

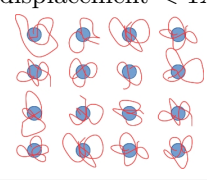
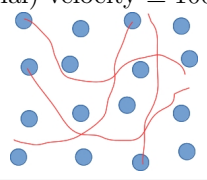
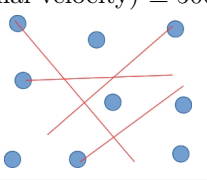
Chapter 1

What is Soft Matter

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1 Introduction

- Traditionally, 3 states of matter: solid, liquid, gas
- classification based on symmetry, density, and amplitude of cohesive energy.

solids	liquids	gas
There is a reference state. Store energy when under stress. When stress is released, energy is restored & comes back to reference state.	No reference state. Flow under infinitesimal stress.	
Macroscopic response characterized by elastic moduli [Pa].	Macroscopic response characterized by viscosities [Pa.s].	
cohesive energy $\varepsilon_c \gg k_B T$	$\varepsilon_c \sim k_B T$	$\varepsilon_c \ll k_B T$
displacement $< 1\text{\AA}$ 	(thermal) velocity $\simeq 100\mu\text{m/s}$ 	(thermal velocity) $\simeq 500\text{m/s}$ 
atomic scale $a \simeq 1\text{\AA}$	$a \simeq 1\text{\AA}$	$a \simeq 1\text{\AA}$
interatomic distance $d \simeq a$	$d \simeq a$	$d \gg a$. Ideal gas: $d = (V/N)^{1/3} = (k_B T/P)^{1/3} \simeq 3\text{ mm @ } 300\text{K, } 1\text{ atm}$
mean free path $\bar{l} \simeq d$	$\bar{l} \simeq d$	$\bar{l} \simeq \frac{d^3}{4\pi a^2} \gg d$

- This classification is ambiguous: for instance, a glass = density of solid, but symmetry of liquid.
- solid, liquid, gas = ideal behaviors, rather than real materials. Note: solid or fluid behavior depends on:
 - time scale (eg: mantle of Earth, glacier)
 - length scale
 - amplitude of applied stress (eg: sand & granular materials, foams)

2 Soft matter: main features

- Soft Matter: term popularized by P.G. de Gennes at the occasion of his Nobel Prize lecture in 1991.
- Still a very active research area: note that since 2015, the Lucasian chair of Mathematics (Cambridge) is hold by Michael Cates (succeeding to Newton, Dirac, Stokes, Hawking,...)

- **definitions (common features) of soft matter :**

- *mechanic* = term “soft” refers to weak rigidity/weak interactions in these systems. Also called **complex materials**.

- *thermodynamic* = very sensitive to perturbations because $\varepsilon_c \sim k_B T$: a large modification of its properties for a small modification of one of the control parameters; e.g. 1% sulphur with latex form latex rubber, electric field applied to liquid crystals.

- *structural* = usually existence of a mesoscopic scale \gg size of the constituents but \ll sample size, because $\varepsilon_c \lesssim k_B T$

- Thermal systems ($\varepsilon_c \sim k_B T$):

- Boltzmann constant: $k_B = 1.4 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$

- typical energy per molecule: $k_B T_{amb} = 4.2 \cdot 10^{-21} \text{ J}$ (e.g.: ideal gas: $E = (3/2)Nk_B T$);

- adapted unit for microscopic world: $1 \text{ eV} = 1,6 \cdot 10^{-19} \text{ J}$;

- $k_B T_{amb} = 25 \text{ meV} = 4,1 \cdot 10^{-21} \text{ J}$

- this is the order of magnitude of energy fluctuations (“thermal fluctuations”)

- When thermal fluctuations become important ?

e.g. sedimentation of colloidal suspension: particles with radius R , density ρ_s in a liquid with density ρ and viscosity η : velocity of sedimentation: $v = \Delta\rho g \frac{4}{3}\pi R^3 \cdot \frac{1}{6\pi\eta R}$. Diffusive velocity $v_D = D/R$ where D is the diffusive coefficient. Einstein relation relates D , T , R and η : $D = \frac{k_B T}{6\pi\eta R}$.

Fluctuations become important when $v_D > v$, that is, when $R < \left(\frac{3k_B T}{4\pi\Delta\rho g}\right)^{1/4} \sim 1\mu\text{m}$.

- **Entropic-driven transitions**

- Usual interpretation of phase transition: equilibrium configuration corresponds to minimization of free energy $F = U - TS$. Competition between energetic and entropic terms. Ordered structure minimizes U and so F at low temperature, while disordered structure maximizes S and so minimizes F at high temperature.

- Very often phase transitions in soft matter are driven by a change of entropy only. This is the case when objects can be modeled with hard-core interactions. In that case the maximization of entropy may favourize ordering of the system ! Three examples of entropic-driven transitions, from the most to the less obvious one:

- **depletion forces in a bidisperse system of hard-core particles.** e.g.: colloids + small globular particles.

Large particles with diameter D , small particles with diameter d . *Excluded volume:* $V_E =$

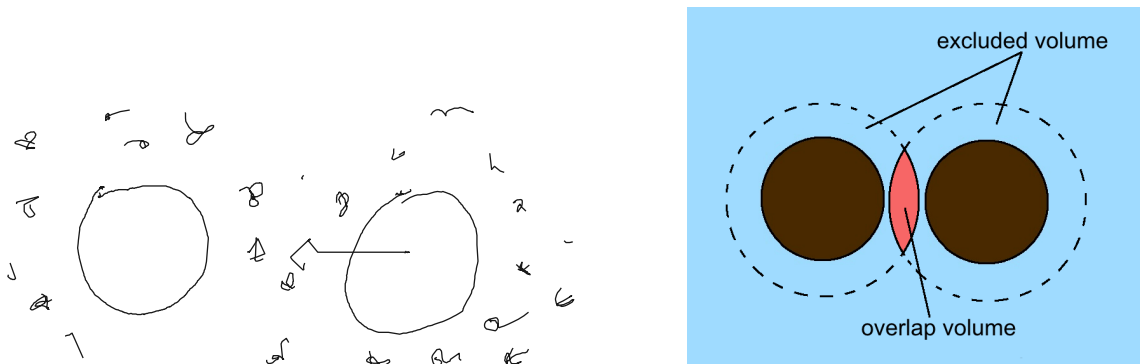


Figure 1: (a) Depletion force: the pressure caused by the small particles over the large particles generates an effective attractive force; (b) excluded and overlap volumes.

$\pi(D + d)^3/6$: volume surrounding a large particle which is inaccessible to the center of a small particle.

At high concentration, excluded volumes can overlap. *Reduced excluded volume:*

$$V'_E = V_E - \frac{2\pi}{3} l^2 \left[\frac{3(D+d)}{2} - l \right],$$

- *Mechanical interpretation:* more collisions of small particles on the outside part of the large particles causes an attractive net force.
- *Thermodynamic interpretation:* Free energy: $F = -TS_{large} - TS_{small}$. The available volume for small particles is:

$$V_A = \begin{cases} V - V_E, & \text{if } h \geq D + d \\ V - V'_E, & \text{if } h < D + d \end{cases} \quad (1)$$

Reduced excluded volume \Rightarrow increase of available volume for small particles $\Rightarrow S_{small} \nearrow$.
 But also Reduced excluded volume $\Rightarrow S_{large} \searrow$.
 Flocculation (demixing) as soon as $|\Delta S_{small}| > |\Delta S_{large}|$.

– **Isotropic-nematic transition of rod-like particles:**

Explained first by Onsager (1949): Excluded volume for rod with diameter D and length $L \gg D$ is minimal ($\pi D^2 2L$) when rods are aligned, and maximal ($L^2 2D$) when they are perpendicular. Alignment decreases orientational entropy, but increases translational entropy. When density $> d_c$, transition from disordered, isotropic phase to the ordered nematic phase.

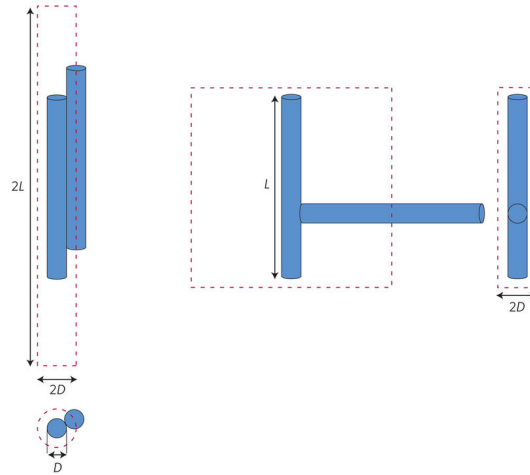


Figure 2: Excluded volume when rods are aligned or perpendicular.

– **crystallization of hard-spheres:**

There has been a long debate between physicists in the 1950's on the possible existence of crystallized phase of hard spheres.

In the two preceding examples, transition originates from a contrast of size of the particles, or from their anisotropic shape. But here all the particles are identical and isotropic.

One of the very first success of numerical simulations has been to "prove" the existence of such a transition. It can be qualitatively explained this way: At 3D, the densest packing fraction of hard-spheres is 74%, while a random close packing cannot exceed $\simeq 64\%$. This suggests that passing from a random close packing to an ordered one at fixed density will allow more space for each particle, and so will increase the configurational entropy. It is simpler to visualize at 2D: the densest packing is the hexagonal packing: each disc is then surrounded by 6 disc (this is defined as the 'kissing number'). Now imagine a disordered structure in which 6 (or more) discs are touching each other and forming a loop: the space inside the loop cannot be visited by any disc and so is lost for the configurational entropy. If the packing fraction is high enough, discs are stuck around these

positions and the packing is ‘jammed’. The excluded volume is then larger than for an ordered packing. Order increases the entropy of the system !

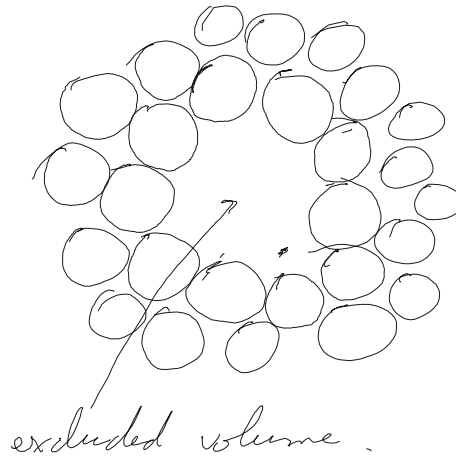


Figure 3: At high concentration, hard-core spheres obstruct each other, such that some portions of space are never visited.

3 Non-exhaustive list of complex systems

3.1 Macromolecules

- polymers (=chains of monomers linked by covalent bonds), means "many parts" in ancient greek.

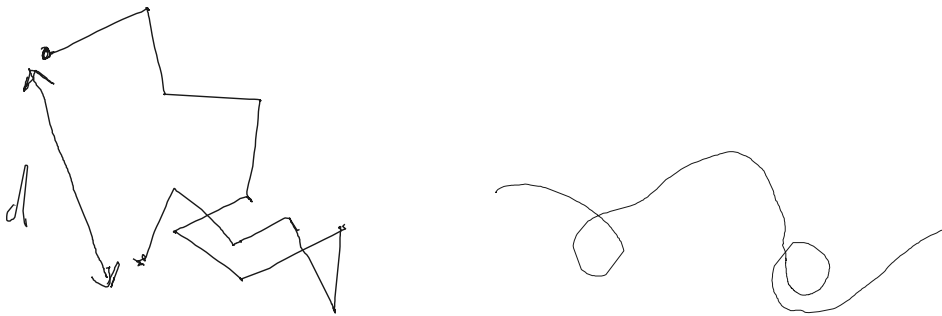


Figure 4: (a) ideal polymer: similar to a random walk with constant step size a . (b) worm chain model: continuous description.

- natural polymers DNA, proteins, silk, wool, rubber,...
- synthetic polymers: polystyrene, silicone, nylon, PVC, polypropylene,...
- Ideal polymer \equiv random walk.
- Suppose one end at position $\mathbf{r} = \mathbf{0}$. density of probability that second end is at position \mathbf{r} :

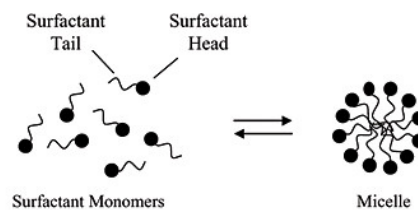
$$P_N(\mathbf{r}) = \left(\frac{3}{2\pi N a^2} \right)^{3/2} e^{-\frac{3r^2}{2N a^2}}.$$

- this is the solution to diffusion equation: exact analogy between polymer and random walk.
- distance between two ends: $d = \alpha\sqrt{N}$ (obvious from central limit theorem: $\langle \mathbf{R}^2 \rangle = \sum_{i=1}^N \langle \mathbf{a}_i^2 \rangle = N a^2$)

- interaction between successive monomers changes the value of α .
- interaction (e.g.: steric constraint) between adjacent monomers changes the power-law coefficient.
- continuous approach (worm chain) \equiv path integral.

3.2 Amphiphilic molecules (surfactant)

- “Amphiphilic” = “who likes in two different ways”.
- “Surfactant” = SURFace ACTive AgeNT.
- Structure: molecule with two distinct part connected to each other (covalent bonds):
 - a non-polar, hydrophobic, part: usually a long carbon chain (*aka* “tail”). CH_2 : +0,1 nm per carbon group \times 0,19 nm² per chain
 - a polar or ionic part, hydrophilic, usually smaller (*aka* “head”)
- Properties: spontaneous formation of larger objects (*self-assembly*)
 - At low concentration, most of the molecules are at the surface (surface tension, and so free energy, decrease)
 - Above a critical concentration value (“Critical Micelle Concentration” CMC), molecules form spherical shell with hydrophobic parts inside: *micelles* (first order phase transition)



Schematic illustration of the reversible monomer-micelle thermodynamic equilibrium (Based on Liu et al., 1996). The black circles represent the surfactant heads (hydrophilic moieties) and the black curved lines represent the surfactant tails (hydrophobic moieties). When micelles form in aqueous solution above the CMC, the surfactant monomers aggregate (self-assemble) with the tails inside the micelle shielded from water and the heads at the micelle surface in contact with water.

- Depending on the molecule geometry, they form objects with other geometries, *e.g.* lamellar phase, membranes.
- CMC \nearrow when $T \nearrow$.

- natural amphiphilic molecules: lipids of biological membranes,... Synthetic amphiphilic molecules: detergent,...

3.3 Liquid Crystals

- Rods-like molecules that have dual properties of liquids (flows) and solids (positional and/or orientational order). Different phases, among which:
 - isotropic phase: no orientational and no positional orders.
 - nematic phase: orientational order, but no positional order.
 - smectic phase: orientational order + positional order in one direction (well-defined layers).
 - cholesteric phase: similar to smectic phase but with twist of molecule orientations along the director axis.

3.4 Dispersed systems

- Phase (solid, liquid, gas) dispersed in another (solid, liquid, gas). 3×3 combinations:

continuous phase : dispersed phase :	solid	liquid	gas
solid	<i>(micro- or nano-composite)</i>	colloidal suspension	<i>(smoke, dry granular)</i>
liquid	gel	emulsion	<i>(aerosol)</i>
gas	aerogel <i>(solid foam)</i> <i>(porous medium)</i>	liquid foam	NONE (all gases are mutually miscible)

(in italics, what are not objects of soft matter)

- colloidal suspension:
 - electrostatic forces: coupling between repartition of charges and generated electrostatic potential: Poisson-Boltzmann equation (mean-field approx.), screening length...
 - depletion forces: binary mixtures (small and large “particles” (e.g. polymers and colloids) *flocculation* or *crystallisation* of larger particles
- interface/membrane:
 - main features of these systems: surface energy dominates over other contributions of energy.
 - Energy per unit surface: *surface tension*: different quantities regrouped under this name.
 - Numerical simulations of interface: analogy between interface and Ising hamiltonian.
 - generalization for many interfaces (emulsion of foam): Potts model

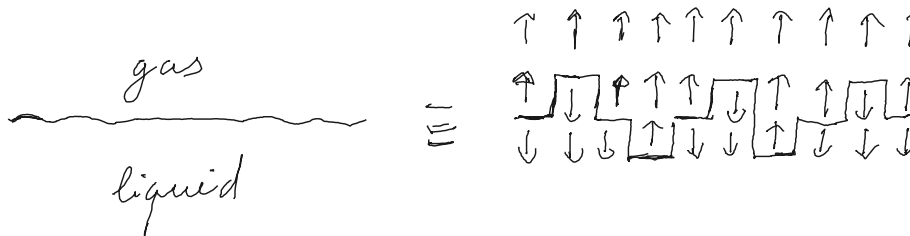


Figure 5: Analogy between liquid-gas interface (energy $\mathcal{H} = \gamma\mathcal{L}$, where γ is the surface tension and \mathcal{L} the length of the interface) and Ising model ($\mathcal{H} = \text{cst} + \sum_{\langle i,j \rangle} J(1 - \delta_{\sigma_i, \sigma_j})$ with $\sigma_i = \pm 1$).

- membrane: surface tension + bending energy
- thermal fluctuations: introduction to functional integration
- repulsion due to thermal fluctuations: longer interaction range than Van der Waals interaction.

3.5 Active matter:

- consumes energy to produce motion
 - eg: motility of biological cells, groups of animals (fishes, birds,...), vibrated sand.
 - biophysics (at scale of molecules, cells, or tissues), morphogenesis
 - collective motion/behavior: structures at large scale independent of details of interactions between units (as for the phase transitions of thermal systems at equilibrium).

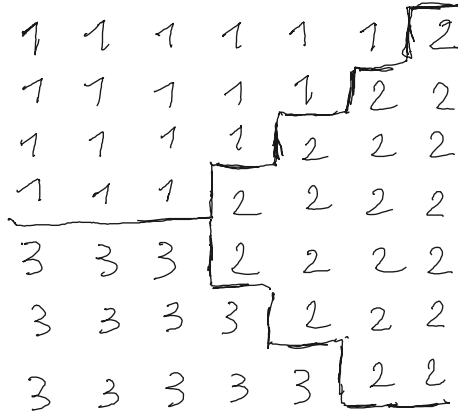
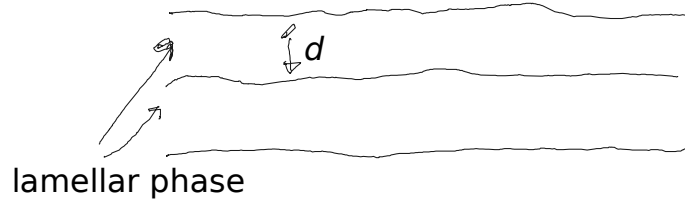


Figure 6: Generalization to N interfaces to modelize foams or emulsions. Potts model: $\mathcal{H} = \sum_{\langle i,j \rangle} J(1 - \delta_{\sigma_i, \sigma_j})$, with $\sigma_i = 1, 2, \dots, N$.



– note: out-of-equilibrium from the point of view of thermodynamics.

- Two kinds of out-of-equilibrium systems:
 - Systems trapped in one of the many metastable state. *e.g.*: glass.
 - Systems in contact with a non-thermal source of energy. Energy consumed through motion. *e.g.*: biological systems (cells, bacteria, groups of animals,...), active particles. This is active matter.

4 Recap: microscopic origins of elasticity and viscosity

4.1 Elasticity of Solids

- Hooke's law (linear elasticity): the elongation $\Delta l/l$ of a rod with length at rest l is proportional to the force per unit surface area σ (=stress) acting on it :

$$\sigma = Y \frac{\Delta l}{l}.$$

Y is the *Young's modulus*. $[Y] = \text{Pa}$.

– Generalization to 3D:

$$\sigma_{ij} = \sum_{k,l} C_{ijkl} u_{kl}$$

where σ and \mathbf{u} are the stress and strain tensors, respectively. \mathbf{C} is the elastic tensor. Its number of independent components depends on the symmetry of the material. For an isotropic body, only 2 independent elastic coefficients, *e.g.*: Lam coefficients λ and μ .

– Navier equation:

$$\rho \frac{\partial^2 \mathbf{u}}{\partial t^2} = \rho \mathbf{g} + \mu \nabla^2 \mathbf{u} + (\lambda + \mu) \nabla (\nabla \cdot \mathbf{u})$$

- For a given temperature T and strain field $\{u_{ij}(\mathbf{r})\}$ ($u_{ij} = (\partial u_i / \partial x_j + \partial u_j / \partial x_i) / 2$), the free energy *per unit volume* $f = \bar{e} - T s$ of a solid is minimal as thermodynamic equilibrium. ($(T, \{u_{ij}(\mathbf{r})\})$):

state variables).

– Suppose uniform uniaxial deformation of a solid bar with length $L \rightarrow L + dL$, under isothermal conditions. Associate change of energy: $d\bar{E} = TdS + FdL$, where $\bar{E} = eV$ and $S = sV$ are the total energy and entropy of the body.

– $F = \left(\frac{\partial \bar{E}}{\partial L}\right)_T$ where \bar{E} denotes the free energy: $\bar{E} = \bar{E} - TS$.

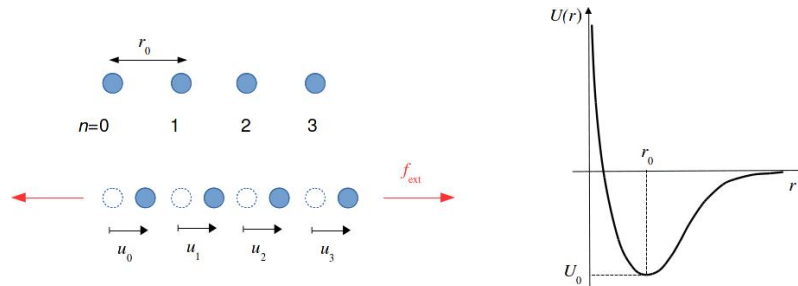
– Hence, two contributions for the restoring force:

$$F = \left(\frac{\partial \bar{E}}{\partial L}\right)_T - T \left(\frac{\partial S}{\partial L}\right)_T.$$

4.1.1 Solids with high cohesive energy

• Solids made of atoms or small molecules: $\bar{E} \gg TS$ as long as $T <$ melting temperature. Then $F \simeq \left(\frac{\partial \bar{E}}{\partial L}\right)_T$.

• Interaction energy between 2 atoms: repulsive at short distance, attractive at long distance \rightarrow equilibrium distance r_0 .



• Consider 1D crystal of N atoms under applied force f_{ext} .

– Harmonic approximation:

$$U(r) \simeq U_0 + \frac{1}{2} \left(\frac{\partial^2 U}{\partial r^2}\right)_{r=r_0} (r - r_0)^2.$$

– Similar to a spring with spring constant $k = \left(\frac{\partial^2 U}{\partial r^2}\right)_{r=r_0}$.

– Total elastic energy:

$$\mathcal{E} = \sum_{n=0}^{N-1} U(r_0 + u_{n+1} - u_n) \simeq \mathcal{E}_0 + \frac{k}{2} \sum_{n=0}^{N-1} (u_{n+1} - u_n)^2.$$

– Under load, each spring experiences same force f_{ext} , and so has elongation $\Delta r = f_{ext}/k$

– Total chain elongation $\Delta L = N\Delta r$, and $L = Nr_0$.

– Relation between force and strain $\gamma = \Delta L/L$: $f_{ext} = kr_0\gamma$.

• Consider now 3D crystal:

– lateral surface area $S = (pr_0)^2$.

– Applied force $F_{ext} = \sigma S$; σ : stress.

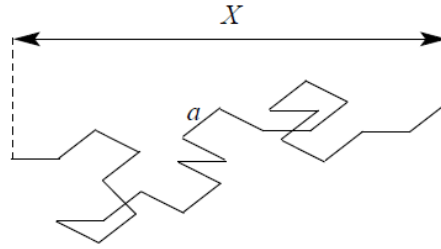
– Applied force per chain: $f_{ext} = F_{ext}/p^2$.

– Thus, linear relationship between stress and strain: $\sigma = E\gamma$, with $E = k/r_0$: Young's modulus.

4.1.2 Solids with low cohesive energy

• many substances (e.g. rubber, plastic,...) are made of long molecules: polymers (see Sect. 3.1).

– many possible configurations for every chain: $\bar{E} \ll TS$. Then $F \simeq -T \left(\frac{\partial S}{\partial L}\right)_T$.



- Entropic origin of the restoring force: when L increases, the number of conformations decreases.
- Non-linear relationship between F and L , except for very small deformation: $F = kL$ with $k = 3k_B T / (Na^2)$, for a chain made of N monomers with size a . See Practice ??.

4.2 Viscosity of Fluids

- Newtonian fluids: components of viscous stress tensor proportional to velocity gradients:

$$\sigma_{ij} = -p\delta_{ij} + \sum_{k,l} \Lambda_{ijkl} v_{kl}$$

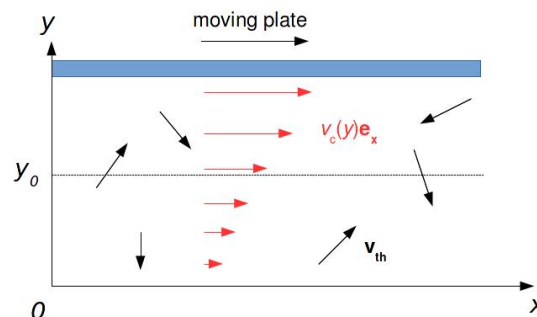
- two independent viscosities for an isotropic fluid: shear viscosity η and bulk viscosity ζ .
- Navier-Stokes equation:

$$\rho \frac{d\mathbf{v}}{dt} = \rho \mathbf{g} - \nabla p + \eta \nabla^2 \mathbf{v} + \left(\frac{\eta}{3} + \zeta \right) \nabla (\nabla \cdot \mathbf{v})$$

- Incompressible fluids: $\nabla \cdot \mathbf{v} = 0$.

4.2.1 Viscosity (and Pressure) of Gas

- Each molecule in a flowing gas has two contributions:
 - macroscopic, convective velocity \mathbf{v}_c
 - and microscopic thermal velocity \mathbf{v}_{th}
 - $\langle \mathbf{v}_{th} \rangle = \mathbf{0}$ (isotropy), but $\langle \|\mathbf{v}_{th}\| \rangle$ (or $\sqrt{\langle v_{th}^2 \rangle}$) $\gg \|\mathbf{v}_c\|$.
 - For ideal (or very diluted) gas: $m \langle \|\mathbf{v}_{th}\|^2 \rangle / 2 = 3k_B T / 2$.
 - Assume fast thermal equilibrium: T is uniform $\rightarrow \langle \|\mathbf{v}_{th}\|^2 \rangle$ not perturbed by the convective flow.



- Origin of viscosity: displacement of an infinite plate in a viscous fluids induces flow within the fluids, and friction on the plate \rightarrow diffusion of macroscopic momentum caused by thermal agitation of the atoms.

Rk: viscous term in Navier-Stokes equation $\eta \nabla^2 \mathbf{v}$ similar to diffusive term: viscosity = diffusion

of momentum

- Two mechanisms: transport and collisions. For diluted gas: mainly transport.
- What is the variation between t and $t + dt$ of the momentum of the gas located in the domain $y \leq y_0$ (**note**: this is an open system, but with fixed mass !) ?
- Simple (yet exact !) model: thermal agitation: molecules move along x, y, z directions only, with velocity $\pm v_{th}$, with $v_{th} = \sqrt{3k_B T/m}$.
- dN_- molecules leave the domain $y \leq y_0$, and dN_+ enter in it.
- steady regime: $dN_- = dN_+ = nv_{th}Sdt/6$, where n is the volumic density, and S the surface area at $y = y_0$.
- each molecule “carries” momentum $\mathbf{p}_{\pm} = m\mathbf{v}_c(y_0 \pm \bar{l}) \mp mv_{th}\mathbf{e}_y$. Note: \bar{l} : is the mean free path (i.e. distance since last collision), and we assumed that $\bar{l} \gg v_{th}dt$ (time between 2 collisions $\gg dt$), so all particles in the layer $[y_0, y_0 + v_{th}dt[$ had their last collision in $y_0 + \bar{l}$ and so carry the same convective velocity (between two collisions, the momentum of a particle is conserved).
- Variation of momentum:

$$d\mathbf{P} = dN_+\mathbf{p}_+ - dN_-\mathbf{p}_-$$

$$\frac{d\mathbf{P}}{dt} \simeq \frac{1}{3}nmS\bar{l}v_{th} \left(\frac{\partial v_c}{\partial y} \right)_{y=y_0} \mathbf{e}_x - \frac{1}{3}nmSv_{th}^2 \mathbf{e}_y$$

Note: Taylor expansion of $\mathbf{v}_c(y_0 \pm \bar{l})$ valid for \bar{l} large but finite (think of small spherical, rather than punctual, particles).

– From Newton’s second law, this variation is equal to the force applied on the domain $y \leq y_0$: $\mathbf{F}_{y_0^+ \rightarrow y_0^-} = S\boldsymbol{\sigma} \cdot \mathbf{e}_y = S(\sigma_{xy}\mathbf{e}_x + \sigma_{yy}\mathbf{e}_y)$, where $\boldsymbol{\sigma}$ is the stress tensor.

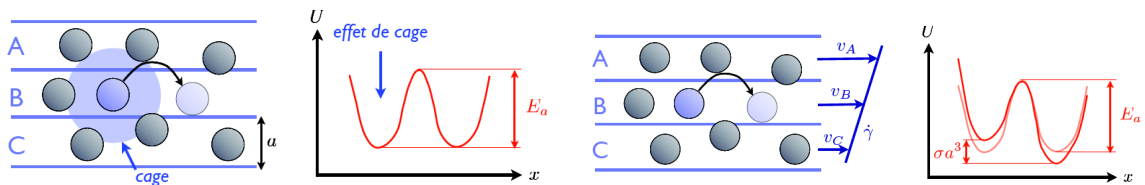
– the shear stress is then proportional to the shear rate $\dot{\gamma} = \left(\frac{\partial v_c}{\partial y} \right)_{y=y_0}$: $\sigma_{xy} = \eta\dot{\gamma}$. The prefactor η is called *shear viscosity*:

$$\eta = \frac{1}{3}nm\bar{l}v_{th}$$

- η increases when T increases for a gas.
- Note: for ideal gas: $\bar{l} \rightarrow \infty$, so uniform convective velocity, and thus $\eta = 0$.
- Pressure $P = -\sigma_{yy} = nk_B T$: this is the ideal gas law !

4.2.2 Viscosity of Liquids (Eyring model)

• Here $\varepsilon_c \sim k_B T$: we cannot neglect the interactions anymore. Eyring model: rows of atoms jumps from 1 “cage” to another with frequency $\nu = \nu_0 e^{-E_a/(k_B T)}$ (Arrhenius law), where E_a is the energy barrier.



- In absence of applied stress: $\nu_+ = \nu_-$.
- If a shear stress is applied in the x direction, the energy landscape is not symmetrical anymore: The barrier to cross to jump in the direction of the applied force is $E_a - W$, and the barrier to cross in the opposite direction is $E_a + W$, where W denotes the work associated with the applied constraint: $W \simeq \sigma a^3/2$.
- Respective frequency of jumps:

$$\nu_{\pm} = \nu_0 e^{-\frac{E_a \mp W}{k_B T}}$$

– Relative displacement per unit time (=velocity) of the row:

$$v = \nu_+ a - \nu_- a = 2a\nu_0 e^{-\frac{E_a}{k_B T}} \operatorname{sh} \left(\frac{\sigma a^3}{2k_B T} \right) \simeq \frac{a^4 \nu_0 \sigma}{k_B T} e^{-\frac{E_a}{k_B T}}$$
$$\Leftrightarrow \sigma \simeq \eta \dot{\gamma},$$

with $\dot{\gamma} = v/a$ (shear rate) and $\eta = \frac{k_B T}{\nu_0 a^3} e^{E_a/(k_B T)}$.

– **The shear viscosity η of a liquid decreases as T increases** (dominant term is the exponential). Here the thermal agitation “struggles” against cohesive interactions in the liquid.