P6: *Implementation of the pressure profile calculation in spherical coordinates*

AIST / CREST-JST

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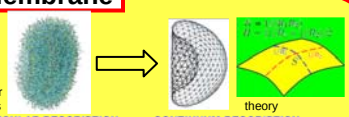
Background: Characterization of inhomogeneous nature

Micro → Pressure Profile → Macro

Fluid Membrane



Elastic coefficients are obtained by the pressure profile

$$P^{\alpha\beta}(x)=\sum_{i=1}^{N_b}\frac{p_i^\alpha p_i^\beta}{m_i}\delta(x-r_i) \qquad F[S]=\int dS\left[\kappa_c(H(S)-H_0)^2+\kappa_g K(S)\right]$$

$$-\sum_{i=1}^{N_b}\nabla_i^\alpha\Phi\int_{\ell=0}^{r_{ij}}d\ell^\beta\delta(x-\ell)$$

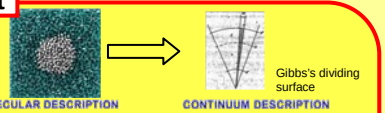
$$\kappa_g=-\int_0^{\lambda_0}d\zeta\zeta^2\left[P^{\mathrm{T}}(\zeta)-P^{\mathrm{N}}(\lambda_0)\right]$$

$$\kappa H_0=\int_0^{\lambda_0}d\zeta\zeta\left[P^{\mathrm{T}}(\zeta)-P^{\mathrm{N}}(\lambda_0)\right]$$

bending modulus
saddle splay modulus
spontaneous curvature

Pressure formula for the flat membrane

Droplet



surface property are obtained by the pressure profile

$$P^{\alpha\beta}(x)=\sum_{i=1}^{N_b}\frac{p_i^\alpha p_i^\beta}{m_i}\delta(x-r_i)$$

$$-\sum_{i=1}^{N_b}\nabla_i^\alpha\Phi\int_{\ell=0}^{r_{ij}}d\ell^\beta\delta(x-\ell)$$

$$\sigma_S=\int_0^\infty dr\left(\frac{r}{R_S}\right)^2\left[P^{\mathrm{N}}(r)-P^{\mathrm{T}}(r)\right]$$

$$R_S^3=\int_0^\infty drr^2\left[P^{\mathrm{N}}(r)-P^{\mathrm{T}}(r)\right]\Big/\int_0^\infty dr\frac{\left[P^{\mathrm{N}}(r)-P^{\mathrm{T}}(r)\right]}{r}$$

$$p_\alpha-p_\beta=\frac{2\sigma_s}{R_s}$$

surface tension
surface of tension
Laplace equation at surface of tension

Implementations of Pressure Profile Calculation (previous work & our work)

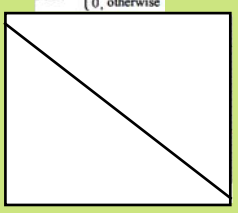
	Ollila et al. (2009)	Goetz et al. (1998)	Our work (2011 JCP)
Target system	Arbitrary shape	planar symmetry	spherical symmetry
Argument of pressure tensor	position vector $\boldsymbol{x}$	Cartesian-coordinate z	Radial-coordinate r
Numerical accuracy	×	○	○

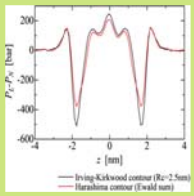
Ollila,et al.,PRL 102, 078101(2009)

Pressure as a function of position vector

$$p_V^{\alpha\beta}=\frac{1}{V}\sum_{i\in V}m_i v_i^\alpha v_i^\beta+\sum_n\frac{1}{nV}\sum_{\langle j\rangle}\sum_{\langle k,l\rangle}(\nabla_{j_k}^\alpha U^n-\nabla_{j_l}^\alpha U^n)\frac{r_{j_l j_k}^\beta}{N}\sum_{\lambda=0}^{N}f_V(\mathbf{r}_{j_l}+\frac{\lambda}{N}\mathbf{r}_{j_l j_k})$$

$$f_V(\mathbf{r})=\begin{cases}1, \text{ if } \mathbf{r}\in V\\ 0, \text{ otherwise}\end{cases}$$





DMPC + Water W. Shinoda, et.al; J. Phys. Chem. B, 114, 6836, (2010)

Pressure as a function of z (= coordinate normal to interface)

$$[\overline{\sigma}_{\mathrm{in}}^{\alpha\beta}]^{(m)}(z_s)=-\frac{1}{mV_{\Delta z}}\sum_{\langle j\rangle}\sum_{\langle k,l\rangle}(\nabla_{j_k}^\alpha U^{(m)}-\nabla_{j_l}^\alpha U^{(m)})r_{j_k j_l}^\beta f(z_{j_k},z_{j_l},z_s)$$

$$f(z_1,z_2,z_s)\equiv\begin{cases}\theta(z_1-z_s)\theta(z_s+\Delta z-z_1) & \text{for } z_1=z_2\\ \dfrac{1}{z_2-z_1}\displaystyle\int_{z_1}^{z_2}d\zeta\theta(\zeta-z_s)\theta(z_s+\Delta z-\zeta) & \text{otherwise}\end{cases}$$

Goetz, et al., J. Chem. Phys. 108, 7397(1998)

Theory

Stress tensor in spherical coordinate system

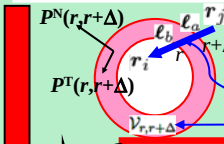
$$\mathbf{P}(\boldsymbol{x})=\sum_{i=1}^{N_f}\frac{\boldsymbol{p}_i\circ\boldsymbol{p}_i}{m_i}\delta(\boldsymbol{x}-\boldsymbol{r}_i)+\sum_{m\geq 2}\sum_{\langle j\rangle}\mathbf{P}_{\langle j\rangle}^{[m]}(\boldsymbol{x})$$

←Decomposition of the pressure to the contribution of the cluster $\langle j\rangle$

$\boldsymbol{P}_{i;j}(\boldsymbol{x})$←$i$-$j$ contour's contribution of the pressure in cluster $\langle j\rangle$

$$\mathbf{P}_{i;j}(r,r+\Delta)=\frac{1}{|\mathcal{V}_{r,r+\Delta}|}\int_{r<|\boldsymbol{x}|\leq r+\Delta}d\boldsymbol{x}\boldsymbol{P}_{i;j}(\boldsymbol{x})$$

← Definition of slice average



Irving-Kirkwood contour (straight line segment)

Volume of the slice

$$|\mathcal{V}_{r,r+\Delta}|=\frac{4\pi\left[(r+\Delta)^3-r^3\right]}{3}$$

$$P_{i;j}^{\mathrm{T}}(r,r+\Delta)=\frac{1}{|\mathcal{V}_{r,r+\Delta}|}\left[\frac{(\boldsymbol{F}\cdot\boldsymbol{r}_{ji})|\boldsymbol{r}_{ji}\times\boldsymbol{\ell}|}{2r_{ji}^2}\arctan\frac{(\boldsymbol{r}_{ji}\cdot\boldsymbol{\ell})}{|\boldsymbol{r}_{ji}\times\boldsymbol{\ell}|}+\frac{(\boldsymbol{F}\times\boldsymbol{r}_{ji})\cdot(\boldsymbol{r}_{ji}\times\boldsymbol{\ell})}{2r_{ji}^2}\ln|\boldsymbol{\ell}|\right]_{\boldsymbol{\ell}=\boldsymbol{\ell}_a}^{\boldsymbol{\ell}=\boldsymbol{\ell}_b}$$

$$P_{i;j}^{\mathrm{N}}(r,r+\Delta)=\frac{\boldsymbol{F}\cdot(\boldsymbol{\ell}_b-\boldsymbol{\ell}_a)}{|\mathcal{V}_{r,r+\Delta}|}-2P_{i;j}^{\mathrm{T}}(r,r+\Delta)$$

Choice of contours for many body force field

Conventions to define local pressure	Pair, Bond (m=2)	Angle (m=3)	Torsion (m=4)
$m(m-1)/2$ contours Both arctan and ln are used	Functions used in convention 1		Every points in are equally treated
m-1 contours Either arctan or ln is used	Functions used in convention 2		"2" is special point in the cluster

Type of the force field

type1
Pair potential
Bond potential
(Coulomb without Ewald)

$$V(\boldsymbol{r}_1,\boldsymbol{r}_2)=V(r)\quad\langle j\rangle=(1,2)$$

type2 Angle potential Torsion potential

$$V(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3)=V(\theta)\quad\langle j\rangle=(1,2,3)$$

$$V(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,\boldsymbol{r}_4)=V(\phi)\quad\langle j\rangle=(1,2,3,4)$$

Type 1

$$\boldsymbol{F}_i^{\mathrm{type1}}\{\boldsymbol{r}_{\langle j\rangle}\}=f_i^{\langle j\rangle}\boldsymbol{r}_{ji}$$

Type 2

$$\boldsymbol{F}_i^{\mathrm{type2}}\{\boldsymbol{r}_{\langle j\rangle}\}=\boldsymbol{f}_i^{\langle j\rangle}\times\boldsymbol{r}_{ji}$$

- Classified to two types
- Either the parallel to $\boldsymbol{r}_{ji}$ force or the normal to $\boldsymbol{r}_{ji}$ exists

Pressure profile formulae to implement

$$P_{i;j}^{\mathrm{T\ type\text{-}2}}(r)=-\frac{(\boldsymbol{F}_{i;j}^{\mathrm{type\text{-}2}}\cdot\boldsymbol{r}_j)}{2|\mathcal{V}_{r,r+\Delta}|}\ln\frac{\ell_b}{\ell_a}$$

$$P_{i;j}^{\mathrm{N\ type\text{-}2}}(r)=\frac{(\boldsymbol{F}_{i;j}^{\mathrm{type\text{-}2}}\cdot\boldsymbol{r}_j)}{|\mathcal{V}_{r,r+\Delta}|}\ln\frac{\ell_b}{\ell_a},$$

$$\sigma_a\equiv(\boldsymbol{r}_{ji}\cdot\boldsymbol{\ell}_a)\ P_{i;j}^{\mathrm{T\ type\text{-}1}}(r)=\frac{f_i^{\langle j\rangle}}{2|\mathcal{V}_{r,r+\Delta}|}\left[\omega\arctan\frac{\sigma}{\omega}\right]_{\sigma=\sigma_a}^{\sigma=\sigma_b}$$

$$\sigma_b\equiv(\boldsymbol{r}_{ji}\cdot\boldsymbol{\ell}_b)$$

$$\omega=|\boldsymbol{r}_{ji}\times\boldsymbol{\ell}|\ P_{i;j}^{\mathrm{N\ type\text{-}1}}(r)=\frac{f_i^{\langle j\rangle}}{|\mathcal{V}_{r,r+\Delta}|}\left[\sigma-\omega\arctan\frac{\sigma}{\omega}\right]_{\sigma=\sigma_a}^{\sigma=\sigma_b}$$

Implement into LAMMPS

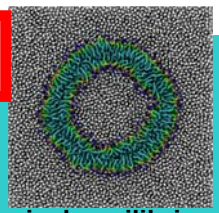
1. **Compute the center of mass of the assembly → global variable**
2. **Add the subroutine for**
   - pair.cpp, bond.cpp angle.cpp, dihedral.cpp, improper.cpp
3. **Call the subroutine just above** "ev_tally"
   - pair_*.cpp, bond_*.cpp, angle_*.cpp, dihedral_*.cpp, improper_*.cpp
4. **Modify compute_pressure.h and .cpp**
   → summation all contribution

- Too many files we need modify!.....

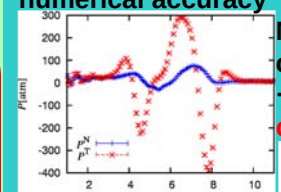
→How to pack them into one file??

Applications

DMPC+water = Liposome



Improvement of numerical accuracy

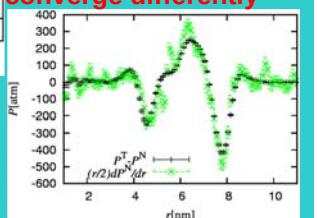


→High resolution evaluation of mechanical property

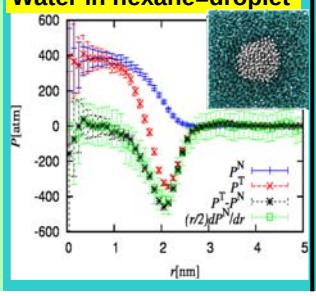
→Clear difference between the inner and outer membrane

Mechanical equilibrium condition $\frac{P^N-P^T}{2}=\frac{r}{2}\frac{dP^N}{dr}$

→two quantities converge differently



Water in hexane=droplet



C12E8+water=Micelle