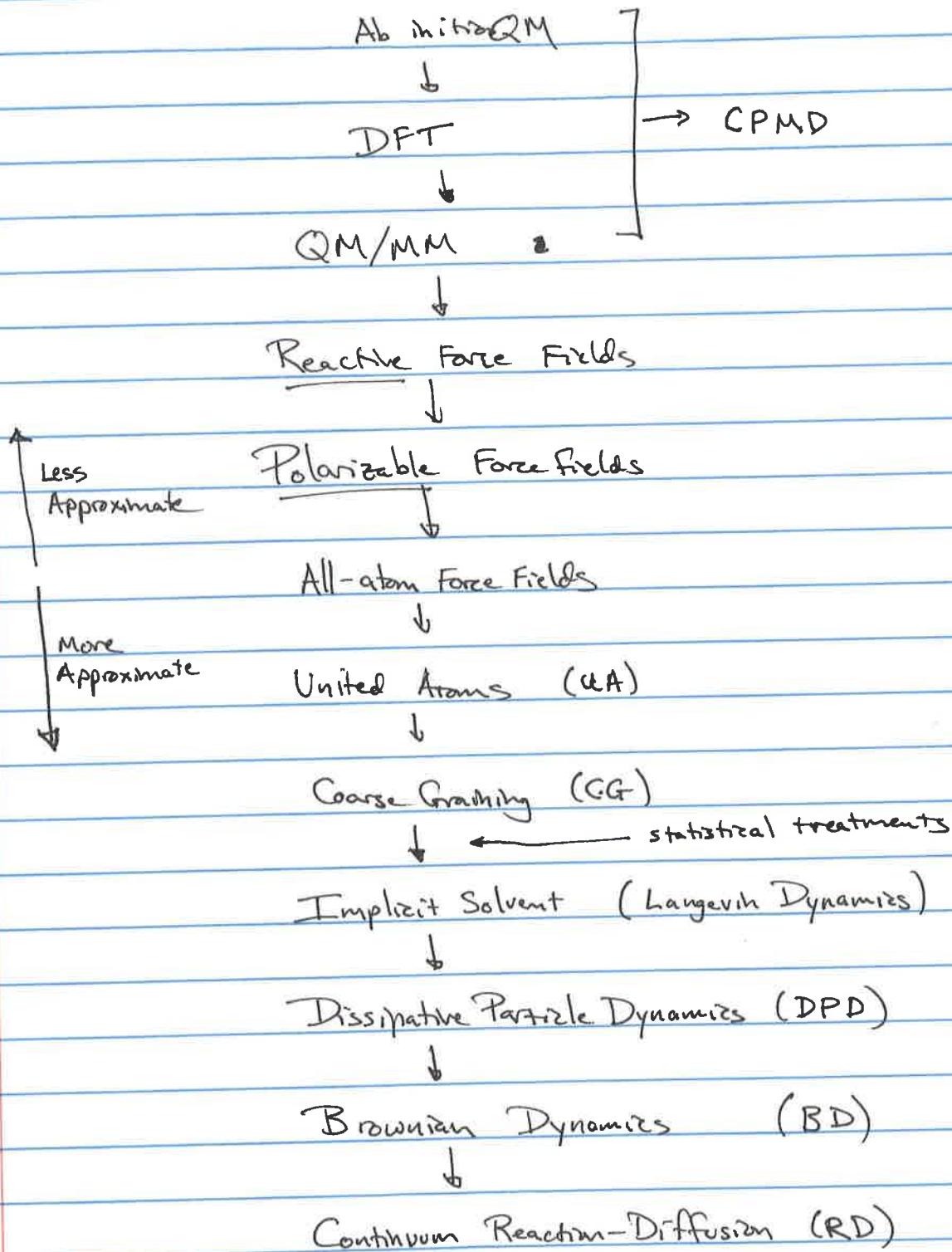


## A hierarchy of simplifications

⑥



(1)

## Simplifying systems

We often want to reduce the number of things we are simulating to save time and to concentrate on only the relevant phenomena.

Suppose our solvent only weakly interacts with our system of interest. We might want to treat the solvent as if it were a continuous medium.

- This might alter electrostatics → continuum dielectric

$$V_{ij} = \frac{q_i q_j}{4\pi \epsilon_0 \epsilon} \leftarrow \text{effective dielectric of solvent}$$

- It also might alter the dynamics of how particles move.

Stokes' Law (1851): frictional force experienced

Ball being dragged through water by a sphere moving with a velocity  $\vec{v}$ :

$$\vec{F}_f = -\zeta \vec{v}$$

$\zeta$  friction coefficient

$$= -6\pi R \eta \vec{v}$$

$R$  radius of ball  $\eta$  dynamic viscosity of fluid

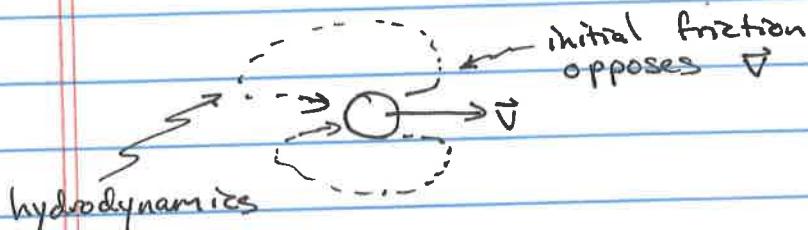
Stokes' Law assumes laminar flow around the sphere



But most fluids are going to be less than laminar around molecules

(2)

A more realistic picture of friction in a fluid takes solvent memory into account:



can make negative friction, but delayed in time

$$\vec{F}_f = - \int_0^t \xi(t-t') \vec{v}(t') dt'$$

$\xi$  previous history is important for hydrodynamic friction kernel

Let's assume we've got a solvent that doesn't have memory

$$\vec{F}_f = - \xi_0 \vec{v}$$

And we'll assume all of our simulated atoms are spheres that interact with the fluid without interference from each other:  $\vec{F}_f = -6\pi R \eta \vec{v}$

A ball in a fluid also experiences random fluctuating forces from the fluid  $\rightarrow$  Brownian Motion

$$m \ddot{x}(t) = \underbrace{-\frac{\partial}{\partial x} V(x)}_{\text{system forces}} - \underbrace{6\pi R \eta \vec{v}(t)}_{\text{Friction}} + \underbrace{R(t)}_{\text{Random}}$$

(from force field)

$R(t)$  is tied to the friction!

$$\langle R(t) \rangle = 0$$

$$\langle R(t) R(t') \rangle = \frac{\delta(t-t') 2k_B T}{M \xi_0}$$

(3)

These equations are called the "second fluctuation-dissipation theorem" and we can say some things about  $R(t)$ :

$R(t)$  is a gaussian random variable with

- 0 mean

- 2<sup>nd</sup> moment =  $\frac{2k_B T}{m \int dt}$

time step

- Friction is tied to Brownian forces!

We can also define the Langevin Equation:

LF:  $m\ddot{x} = -\frac{\partial V(x)}{\partial x} - \zeta \dot{x} + R(t)$

$\zeta$   $\uparrow$  tied together!

For fluids with hydrodynamics the Generalized Langevin equation must be used:

GLE:  $m\ddot{x} = -\frac{\partial V(x)}{\partial x} - \int_0^t dt' \dot{x}(t') \zeta(t-t') + R(t)$

$$\langle R(t)R(t') \rangle = k_B T \zeta(t-t')$$

Random force  
isn't random  
anymore!

Advantages of the Langevin approach:

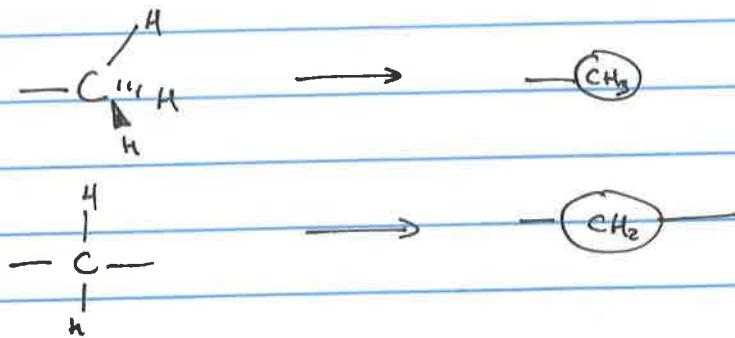
- No solvent degrees of freedom
- Samples NVT for solutes
- Simple

Disadvantages:

- No solvent
- No Solvent-mediated interactions!

(4)

### United Atom



usually the  
simplest and  
easiest to  
unify!

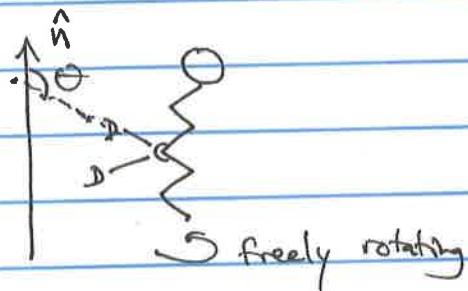
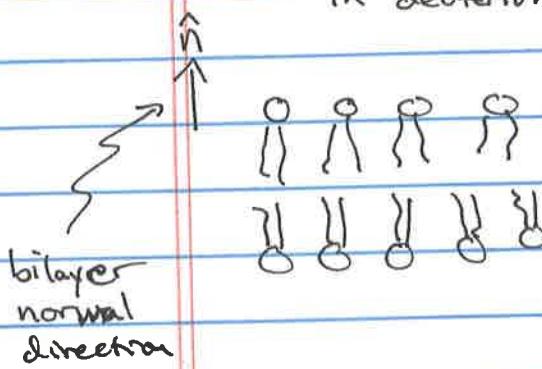
A few minor issues: in lipid bilayers, experiments measure:

$$\Delta \gamma_d = \frac{3}{4} \left( \frac{e^2 q Q}{h} \right) S_{CD}$$

Carbon-deuterium  
order parameter

quadrupolar splitting measured  
in deuterium NMR

quadrupolar coupling constant

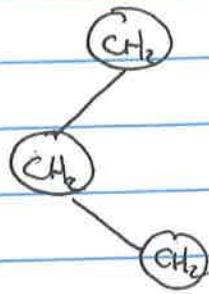


$S_{CD}$  → degree of reorientation that happens on NMR timescales = how ordered C-D bonds are & average orientation

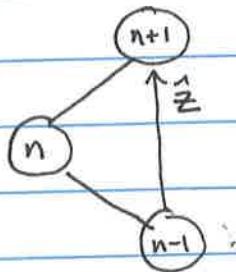
- 1  $S_{CD} \approx -0.2$  order in chain heads  $\perp$  to  $\hat{n}$
- 2  $S_{CD} \approx 0$  disorder in chain tails

Challenges of UA:

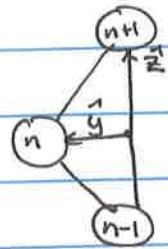
(5)



← where's the CD bond?



$\vec{z}$  = vector from  
 $n-1 \rightarrow n+1$

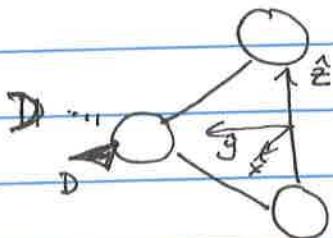


$\vec{y}$  = vector  
from  
 $\vec{z}$  midpoint  
to  $n$

$$\hat{x} = \hat{y} \times \hat{z}$$

$\hat{x}$  is automatic!

CD bonds probably lie in  $x, y$  plane!

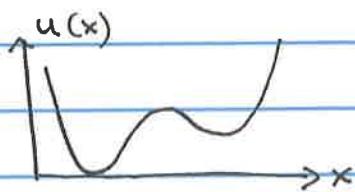


← even in UA models  
we can derive likely  
H-atom positions!

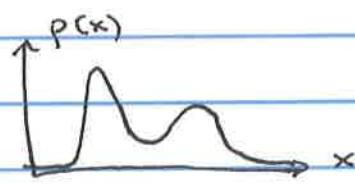
(6)

## Coarse Graining

If we have a potential energy function  $u(x)$ ,



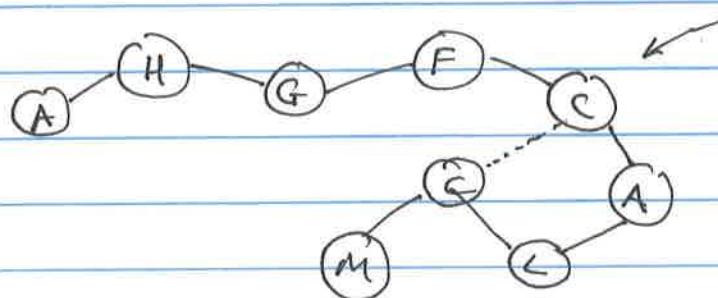
the probability of observing a particular value of  $x$  is proportional to  $e^{-u(x)/k_B T}$



$$p(x) \propto e^{-u(x)/k_B T}$$

Now suppose we observe a probability distribution in real life  $p(x)$ . We can theorize about the existence of a statistical potential  $U(x) = -k_B T \ln p(x)$

A statistical potential is exactly this: A number of protein force fields have been created by scanning the entire protein data bank (PDB) to accumulate statistics on the relative appearance statistics of amino acid distance pairings. From this, a potential library at the amino acid residue level can be compiled



Residue-level beads is a form of coarse-graining

## Other non-statistical CG approaches

(7)



SCB, one of a class of liquid crystalline molecules

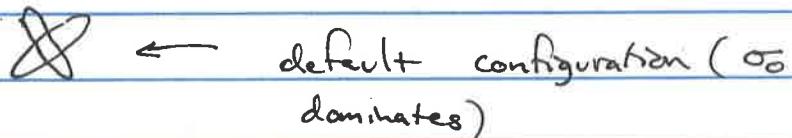
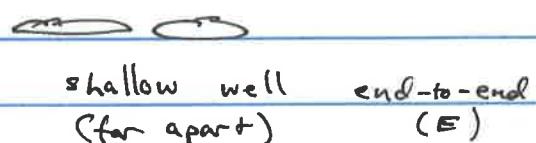
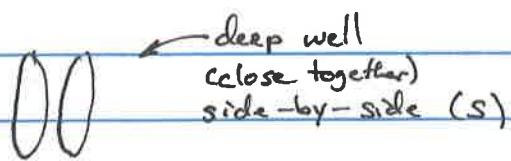
In many liquid crystals the molecule is made up of 1 or 2 rigid rod-like structures, decorated with various polar or non-polar functional groups.

A common CG method in LC simulations is the Gay-Berne potential which is an extension of Lennard-Jones to ellipsoidal shapes



$$V_{ij} = 4\epsilon(r_{ij}, \hat{u}_i, \hat{u}_j) \left[ \left( \frac{\sigma_0}{r_{ij} - \sigma(r_{ij}, \hat{u}_i, \hat{u}_j) - \sigma_0} \right)^{12} - \left( \frac{\sigma_0}{r_{ij} - \sigma(r_{ij}, \hat{u}_i, \hat{u}_j) - \sigma_0} \right)^6 \right]$$

$\sigma(r_{ij}, \hat{u}_i, \hat{u}_j)$  and  $\epsilon(r_{ij}, \hat{u}_i, \hat{u}_j)$  are both functions of the relative orientations of the two molecules:

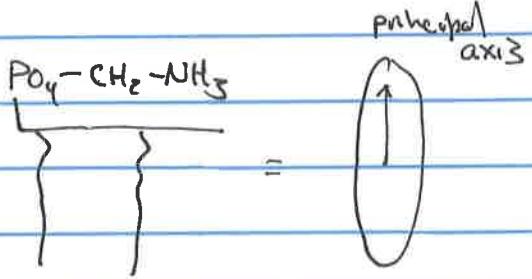


Can also be used for discatics (molecules that are mostly planar)



(8)

## Ordering in rod-like molecules

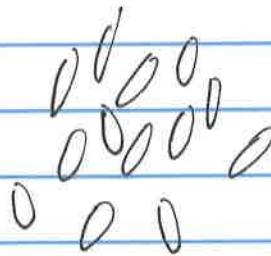


Phases:



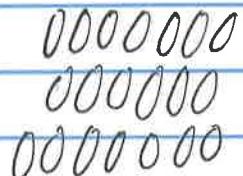
isotropic

(no translational or  
orientational order)



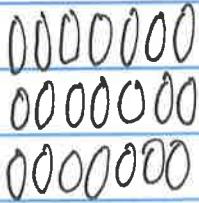
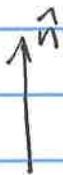
nematic

(only orientational  
order)

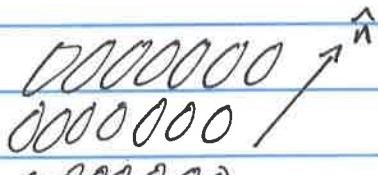


smectic

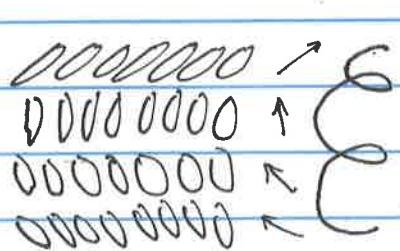
orientational +  
1-D translational  
order



smectic A

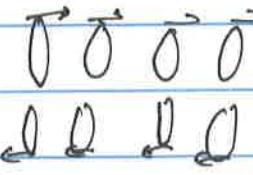


smectic C



smectic C\*  
(polarizes light!)

Lipids also have complicated phases



bilayer

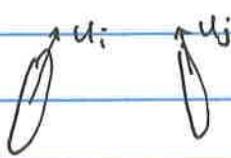


micelles

... bicontinuous, vesicles, etc.

(9)

### Measuring order in long molecules



$\hat{u}_i$  lies along principal axis  
of molecule i

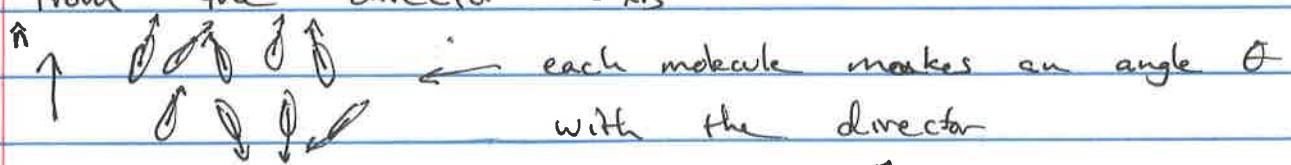
$$\vec{Q} = \begin{pmatrix} Q_{xx} & Q_{xy} & \dots \\ Q_{yx} & Q_{yy} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \text{ or } Q_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^N \left[ \frac{3}{2} \left( U_{i\alpha} U_{i\beta} - \frac{1}{2} \delta_{\alpha\beta} \right) \right]$$

ordering tensor

Diagonalizing  $\vec{Q}$  gives 3 eigenvalues,  $\lambda_+, \lambda_0, \lambda_-$   
which sum to zero.

If  $\lambda_+$  is the largest eigenvalue, the director axis  
 $\hat{n}$  is the eigenvector of  $\vec{Q}$  corresponding to that  
eigenvalue.

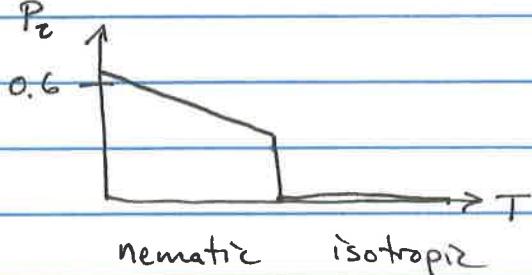
The orientational order parameter measures deviation  
from the director axis



$$\cos \theta_i = \hat{n} \cdot \hat{u}_i$$

$$\overline{P}_2 = \langle P_2(\cos \theta) \rangle = \frac{1}{N} \sum_{i=1}^N \left( \frac{3}{2} \cos^2 \theta_i - \frac{1}{2} \right)$$

$P_2$  2nd Legendre polynomial



$\bar{P}_2$  measures orientational ordering



00000000  
00000000  
00000000

$\rho(z) =$  density projected along director axis  
(can identify smectic A  $\rightarrow$  nematic)

For smectic C, we need more sophisticated  
orderly measures:

$$\rho(r) = \rho_0 + \rho_1 \cos(q_s z - \phi) + \dots$$

$\brace{\text{average density}}$        $\brace{\text{phase angle}}$

$$\psi(\vec{r}) = \rho(\vec{r}) e^{i\phi(\vec{r})}$$

$\brace{\text{density of molecules}}$        $\brace{\text{spatial order of phase angles}}$

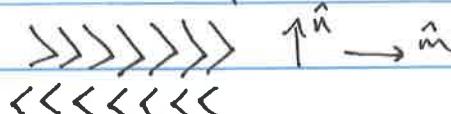
Fourier analysis to find other structure

Other "mesophases"

$$\begin{array}{c} + - \\ \diagup \quad \diagdown \\ \text{II} \end{array} = \begin{array}{c} \uparrow \rightarrow \\ \text{II} \end{array} = 2 \text{ important axes} \quad \begin{array}{l} \hat{u} = \text{principal axis} \\ \hat{v} = \text{dipolar axis} \end{array}$$

or

Molecules without cylindrical symmetry can have multiple  
orientational order parameters: and multiple director axes



chevron phases can  
have non-linear optical props!