Soft Condensed Matter

Xinyu Zhong
Wolfson College

February 13, 2023

Contents

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 surface integral to volume integral.
3. Combining the rate of change in mass and conservation of mass, as both are volume integral:
$$\frac{\partial \rho}{\partial t} = -\boldsymbol{\nabla} \cdot (\rho \mathbf{v})$$
4. For incompressible fluid, ρ is constant, and the continuity equation simplify to $\boldsymbol{\nabla} \cdot \mathbf{v} = 0$.

1.1.2 Momentum Flux and the equation of motion

1. Rate of change in total momentum $P_i(V,t)$
$$\frac{\partial P_i(V,t)}{\partial t} = \frac{\partial}{\partial t}\int_V d^3 r \rho v_i = \int_V (\frac{\partial}{\partial t}\rho) v_i + \rho \frac{\partial}{\partial t} v_i$$
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 contribution for viscous pressure and pressure forces
4.

1.2 Navier-Stokes equation

1. The complete Navier-Stokes equation
$$\rho[\partial_t \boldsymbol{v} + (\boldsymbol{v} \cdot \nabla)\boldsymbol{v}] = -\boldsymbol{\nabla} p + \eta \nabla^2 v + \rho \boldsymbol{g}$$
2. Left-hand side relate to inertial force densities
3. Right-hand side encompass intrinsic viscosity and applied force densities (pressure gradient and gravity)
4. Conservative external forces, including gravity, the eternal force term is absorbed into pressure term.

1.3 Material Derivative

1. Concept of streamline
2. Lagrangian rate of
$$\frac{Df}{Dt} = \frac{\partial f}{\partial t} = (\boldsymbol{v} \cdot \nabla) f$$
3. In particular, the acceleration of fluid element is:
$$\frac{D\mathbf{v}}{Dt} = \frac{\partial \mathbf{v}}{\partial t} = (\boldsymbol{v} \cdot \nabla)\mathbf{v}$$
4.

1.4 Reynold Number and Stokes Flow

When discussing fluid of limit 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 number is inversely proportional to viscosity.
2. Low Reynolds number $Re << 1$, the viscous term dominates over inertia, non-linear Navier-Stokes equation is reduced to linear Stokes equation:
$$0 = -\boldsymbol{\nabla} p + \eta \nabla^2 \boldsymbol{v}$$
3. If an external force is applied, for instance an oscillating boundary, time derivative is given by the external force and is not negligible, which gives time-dependent Navier Stokes Equation
$$\rho \partial_v \boldsymbol{v} = -\boldsymbol{\nabla} p + \eta \nabla^2 \boldsymbol{v}$$

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 which 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 cancelled 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 strategy to break time-reversal symmetry to operator with 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, $\boldsymbol{v} = 0$ relative to contain.
2. Navier-Stokes equation reduce to:
$$0 = -\boldsymbol{\nabla} p - \rho g \boldsymbol{e}_z$$
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 constribution to the pressure is given as the hydrostatic pressure:
$$p_{hs} = -rhogz$$
We can therefore regroup the effects of gravity into the pressure term and write the total pressure as:
$$p_{tot} = p + phs$$
4.

1.8 Couette Flow

Couette flow is a flow induced in a liquid through the movement of one or more walls. No pressure gradiant.
Example: Planar geometry
Bottom plate at $z = 0$ and top plate $z = h$, liquid is moving with speed v_0 while stationary at 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 motion for the flow field is given by 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 diffuse 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 teh shpere experieences due to the motion of the underlying fluid is $\mathbf{F} = 6\pi\eta a\boldsymbol{v}$

1.11.1 Scaling argument

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

$$v_x(z = 0) = 0$$
$$v_x(z = h) = 0$$

Solution is a parabolic

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

Overall flow is characterised by the volumetric flow rate, Q

$$Q = \int_c dydzv_x(y, z)$$

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

$$\begin{aligned}(x,y,z) &= (x, r\cos(\psi), r\sin(\psi))\\ \vec{\mathbf{e}}_x &= \vec{\mathbf{e}}_x\\ \vec{\mathbf{e}}_r &= \cos\psi\vec{\mathbf{e}}_y + \sin\psi\vec{\mathbf{e}}_z\\ \vec{\mathbf{e}}_\psi &= -\sin\psi\vec{\mathbf{e}}_y + \cos\psi\vec{\mathbf{e}}_z\end{aligned}$$

Volumetric flow rate:

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

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 proportionalto the pressure difference at its ends Δp. This relationship holds for any channel geomertry and is known as the Hagen-Poiseuille law. Compare Fluid to Circuits,

Summay

	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 Different 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 diagonaisable

2.1.2 Stress

1. Stress in 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 teh 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 Hookes'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 onlu ahve 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 streches along this direction by strain ϵ_{xx}. Stress and stains 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:
$$E\epsilon_{xx} = \sigma_{xx} \tag{1}$$
$$E\epsilon_{yy} = -\nu\sigma_{xx} \tag{2}$$
$$E\epsilon_{yy} = -\nu\sigma_{xx} \tag{3}$$

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

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 $d\sigma(t)$:

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

   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 viscoelasic 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:

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

$\mathcal{E}$ 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 relationship to the diffusion equation. We then considered the over damped limit of the equation in a system with a potential energy, 'Confined Brownian Motion'.
2. The probability density function is an equivalent approach to the Langevin equation.
3. We also find mean square value of dispalcement 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. $\left\langle\vec{\xi}(t)\cdot\vec{\xi}(t')\right\rangle = \langle\vec{\xi}(t)\rangle\left\langle\vec{\xi}(t')\right\rangle = 0$ for $t \neq t'$. The properties of $\vec{\xi}$ can therefore be summarised as:

$$\langle\vec{\xi}(t)\rangle = 0$$
$$\left\langle\vec{\xi}(t)\cdot\vec{\xi}(t')\right\rangle = c\delta(t-t')$$

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

2.9.2 Solution of Langevin equation and fluctuation-dissipation theorem

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

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

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

$$\begin{aligned}\langle\vec{v}(t)\cdot\vec{v}(t)\rangle =& \vec{v}_0^2 e^{-2\frac{\gamma}{m}t} + \frac{2}{m}\int_0^t e^{-\frac{\gamma}{m}(2t-t')}\vec{v}_0\cdot\underbrace{\left\langle\vec{\xi}(t')\right\rangle}_{=0}dt' &(4)\\ &+\frac{1}{m^2}\int_0^t dt'\int_0^t dt'' e^{-\frac{\gamma}{m}(2t-t'-t'')}\underbrace{\left\langle\vec{\xi}(t')\cdot\xi\left(\vec{t''}\right)\right\rangle}_{=c\delta(t'-t'')} &(5)\\ =& \vec{v}_0^2 e^{-2\frac{\gamma}{m}t} + \frac{c}{2m\gamma}\left(1-e^{-2\frac{\gamma}{m}t}\right) &(6)\end{aligned}$$

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 $t \to \infty$ value of $\langle\vec{v}^2\rangle \to 3k_BT/m\,(k_BT/2$ per degree of freedom). This constraint therefore determines the value of the constant $c = 6\gamma k_BT$ and thus

$$\left\langle\vec{\xi}(t)\cdot\vec{\xi}(t')\right\rangle = 6k_BT\gamma\delta(t-t')$$

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.

2.9.3 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 collioidal particle to diffuse its own diameter
Next, we find that the Probablility function, which is proportional to the concentration satisfies the diffusion equation.

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

2.9.4 Particle flux

Bu considering teh continuity equation:

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

We obtain the Fick's Law

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

2.9.5 Diffusion controlled process

IN 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 forms clusters. We have a solution for c with boundary condition c(r=a)=0:

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

The particle current densit is radial and has form:

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

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

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

2.10 Velocity relaxation

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

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

2.10.1 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.

2.10.2 Confined Brownian Motion

3 Polymers

4 Molecular self-assembly