dt' = \vec{v}_0 e^{-\frac{\gamma}{m}t}.$$

Next, we will **evaluate the mean square velocity and find the constant c**:

$$\langle \vec{v}(t) \cdot \vec{v}(t) \rangle = \vec{v}_0^2 e^{-2\frac{\gamma}{m}t} + \frac{2}{m} \int_0^t e^{-\frac{\gamma}{m}(2t-t')} \vec{v}_0 \cdot \underbrace{\langle \vec{\xi}(t') \rangle}_{=0} dt' \quad (4)$$

$$+ \frac{1}{m^2} \int_0^t dt' \int_0^t dt'' e^{-\frac{\gamma}{m}(2t-t'-t'')} \underbrace{\langle \vec{\xi}(t') \cdot \vec{\xi}(t'') \rangle}_{=c\delta(t'-t'')} \quad (5)$$

$$= \vec{v}_0^2 e^{-2\frac{\gamma}{m}t} + \frac{c}{2m\gamma} (1 - e^{-2\frac{\gamma}{m}t}) \quad (6)$$

Note that solution has a characteristic time scale m/γ , which describes the time of relaxation of the initial condition.

Now we make use of the equipartition theorem to fix the result at $t \approx \infty$: The equipartition theorem fixes the $t \rightarrow \infty$ value of $\langle \vec{v}^2 \rangle \rightarrow 3k_B T/m$ ($k_B T/2$ per degree of freedom). This constraint therefore determines the value of the constant $c = 6\gamma k_B T$ and thus

$$\langle \vec{\xi}(t) \cdot \vec{\xi}(t') \rangle = 6k_B T \gamma \delta(t - t')$$

This result is known as the **fluctuation dissipation theorem**; Equation above relates the amplitude of the fluctuations of a particle induced by a random force to the dissipative drag γ that the same particle experiences when it is actively moved through a fluid.

2.10.2 Mean square displacement and the diffusion equation

In this section, we find the displacement by integrating the velocity and investigated the mean square value of the displacement in the long time limit, in which we define the diffusion coefficient D and the time scale τ_r for a colloidal particle to diffuse its own diameter

Next, we find that the Probability function, which is proportional to the concentration satisfies the diffusion equation.

$$\partial_t c(x, t) = D \nabla^2 c(x, t)$$

2.10.3 Particle flux

By considering the continuity equation:

$$\partial_t c(x, t) = -\nabla \cdot \mathbf{J}(x, t)$$

We obtain the Fick's Law

$$\mathbf{J}(x, t) = -D \nabla \cdot c(x, t)$$

2.10.4 Diffusion controlled process

Incompressible this section, we consider spherical symmetric growth at steady state, This situation corresponds to particles attaching together when they meet reference particle of radius a located at $r=0$ and thus form clusters. We have a solution for c with boundary condition $c(r=a)=0$:

$$c(r) = c_\infty \left(1 - \frac{a}{r}\right) \quad (7)$$

The particle current density is radial and has form:

$$J(r) = -D \frac{dc}{dr} = \frac{D c_\infty a}{r^2} \quad (8)$$

The $1/r^2$ actually shows that total flux crossing any spherical shell is constant and independent of distance from centre, the total flux

$$\frac{dN}{dt} = -J(a)4\pi a^2 = 4\pi D c_\infty a \quad (9)$$

2.10.5 Velocity relaxation

Memory of the original velocity \vec{v}_0 is lost over a time scale

$$\tau_v := \frac{m}{\gamma}$$

2.10.6 Overdamped limit

If observations are made on time scales which are much larger than the velocity relaxation time $\tau_v = m/\gamma$, then the particle effectively has no acceleration or inertia. The Langevin equation therefore becomes:

$$0 = -\gamma \vec{v} + \vec{\xi}(t)$$

or which is known as the Smoluchowski or overdamped limit. can be integrated to yield an expression for the particle position in the overdamped limit

$$\vec{x}(t) = \vec{x}_0 + \frac{1}{\gamma} \int_0^t \vec{\xi}(t') dt'$$

where x_0 is the initial position of the particle.

2.11 System with Potential energy

We now consider a system with a potential energy

2.11.1 Confined Brownian Motion

New solution for the Langevin equation:

$$\vec{x}(t) = \vec{x}_0 e^{-\frac{k}{\gamma}t} + \int_0^t e^{\frac{k}{\gamma}(t-t')} \frac{1}{\gamma} \vec{\xi}(t') dt'$$

As expected, $\langle \vec{x}(t) \rangle = \vec{x}_0 e^{-\frac{k}{\gamma}t} \rightarrow 0$, when $t \rightarrow \infty$ and the mean square deviation can be computed to yield

$$\langle \vec{x}(t)^2 \rangle = \vec{x}_0^2 e^{-2\frac{k}{\gamma}t} + \frac{3k_B T}{k} \left(1 - e^{-2\frac{k}{\gamma}t}\right).$$

2.11.2 Diffusion in external potentials

The particle current flux density:

$$\vec{J}(\vec{x}) = -D \vec{\nabla} c(\vec{x}, t) - \frac{1}{\gamma} \vec{\nabla} U(\vec{x}) c(\vec{x}, t)$$

2.12 Escape over a potential barrier

In this section, we get the escape rate of a particle escape from a metastable state separated by a barrier from reaching thermodynamic equilibrium by considering the flux density, therefore the escape rate is:

$$r = D \frac{\sqrt{\kappa_A \kappa^\ddagger}}{2\pi k_B T} e^{-\beta U^\ddagger}$$

This result shows that the escape rate is proportional to the Boltzmann factor of the barrier. This type of exponential behaviour was discovered empirically to apply for many chemical reactions by Arrhenius.

2.13 Reaction controlled processes

2.14 Microrheology

Microrheology is a technique to measure the viscoelastic properties of a material by monitoring the trajectories of an ensemble of small and inert tracer particles embedded in it.

3 Polymers

3.1 Polymer definition and examples

3.2 Polydispersity

3.3 The ideal chain

Definition of constants:

1. \vec{u} : bond vector, $\vec{u}_i = \vec{r}_{i+1} - \vec{r}_i$
2. \vec{R} : end-to-end vector, $\vec{R} = \vec{r}_N - \vec{r}_0$
3. b_0 : bond length
4. $\sqrt{\langle \vec{R}^2 \rangle}$: end-to-end distance

WE discussed three ideal chain models: Random walk, Freely rotating chain, and Beads and springs and discussed here Kuhn length

Model	Kuhn length
Random walk	b_0
Freely rotating chain	$b_0 \sqrt{\frac{1+\cos\theta}{1-\cos\theta}}$
Beads and springs	$\sqrt{\frac{3k_B T}{\kappa}}$

The quantity l_p is known as the persistence length.

Definition Persistence length:

$$l_p = \vec{R} \cdot \frac{\vec{u}_0}{b_0} = \frac{2b_0}{\theta}$$

is the mean value of projection of the end-to-end distance on the first segments. Note that θ is the angle between two adjacent bonds.

3.3.1 Random walk

3.4 Freely joint chain

We construct an equivalent freely joint chain with the same end-to-end distance and the same contour length as the actual polymer by considering a polymer formed N effective Kuhn segments, each one with an effective bond length. Also known as worm-like chain.

End-to-end distance of a freely joint chain is $\sqrt{\langle \vec{R}^2 \rangle} = N^{1/2} b_0$

In reality, Kuhn length is much larger than true size, as chains retain its memory of its orientation over a significant length.

Here θ determine the mean end-to-end distance:

The contour length L and the mean end-to-end distance $\langle R^2 \rangle$ are related to the persistence length l_p by:

$$\langle R^2 \rangle = 2l_p^2 [\exp(-L/l_p) - 1 + L/l_p].$$

If $L \ll l_p$, then $\langle R^2 \rangle \approx L^2$ and the chain is stiff. If $L \gg l_p$, then $\langle R^2 \rangle \approx 2l_p^2$ and the chain is flexible.

3.5 Freely rotating chain

End-to-end distance of a freely rotating chain is $N b_0^2 \frac{1+\cos\theta}{1-\cos\theta}$

3.5.1 Bead springs model

We can also describe an ideal chain as a series of $N + 1$ beads $i = 0 \dots N$ connected linearly by springs with spring constant κ , leading to an energy of the form $U = \frac{\kappa}{2} (\vec{r}_{i+1} - \vec{r}_i)^2$.

The end-to-end distance can then be evaluated as:

$$l \langle R^2 \rangle = \frac{\int Z(R) R^2 d^3 R}{\int Z(R) d^3 R} = \underbrace{\frac{3k_B T}{\kappa}}_{=b_0^2} N$$

3.6 Entropy of Real Chains

For an ideal Gaussian chain Eq. (4.17) shows that the probability of observing an end-to-end distance \vec{R} for a chain with N segments is

$$P(\vec{R}, N) = \left(\frac{3}{2\pi N b_0^2} \right)^{\frac{3}{2}} e^{-\frac{3\vec{R}^2}{2N b_0^2}}$$

We have $S = k_B \ln(P)$ and $F = U - TS$:

$$F(\vec{R}, N) = k_B T \frac{3}{2} \frac{\vec{R}^2}{N b_0^2} + F(0)$$

since

$$S(\vec{R}, N) = -k_B \frac{3}{2} \frac{\vec{R}^2}{N b_0^2} + S(0)$$

where $F(0)$ and $S(0)$ represent the constants that do not depend on R .

3.7 Real chains: excluded volume

Real chains have excluded volume which reduces the number of ways of assembly and hence reduces the entropy and then an extra term in the Helmholtz free energy. The size of R is then found by minimising the free energy.

1. Reduced Entropy:

$$S_{\text{ex}} = S_{\text{id}} - k_B \frac{N^2 v}{V}$$

2. Then will have excess term in Helmholtz free energy:

$$F_{\text{excl}} = \frac{3k_B T v N^2}{4\pi R^3}$$

3. The new equilibrium can be found at minimized F :

$$F = k_B T \frac{3v N^2}{4\pi R^3} + k_B T \frac{3R^2}{2N b_0^2}$$

4. Therefore the size of the polymer coil is given as:

$$R = \left(\frac{3v b_0^2}{4\pi} \right)^{1/5} N^{3/5}$$

Note that the ideal chain relationship is $R = \sqrt{N} b_0$.

3.8 Coil-globule transition

In this section, we consider a negative exclude volume due to attractive interaction. Chains with negative excluded volume will collapse into a globule.

1. The change in Helmotz free energy in the chain:

$$\frac{F_{\text{int}}}{V} = k_B T v(T) n^2$$

with

$$v(T) = v_0 - \frac{a}{k_B T} = v_0 \left(1 - \frac{a}{v_0 k_B T} \right)$$

2. Definition Flory parameter:

$$\chi(T) = \frac{1}{2} (1 - v(T)/v_0)$$

is introduced such that $v(T) = v_0(1 - 2\chi(T))$, $\chi \sim T^{-1}$ is typically observed

3. In particular, there is a temperature at which the excluded volume interaction vanishes: this is known as the θ temperature and is given by $\theta = a/(v_0 k_B)$ or $\chi(\theta) = 1/2$. Note that with θ defined, we can now rewrite $v(T) = v_0(1 - \frac{\theta}{T})$ and $\chi(T) = \frac{\theta}{2T}$.

3.8.1 Flory Huggins free energy

In this section, we try to find out the physical origin of the χ , by considering regular solutions which are mixtures of low molecular weight species A with solvent molecules B AND STUDY ITS FREE ENERGY DENSITY:

Taken together, we can express the free energy density $f = \Delta F/M = \Delta U/M - T\Delta S/M$ of mixing as

$$f_{\text{mix}} = k_B T \left[\frac{\Phi}{N} \ln \Phi + (1 - \Phi) \ln(1 - \Phi) + \chi \Phi(1 - \Phi) \right]$$

We will see this energy used in derivation of Osmotic pressure and chemical potential

3.9 Osmotic pressure and chemical potential of polymer solutions

Definition Osmotic pressure Π :

$$\Pi = - \left. \frac{\partial \Delta F}{\partial V} \right|_{N_A} = - \frac{1}{b_0^3} \frac{\partial (Mf)}{\partial M} = - \frac{1}{b_0^3} \left(f + M \frac{\partial f}{\partial M} \right) = \frac{1}{b_0^3} \left(-f + \Phi \frac{\partial f}{\partial \Phi} \right)$$

is pressure exerted by molecules in solution against a membrane which is impenetrable to them but allows the flow of solvent molecules and can be obtained from the change in the free energy of the system as a function of volume with constant number of solutes N_A

Definition Chemical potential of polymer:

$$\mu = \frac{\partial \Delta F}{\partial N_A} = M \frac{\partial f}{\partial N_A} = M \underbrace{\frac{\partial \Phi}{\partial N_A}}_{=M^{-1}} \frac{\partial f}{\partial \Phi} = \frac{\partial f}{\partial \Phi}$$

given as the rate of change in the free energy as a function of the number of polymers in solution

4 Molecular self-assembly

4.1 Driving Forces behind molecular self-assembly

5 Self-assembly II

In this section we discuss lipid membrane, which are diffusion barrier for charged molecules and ions.

We will discuss the properties of bilayers that are a direct consequence of the self-assembly. Shape, Phase, curvature and membrane fluctuations.

5.1 Simple argument for the shape

Lipid bilayers consists of double layer of amphiphilic molecules:

1. The head area a_0 . This results from a balance of repulsions between the surfactant molecules (electrostatic, excluded volume, etc), and an effective attraction to minimise the contact area of hydrocarbon tails with water.

2. The critical chain length l_{c^*} . This is the maximum length of the hydrocarbon chain if stretched.
3. The hydrocarbon volume v . This is the volume occupied by the chain, irrespective of the conformation.

5.2 Shape of assembly

1. Sphere
2. Cylinder
3. Bilayer

5.3 Bilayers

5.3.1 Phase transition

Three main states called L_α , L_β and P_β . The three states L_β , P_β and L_α are indicated as well as the two transition temperatures, pre transition $L_\beta \leftrightarrow P_\beta$ at T_P , and main transition T_m at $P_\beta \leftrightarrow L_\alpha$, observable due to a clear change in c_p . The enthalpy corresponding to the transition can be deduced from the melting curve:

$$\Delta H = \int_{T_0}^{T_1} \Delta c_p dT$$

while the corresponding entropy is

$$\Delta S = \int_{T_0}^{T_1} \frac{\Delta c_p}{T} dT$$

The last equation can be simplified if the melting transition is very sharp and resembles a delta function ($c_p/T \approx c_p/T_m$) one can define

$$\Delta S = \Delta H/T_m$$

5.3.2 Influence of pressure on phase transition temperature

Pressure could shift the phase transition temperature by changing ΔH , It will also result in a volume change.

$$\Delta T_m = \frac{\Delta p \Delta V}{\Delta S} = \Delta p T_m \frac{\Delta V}{\Delta H_0}$$

$$\Delta V = \frac{\Delta T_m \Delta H_0}{T_m \Delta p}$$

5.3.3 Micelles, Nematic, Hexagonal and Lamellar phases

Balance between translational entropy and curvature energies gives rise to complex phase diagrams **at high concentration**, as interaction between the assembled structures become more significant.

5.4 Soft Membranes

differential geometry

Deformation causes stretch For a small displacement h relative to the average membrane plane $z = 0$, the area of a surface element can be obtained by expanding eq. 7.10:

$$dA = \left(1 + \frac{1}{2}(\nabla h)^2 \right) dxdy$$

is the actual increase in the infinitesimal area is $dA - dxdy$

Deformation causes curvature $H = \frac{1}{2} \nabla \cdot \frac{\nabla h(\mathbf{x})}{[1+(\nabla h(\mathbf{x}))^2]} \simeq \frac{1}{2} \nabla^2 h(\mathbf{x})$

Increase in energy due to the work against membrane tension and the bending of the membrane is (to first order)

$$\begin{aligned} \delta E &= \delta E_\sigma + \delta E_B \\ &= \sigma \int_0^L \int_0^L \frac{1}{2} \left[\left(\frac{\partial h}{\partial x} \right)^2 + \left(\frac{\partial h}{\partial y} \right)^2 \right] dx dy + \\ &\quad + \kappa \int_0^L \int_0^L \frac{1}{2} \left[\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} \right]^2 dx dy \end{aligned}$$

Minimising the energy The membrane will try to minimise the free energy of the equation above given the boundary conditions.

6 Surface energy

The work required to create a new surface of area δA is

$$\delta E = \gamma \delta A$$

where γ is the surface tension, has the unit of Newton over meter.

7 Colloids

Colloids are small particles with size around 10^{-7}

7.1 Forces between colloids

1. Exclude volume interaction
2. Dispersion forces, i.e. van der Waals forces
3. Coulomb interaction
4. Depletion forces
5. Steric interactions

We will many focus on the van der Waals forces and Coulomb interaction, which is the dominant force between colloids.

7.2 Dispersion

Dispersion forces are from the induced dipole momentum *Definition Induced dipole:*

$$\mu_{\text{ind}} = \alpha E$$

is the dipole moment induced by an external electric field

Definition Dispersion force:

$$V(r) = -\frac{B}{r^6}$$

is the force between two atoms or molecules caused by the attraction of instantaneous multipoles

This is the force that encourages aggregation

7.3 Coulomb interactions

Coulomb interaction is the repulsive force that stops the aggregation

Definition Bjerrum length:

$$\lambda_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T}$$

is the distance at which the electrostatic interaction energy between two elementary charges is equal to the thermal energy, it is derived by equation the electrostatic energy to the thermal energy $k_B T$. Its physical meaning is the closet distance that two like-charged ions can have at a certain temperature

7.3.1 Poisson-Boltzmann Equation

Definition Poisson-Boltzmann Equation:

$$\nabla^2 \phi(\mathbf{r}) = \frac{1}{\epsilon_0 \epsilon_r} \rho(\mathbf{r})$$

is the equation that describes the electrostatic potential $\phi(\mathbf{r})$ due to a set of point charges $z_i e$ in a medium with dielectric constant ϵ_r . The average concentration of charged molecules follows the Boltzmann distribution:

$$n_{\pm}(\mathbf{r}) = n_{\pm}^0 \exp\left(-\frac{e \mp \phi(\mathbf{r})}{k_B T}\right)$$

Assuming z is singly charged.

Note that ρ is the charge density, and n is the number density, with a connection of $\rho = \sum_{i=1}^N e z_i n_i(\mathbf{r})$.

Combining the Poisson equation and Boltzmann distribution, we have:

$$\nabla^2 \phi(\mathbf{r}) = -\frac{e}{\epsilon_0 \epsilon_r k_B T} \sum_{i=1}^N z_i n_i^0 \exp\left(-\frac{e z_i \phi(\mathbf{r})}{k_B T}\right)$$

7.4 Solving PE equation (linear)

PB is not linear so quite difficult to solve, but we can linearize it by assuming ϕ is small, i.e. $e z_i \phi(\mathbf{r}) / k_B T \ll 1$. This is known as the Debye-Huckel equation, with the definition of the Debye length:

Definition Debye length:

$$\kappa^{-1} = \sqrt{\frac{\epsilon_0 \epsilon_r k_B T}{2 \sum_{i=1}^N z_i^2 n_i^0}}$$

is the length scale at which the electrostatic screening due to mobile ions in solution becomes significant. Note the difference in Debye length and Bjerrum length, the former is the length scale at which the electrostatic screening due to mobile ions in solution becomes significant, while the latter is the closet distance that two like-charged ions can have at a certain temperature, and is independent of the concentration of the ions.

7.5 DLVO

Combining the effect of all the interaction forces, we have the DLVO theory, which is the sum of the van der Waals and the electrostatic interactions. There is a local minimum force the potential energy and a barrier preventing that from going to 0.

8 Electrokinetic Phenomena

There are two types of electrokinetic phenomena:

1. Electro-osmosis: The electro-osmotic flow is the uniform velocity that is far from a charged surface in contact with a liquid electrolyte solution

2. Electrophoresis: motion of the colloids under the influence of an external electric field

8.1 Navier-Stoke Equation

Definition Navier-Stoke Equation:

s

is the equation that describes the motion of viscous fluid substances