Selective topics on single-component and multi-component hydrodynamics

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Multiscale modeling

- Many applications on mesoscopic modeling of soft matter and complex fluid systems (biomembrane, colloid, polymer melt, $\cdots$)

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Multiscale modeling

- Many applications on mesoscopic modeling of soft matter and complex fluid systems (biomembrane, colloid, polymer melt, $\cdots$)
- ***Question I***: why macroscopic/mesoscopic modeling equations are approximately self-determined?
- ***Question II***: where the macroscopic/mesoscopic modeling parameters (e.g., viscosity, surface tension) are originated from?

Governing principle

"...if we were to name the most powerful assumption of all, which leads one on and on in an attempt to understand life, it is that all things are made of atoms, and that everything that living things do can be understood in terms of the jigglings and wigglings of atoms."
– RICHARD FEYNMAN

Connection to reduced model

- Establish connection between macroscopic/mesoscopic models and microscopic model governed by Hamiltonian $H(\mathbf{r}, \mathbf{p})$

  $H(\mathbf{r}, \mathbf{p}) = \frac{1}{2}\mathbf{p}^T \mathbf{M}^{-1}\mathbf{p} + V(\mathbf{r})$,

  $\mathbf{r} = (\mathbf{r}_1^T, \mathbf{r}_2^T, \cdots, \mathbf{r}_N^T)^T, \mathbf{p} = (\mathbf{p}_1^T, \mathbf{p}_2^T, \cdots, \mathbf{p}_N^T)^T.$
- Linearized one-component hydrodynamics
  - Macro - Micro linkage
  - Micro - Macro linkage
- Multiphase/multicomponent flow systems
  - Surface tension: macroscopic limit
  - Thermal fluctuating interface

Outline

One-component linearized hydrodynamics

- Macro-micro linkage
- Micro-Marco linkage

Multicomponent interfacial flow

Application

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- One-component linearized hydrodynamics
  - Macro-micro linkage
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- Multicomponent interfacial flow
- Application

Governing conservation law

- Conservation of local mass, momentum and energy

$$m\frac{\partial}{\partial t}\rho(\mathbf{r},t) + \nabla\cdot\mathbf{p}(\mathbf{r},t) = 0 \tag{1.1a}$$

$$\frac{\partial}{\partial t}\mathbf{p}(\mathbf{r},t) + \nabla\cdot\mathbf{\Pi}(\mathbf{r},t) = 0 \tag{1.1b}$$

$$\frac{\partial}{\partial t}e(\mathbf{r},t) + \nabla\cdot\mathbf{J}^e(\mathbf{r},t) = 0 \tag{1.1c}$$

  $\mathbf{p}$-momentum, $\mathbf{\Pi}$-stress tensor, $\mathbf{J}^e$-energy flux
- We assume mean velocity $\langle\mathbf{u}(\mathbf{r},t)\rangle = 0$, local deviations of the hydrodynamic variables is small.
- Linearized transport equations can be established by choosing proper constitutive models of $\mathbf{p}(\mathbf{r},t)$, $\mathbf{\Pi}(\mathbf{r},t)$ and $\mathbf{J}^e(\mathbf{r},t)$.

Balescu, R., *Statistical dynamics: matter out of equilibrium*, 1997

Conservation of mass

- First order approximation of $\mathbf{p}(\mathbf{r}, t)$

$$\mathbf{p}(\mathbf{r}, t) = m\left[\rho + \delta\rho(\mathbf{r}, t)\right]\mathbf{u}(\mathbf{r}, t) \approx m\rho\mathbf{u}(\mathbf{r}, t) := m\mathbf{j}(\mathbf{r}, t) \tag{1.2}$$

ρ- bulk number density, $\mathbf{j}$- particle number current

- Mass transport equation

$$\frac{\partial}{\partial t}\delta\rho(\mathbf{r}, t) + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0 \tag{1.3}$$

Conservation of momentum

- Macroscopic modeling of stress tensor

$$\Pi^{\alpha\beta}(\mathbf{r},t) = \delta_{\alpha\beta}P(\mathbf{r},t) - \eta\left(\frac{\partial u_\alpha(\mathbf{r},t)}{\partial r_\beta} + \frac{\partial u_\beta(\mathbf{r},t)}{\partial r_\alpha}\right) + \delta_{\alpha\beta}\left(\frac{2}{3}\eta - \zeta\right)\nabla\cdot\mathbf{u}(\mathbf{r},t) \quad (1.4)$$

  η- shear viscosity, ζ- bulk viscosity, $P(\mathbf{r},t)$- local pressure, α,β- x,y,z.

- Momentum transport equation

$$\frac{\partial}{\partial t}\mathbf{p}(\mathbf{r},t) + \nabla\cdot\mathbf{\Pi}(\mathbf{r},t) = 0, \qquad \mathbf{p}(\mathbf{r},t) \approx m\mathbf{j}(\mathbf{r},t)$$

$$\frac{\partial}{\partial t}\mathbf{j}(\mathbf{r},t) + \frac{1}{m}\nabla P(\mathbf{r},t) - \nu\nabla^2\mathbf{j}(\mathbf{r},t) - \frac{\eta/3+\zeta}{\rho m}\nabla\nabla\cdot\mathbf{j}(\mathbf{r},t) = 0$$

  $\nu = \eta/\rho m$ - kinetic viscosity

Landau, L. D. and Lifshitz, E. M., *Fluid Mechanics*, 1987

Conservation of momentum

- First order approximation of local pressure $P(\mathbf{r}, t)$

$$\begin{aligned}\delta P(\mathbf{r}, t) &= \left(\frac{\partial P}{\partial \rho}\right)_T \delta\rho(\mathbf{r}, t) + \left(\frac{\partial P}{\partial T}\right)_\rho \delta T(\mathbf{r}, t) \\ &= \frac{1}{\rho \chi_T}\delta\rho(\mathbf{r}, t) + \beta_v \delta T(\mathbf{r}, t)\end{aligned} \tag{1.5}$$

$\chi_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T$ - isothermal compressibility, $\beta_v = \left(\frac{\partial P}{\partial T}\right)_\rho$ - thermal pressure coefficient.

- Linearized momentum transport (Navier-Stokes) equation can be written as

$$\frac{1}{\rho m \chi_T}\nabla\delta\rho(\mathbf{r}, t) + \frac{\beta_v}{m}\nabla\delta T(\mathbf{r}, t) + \left(\frac{\partial}{\partial t} - \nu\nabla^2 - \frac{\eta/3 + \zeta}{\rho m}\nabla\nabla\cdot\right)\mathbf{j}(\mathbf{r}, t) = 0 \tag{1.6}$$

- Energy transport equation can be formulated in a similar manner

Long wave length limit

- Define Fourier-Laplace transform

$$\tilde{\mathbf{f}}_{\mathbf{k}}(s) = \int_0^\infty dt e^{ist} \int \mathbf{f}(\mathbf{r}, t) e^{-i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} \tag{1.7}$$

- Mass and momentum transport equations can be re-written as

$$\begin{cases} \frac{\partial}{\partial t}\delta\rho(\mathbf{r}, t) + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0 \\ -is\tilde{\rho}_{\mathbf{k}}(z) + i\mathbf{k} \cdot \tilde{\mathbf{j}}_{\mathbf{k}}(s) = \rho_{\mathbf{k}} \end{cases} \tag{1.8}$$

$$\begin{cases} \frac{\nabla\delta\rho(\mathbf{r}, t)}{\rho m \chi_T} + \frac{\beta_v}{m}\nabla\delta T(\mathbf{r}, t) + \left(\frac{\partial}{\partial t} - \nu\nabla^2 - \frac{\eta/3 + \zeta}{\rho m}\nabla\nabla\cdot\right)\mathbf{j}(\mathbf{r}, t) = 0 \\ \frac{\tilde{\rho}_{\mathbf{k}}(s)}{\rho m \chi_T} i\mathbf{k} + \frac{\beta_v}{m} i\mathbf{k}\tilde{T}_{\mathbf{k}}(s) + \left(-is + \nu k^2 + \frac{\eta/3 + \zeta}{\rho m}\mathbf{k}\mathbf{k}\cdot\right)\tilde{\mathbf{j}}_{\mathbf{k}}(s) = \mathbf{j}_{\mathbf{k}} \end{cases} \tag{1.9}$$

$\rho_{\mathbf{k}}$, $\mathbf{j}_{\mathbf{k}}$- Fourier mode of $\delta\rho(\mathbf{r}, 0)$, $\mathbf{j}(\mathbf{r}, 0)$

Long wave length limit

- Taking $\mathbf{k}$ along z direction, momentum transport equation Eq. (1.9) can be written by

$$\begin{cases} \frac{\tilde{\rho}_{\mathbf{k}}(s)}{\rho m \chi_T} i\mathbf{k} + \frac{\beta_v}{m} i\mathbf{k}\tilde{T}_{\mathbf{k}}(s) + \left(-is + \nu k^2 + \frac{\eta/3+\zeta}{\rho m}\mathbf{k}\mathbf{k}\cdot\right)\tilde{\mathbf{j}}_{\mathbf{k}}(s) = \mathbf{j}_{\mathbf{k}} \\ \frac{1}{\rho m \chi_T} ik\tilde{\rho}_k(s) + \frac{\beta_v}{m} ik\tilde{T}_k(s) + \left(-is + \frac{\frac{4\eta}{3}+\zeta}{\rho m}k^2\right)\tilde{j}^z_k(s) = j^z_k \\ \left(-is + \nu k^2\right)\tilde{j}^\alpha_k(s) = j^\alpha_k, \alpha = x, y \end{cases}$$

- In particular, we analyze the transverse mode along x, y direction.

Long wave length limit

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$$\begin{cases} \frac{\tilde{\rho}_{\mathbf{k}}(s)}{\rho m \chi_T} i\mathbf{k} + \frac{\beta_v}{m} i\mathbf{k}\tilde{T}_{\mathbf{k}}(s) + \left(-is + \nu k^2 + \frac{\eta/3+\zeta}{\rho m}\mathbf{k}\mathbf{k}\cdot\right)\tilde{\mathbf{j}}_{\mathbf{k}}(s) = \mathbf{j}_{\mathbf{k}} \\ \frac{1}{\rho m \chi_T} ik\tilde{\rho}_k(s) + \frac{\beta_v}{m} ik\tilde{T}_k(s) + \left(-is + \frac{\frac{4\eta}{3}+\zeta}{\rho m}k^2\right)\tilde{j}^z_k(s) = j^z_k \\ \boxed{\left(-is+\nu k^2\right)\tilde{j}^\alpha_k(s) = j^\alpha_k}, \alpha = x, y \end{cases}$$

- In particular, we analyze the transverse mode along x, y direction.

Transverse mode analysis I

- Transverse current follows

$$\frac{\partial}{\partial t} j_k^x(t) = -\nu k^2 j_k^x(t) \tag{1.10}$$

- Multiply $j_{-k}^x(0)$, taking ensemble average yields

$$\frac{\partial}{\partial t} C_t(k,t) + \nu k^2 C_t(k,t) = 0 \tag{1.11}$$

where $C_t(k,t) = \frac{k^2}{N} \left\langle j_k^x(t) j_{-k}^x(0) \right\rangle$ is the transverse current correlation

$$C_t(k,t) = C_t(k,0) e^{-\nu k^2 t} = \omega_0^2 e^{-\nu k^2 t}, \omega_0^2 = \frac{k_B T}{m} k^2 \tag{1.12}$$

Transverse mode analysis II

- Taking $\lim_{\epsilon\to 0^+} s = \omega + i\epsilon$, $\tilde{C}_t(k,\omega)$ is approximated by

$$\tilde{C}_t(k,\omega) = \frac{\omega_0^2}{-i\omega}\left(1 - \frac{\nu k^2}{i\omega}\right)^{-1} \approx \frac{\omega_0^2}{-i\omega}\left(1 + \frac{\nu k^2}{i\omega}\right), k \ll 1. \quad (1.13)$$

- Shear viscosity η is related to $\tilde{C}_t(k,\omega)$ through

$$\eta = \beta\rho m^2 \lim_{\omega\to 0}\lim_{k\to 0}\frac{\omega^2}{k^4}\mathrm{Re}\left[\tilde{C}_t(k,\omega)\right] \quad (1.14)$$

- Following the definition of $\tilde{C}_t(k,\omega)$, for small k

$$\lim_{k\to 0}\mathrm{Re}\left[\frac{k^2}{N}\int_0^\infty \left\langle \dot{j}_k^x(t)\dot{j}_{-k}^x\right\rangle\right] e^{i\omega t}dt = \lim_{k\to 0}\omega^2\mathrm{Re}\left[\tilde{C}_t(k,\omega)\right] \quad (1.15)$$

Transverse mode analysis III

- Substitute Eq. (1.15) into Eq. (1.14) gives

$$\eta = \frac{\beta m^2}{V} \lim_{\omega \to 0} \lim_{k \to 0} \mathrm{Re} \left[\int_0^\infty \frac{1}{k^2} \left\langle \dot{j}_k^x(t) \dot{j}_{-k}^x \right\rangle e^{i\omega t} dt \right] \tag{1.16}$$

- Using $\dot{j}_k^x(t) + \frac{ik}{m} \Pi_k^{xz}(t) = 0$, η is given by

$$\eta = \frac{\beta}{V} \int_0^\infty \langle \Pi_0^{xz}(t) \Pi_0^{xz} \rangle \, dt \tag{1.17}$$

- Diffusion coefficient D can be derived in a similar manner. (Hint: using mass transport equation and $\mathbf{j}(\mathbf{r}, t) = -D \nabla \rho(\mathbf{r}, t)$.)

Stress tensor in microscopic scale I

- Relate stress tensor Π to microscopic modeling of Hamiltonian system $H(\mathbf{r}, \mathbf{p}) = \frac{1}{2}\mathbf{p}^T\mathbf{M}^{-1}\mathbf{p} + V(\mathbf{r})$
- Microscopic flux mode j_k^α evolves

$$\mathbf{j}_k(t) = \sum_{i=1}^{N} \mathbf{u}_i(t)e^{-i\mathbf{k}\cdot\mathbf{r}_i}$$
$$m\frac{\partial}{\partial t}j_k^\alpha = m\sum_{i=1}^{N}(\dot{u}_{i\alpha} - ik_\beta u_{i\alpha}u_{i\beta})e^{-i\mathbf{k}\cdot\mathbf{r}_i} \tag{1.18}$$

α - x/y direction, β - z direction.

Stress tensor in microscopic scale II

- Assuming $V(\mathbf{r})$ can be approximated by pairwise potential $v(|\mathbf{r}|)$, $m\dot{u}_{i\alpha}e^{-i\mathbf{k}\cdot\mathbf{r}_i}$ can be written as

$$\begin{aligned} m\sum_{i=1}^{N}\dot{u}_{i\alpha}e^{-i\mathbf{k}\cdot\mathbf{r}_i} &= \sum_{i=1}^{N}\sum_{j\neq i}^{N}\frac{r_{ij,\alpha}}{r_{ij}}v'(r_{ij})e^{-i\mathbf{k}\cdot\mathbf{r}_i} \\ &= \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\frac{r_{ij,\alpha}}{r_{ij}}v'(r_{ij})\left[e^{-i\mathbf{k}\cdot\mathbf{r}_i}-e^{-i\mathbf{k}\cdot\mathbf{r}_j}\right] \end{aligned} \tag{1.19}$$

Stress tensor in microscopic scale III

- Therefore, $\Pi_k^{\alpha\beta}$ can be rewritten by

$$\Pi_k^{\alpha\beta} = \sum_{i=1}^{N} \left(m u_{i\alpha} u_{i\beta} + \frac{1}{2} \sum_{j \neq i} \frac{r_{ij,\alpha} r_{ij,\beta}}{r_{ij}^2} \phi_k(r_{ij}) \right) e^{-i\mathbf{k}\cdot\mathbf{r}_i}, \quad (1.20)$$

where $\phi_k(r_{ij}) = r v'(r) \left(\frac{e^{i\mathbf{k}\cdot\mathbf{r}} - 1}{i\mathbf{k} \cdot r} \right)$.

- Taking $k \to 0$, $\Pi^{\alpha\beta}$ recovers the Kirkwood formulation

$$\Pi_0^{\alpha\beta} = \sum_{i=1}^{N} \left(m u_{i\alpha} u_{i\beta} + \frac{1}{2} \sum_{j \neq i} \frac{r_{ij,\alpha} r_{ij,\beta}}{r_{ij}} v'(r_{ij}) \right) \quad (1.21)$$

- Accordingly, shear viscosity η is related to microscopic model through

$$\eta = \frac{\beta}{V} \int_0^\infty \langle \Pi_0^{xz}(t) \Pi_0^{xz} \rangle \, dt \quad (1.22)$$

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Multicomponent interfacial flow

Application

- For Hamiltonian system $H(\mathbf{r}, \mathbf{p})$, state variable $A(\Gamma)$ evolves

$$\frac{dA}{dt} = e^{Lt}(\mathcal{P} + \mathcal{Q})LA(0) = e^{Lt}\mathcal{P}LA(0) + e^{Lt}\mathcal{Q}LA(0), \tag{1.23}$$

- Define projection operator $\mathcal{P}$

$$\mathcal{P}LB = \langle LBA^T \rangle \langle AA^T \rangle^{-1} A \tag{1.24}$$

- Using identity

$$e^{Lt}\mathcal{Q} = e^{\mathcal{Q}Lt} + \int_0^t e^{L(t-s)}\mathcal{P}Le^{\mathcal{Q}Ls}ds, \tag{1.25}$$

Eq. (1.24) can be written as

$$\begin{aligned}\frac{dA}{dt} &= e^{Lt}\mathcal{P}LA(0) + e^{\mathcal{Q}Lt}\mathcal{Q}LA(0) + \int_0^t e^{L(t-s)}\mathcal{P}Le^{\mathcal{Q}Ls}\mathcal{Q}LA(0)ds \\ &= e^{Lt}\mathcal{P}LA(0) - \int_0^t K(s)A(t-s) + e^{\mathcal{Q}Lt}\mathcal{Q}LA(0)\end{aligned}$$

where kernel $K(t)$ is given by

$$K(t) = \left\langle e^{\mathcal{Q}Lt}\mathcal{Q}LA\mathcal{Q}LA^T \right\rangle \left\langle AA^T \right\rangle^{-1}$$

Hydrodynamics limit mode

- For low wave number mode $k \ll 1$

$$\frac{dA}{dt} = LA = O(k), \tag{1.26}$$

- Accordingly projection dynamics

$$\frac{dA}{dt} \approx e^{Lt}\mathcal{P}LA(0) + \int_0^\infty K(s)ds A(t) + e^{\mathcal{Q}Lt}\mathcal{Q}LA(0)$$

- Orthogonal operator and Kernel $K(s)$ satisfy

$$\begin{aligned} e^{\mathcal{Q}Lt} &= e^{Lt} + O(k) \\ K(t) &= \left\langle e^{\mathcal{Q}Lt}\mathcal{Q}LA\mathcal{Q}LA^T \right\rangle \left\langle AA^T \right\rangle^{-1} \\ &= \left\langle e^{Lt}\mathcal{Q}LA\mathcal{Q}LA^T \right\rangle \left\langle AA^T \right\rangle^{-1} + O(k^3) \end{aligned}$$

Hydrodynamic limit I

- Consider N particles at $\mathbf{r} = (\mathbf{r}_1^T, \mathbf{r}_2^T, \cdots, \mathbf{r}_N^T)^T$. Momentum density given by

$$m\rho u_x(\mathbf{r}') = \sum_j p_{jx}\delta(\mathbf{r}' - \mathbf{r})$$

- Taking Fourier mode along $\mathbf{k} = k\hat{z}$

$$m\rho u_k^x = \sum_j p_{jx}e^{iqz_j}$$

Hydrodynamic limit II

- Define projection variable A as $m\rho u_k^x$ for low wave number limit $k \ll 1$.

$$L\left(m\rho u_k^x\right) = ik \sum_j L(p_{jx} z_j) + O(k^2) \approx ik\Pi_{xz}$$

$$\Pi_{xz} = \sum_j \left(\frac{p_{jx} p_{jz}}{m} + F_{ix} z_j \right)$$

- Kernel $K(t)$ can be rewritten as

$$\begin{aligned} K(t) &= \left\langle e^{Lt} \mathcal{Q} L A \mathcal{Q} L A^T \right\rangle \left\langle A A^T \right\rangle^{-1} \\ &= \left\langle e^{Lt} L A L A^T \right\rangle \left\langle \sum_j m k_B T \right\rangle^{-1} \\ &= -k^2 \frac{\langle \Pi_{xz}(t) \Pi_{xz}(0) \rangle}{m k_B T N}, \quad \text{since} \quad \mathcal{P} L A \equiv 0. \end{aligned}$$

Hydrodynamic limit III

- Mode $m\rho v_k^x$ evolves as

$$\frac{d}{dt} m\rho v_k^x = -k^2 \frac{\int_0^\infty \langle \Pi_{xz}(t)\Pi_{xz}(0)\rangle \, dt}{m k_B T N} m\rho v_k^x$$
$$= -k^2 \eta v_k^x$$

where η is the shear viscosity

$$\eta = \frac{\beta}{V} \int_0^\infty \langle \Pi_{xz}(t)\Pi_{xz}(0)\rangle \, dt$$

- Time domain recovers

$$m\rho \frac{\partial}{\partial t} u_x = \eta \frac{\partial^2}{\partial z^2} u_x$$

Outline

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One-component linearized hydrodynamics

Multicomponent interfacial flow

- Low temperature limit
- Fluctuating interface

Application

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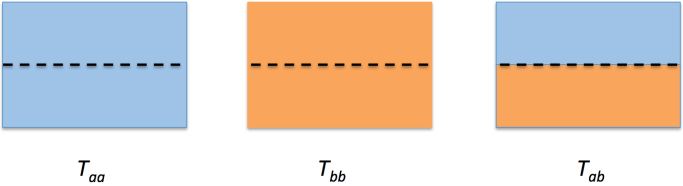
Interfacial flow

- Interface appears due to the break symmetry of hydrogen bonds across boundary of multicomponent/multiphase flow
- Macroscopic scale: Young-Laplace relationship across fluid interface

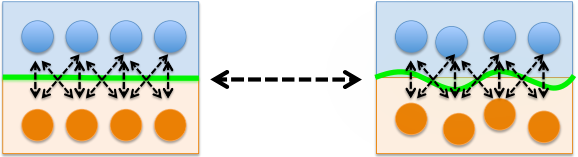
$$(\mathbf{\Pi}_a - \mathbf{\Pi}_b)\mathbf{n} = \kappa\sigma\mathbf{n}, \quad \mathbf{r} \in \Gamma \tag{2.1}$$

  $\mathbf{\Pi}_a, \mathbf{\Pi}_b$ - stress of fluid a and b, σ - surface tension, Γ - fluid interface, κ - interface curvature
- Microscopic scale: interfacial energy difference $T_{aa} + T_{bb} - 2T_{ab}$ due to microscopic particle interaction



Interfacial flow

- Macroscopic limit: establish connection between macroscopic surface tension (σ_0) and microscopic interaction.
- Mesoscopic scale: surface tension ($\sigma(k_B T)$) across thermal induced fluctuating interface.



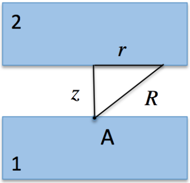
Macroscopic scale: near-flat interface   Mesoscopic scale: fluctuating interface

Interfacial energy: microscopic perspective

- Assume the particle interaction is pairwise function $f(r)$

- Two slabs of fluid consists of fluid a particle with uniform density n, interaction between a tagged particle A and a thin layer $[z, z+dz]$

$$\int_0^\infty 2\pi r dr n f(R)\cos\theta$$
$$= \int_z^\infty 2\pi n \frac{d\left(R^2 - z^2\right)}{2} f(R) \frac{z}{R}$$
$$= \int_z^\infty 2\pi n z f(R) dR$$



Interfacial energy: microscopic perspective I

- Taking integration over the whole fluid slab yields the total interaction $\psi(z)$ between particle A and the slab.

$$
\begin{aligned}
&\int_z^\infty dz' \int_{z'}^\infty 2\pi n z' f(R) dR \\
&= \int_z^\infty dz' z' 2\pi n \int_{z'}^\infty f(R) dR \\
&= \int_z^\infty 2\pi n z' \phi(z') dz',
\end{aligned}
$$

where $\phi(z) = \int_{z'}^\infty f(R)dR$ is the potential energy.

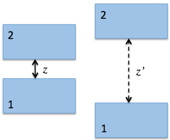
Interfacial energy: microscopic perspective II

- The whole interaction between slab 1 and slab 2 (unit area) with distance z is $\theta(z)$ given by

$$\theta(z) = \int_z^\infty \psi(z) n dz$$

- The interfacial energy T_{aa} of each slab of fluid a is the mechanic work to pull the two fluid layers apart from 0 to ∞.

$$\frac{1}{2}\int_0^\infty \theta(z)dz = \frac{1}{2}\theta(z)z\Big|_0^\infty + \int_0^\infty \frac{n}{2} z\psi(z)dz$$
$$= \int_0^\infty \frac{z^3}{4} 2\pi n^2 \phi(z)dz = \int_0^\infty \frac{\pi}{8} n^2 z^4 f(z)dz$$



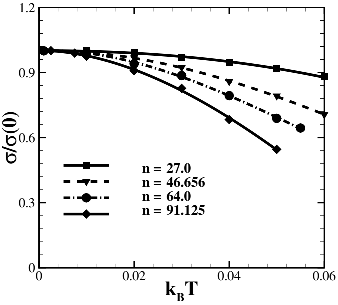
Interfacial energy: microscopic perspective III

- Macroscopic low temperature limit, Γ is nearly flat and smooth and particle density n is homogeneous
- Surface tension σ_0 between fluid a and b is $T_{aa} + T_{bb} - 2T_{ab}$, and can be related to force interaction f^{int} by

$$\sigma_0 = \frac{\pi}{8} n_{eq}^2 \int_0^\infty \left[f_{aa}^{\text{int}}(r) + f_{bb}^{\text{int}}(r) - 2 f_{ab}^{\text{int}}(r) \right] r^4 dr \qquad (2.2)$$

- Eq. (2.2) can be used to model multiphase/multicomponent flow (e.g., with Lagrangian particle framework) where thermal fluctuation is not pronounced.

Numerical example



Surface tension computed at different $k_B T$.

- σ deviates from low temperature prediction σ_0 for intermediate thermal fluctuation $k_B T$.
- Relationship between σ and $k_B T$ further depends on model resolution n.
- How to relate σ to $(k_B T, f^{\text{int}}, n)$?

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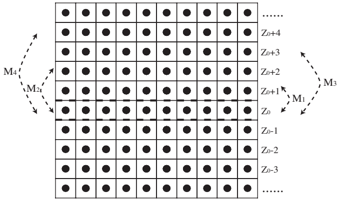
A Coarse-grained lattice model I



- Map the Lagrangian particles back to discrete lattice under mean field ϵ

$$u^L = \epsilon n^L, \quad \epsilon \approx \int_0^\infty 4\pi u(r) r^2 dr,$$

n^L, u^L- number density and potential energy of individual lattice.

A Coarse-grained lattice model II

- The activity of each lattice unit $\zeta(n^L, k_B T)$ is determined by the probability to fill a lattice site, i.e.,

$$n^L/\zeta(n^L, k_B T) = (1 - n^L)e^{-u^L/k_B T}$$

- Equilibrium activity ζ satisfies the equal-areas rule

$$\int_{n_g^L}^{n_l^L} \ln\left[\frac{\zeta(n', k_B T)}{\zeta}\right] dn' = 0,$$

$$\zeta = e^{\epsilon/2k_B T}, \quad \zeta(n_g^L) = \zeta(n_l^L)$$

n_g^L and n_l^L- nontrivial solutions ($\neq 0.5$) corresponding to the coexisting densities of the gas and liquid phase.

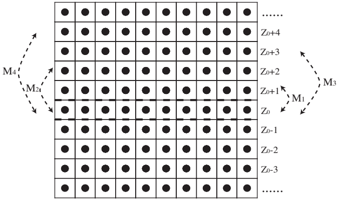
Inhomogeneous density distribution I

- Energy $u^L(z_0)$ of a lattice unit at layer z_0 determined by the interaction with the neighboring layers

$$u^L(z_0) = \epsilon n^L(z_0) + \sum_{l=1}^{L} M_l \Delta_l^2 n^L(z_0)$$

$$\Delta_l^2 n^L(z_0) = n^L(z_0 + l) + n^L(z_0 - l) - 2n^L(z_0),$$

$\epsilon n^L(z_0)$- energy of the lattice layer z_0 under homogeneous assumption; M_l- interaction energy between layer z_0 and $z_0 + l$.



The lattice layer z_0 interact with the neighboring layers $z_0 \pm 1$, $z_0 \pm 2$, ..., $z_0 \pm L$ with interaction energy M_1, M_2, ..., M_L, respectively.

Inhomogeneous density distribution II

- Alternatively, u^L can also be determined by mean field activity

$$n^L/\zeta = (1 - n^L)e^{-u^L/k_BT}, \quad \zeta = e^{\epsilon/2k_BT}$$

- By using $u^L(z_0) = \epsilon n^L(z_0) + \sum_{l=1}^{L} M_l \Delta_l^2 n^L(z_0)$
  - M_l depends on particle interaction $u(r)$ and can be computed in an iterative way.
- $n^L(z)$ can be obtained by solving the self-consistent field equation

$$-\sum_{l=1}^{L} M_l \Delta_l^2 n^L(z) = F'\left[n^L(z)\right],$$

$$F'\left[n^L(z)\right] = -\epsilon\left(\frac{1}{2} - n^L(z)\right) + k_BT \ln\left[n^L/(1 - n^L)\right].$$

Inhomogeneous density distribution III

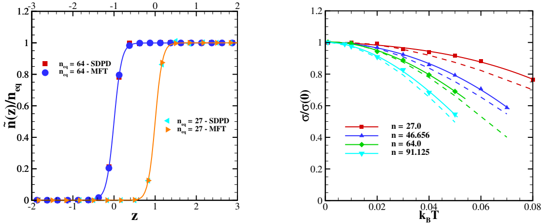
- Surface tension determined by Van der Waals theory

$$\sigma = \sum_{z=-\infty}^{\infty} \left\{ F\left[n^L(z)\right] + \frac{1}{2}\sum_{l=1}^{L} M_l \left[\Delta_l n^L(z)\right]^2 \right\}$$

$$\Delta_l n^L(z) = n^L(z+l) - n^L(z), \quad F(n) = \int_{n_g^L}^{n} F'(n')dn'.$$

Inhomogeneous density distribution IV

Density and surface tension obtained from mean field theory and direct simulation, σ is resolution dependent!



(a) (b)

Figure: (a) Normalized interfacial density profile at $k_B T = 0.03$. (b) Normalized surface tension obtained at different $k_B T$.

Scaling analysis I

- Lattice model defines transition temperature $k_B T_c^L$

$$\int_{n_g^L}^{n_l^L} \ln\left[\frac{\zeta(n', k_B T)}{\zeta}\right] dn' = 0,$$

$$-\epsilon^L/(k_B T_c)^L = 4, \quad \zeta(n_g^L) = \zeta(n_l^L) = 0.5$$

- Scaling of particle model can be established by

$$-\frac{\epsilon/(dp)^5}{k_B T_c/(dp)^2} = 4.$$

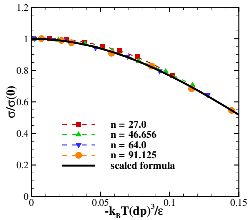
- For same σ_0, $k_B T_c$ is different for different model resolution n!

Scaling analysis II

- Scaling of surface tension σ in Lagrangian particle model given by

$$\boxed{\sigma(k_B T, n_{eq}, \epsilon) = f\left(\frac{k_B T}{n_{eq}\epsilon}\right)}$$

- Surface tension σ predicted by $\sigma = \sigma_0 \left(1 - b\left(\frac{k_B T}{n_{eq}\epsilon}\right)^2\right)^2$



Outline

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One-component linearized hydrodynamics

Multicomponent interfacial flow

Application
- Bubble coalescence
- Capillary wave spectrum

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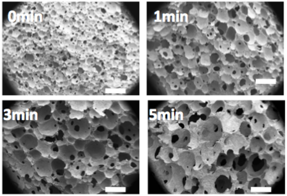
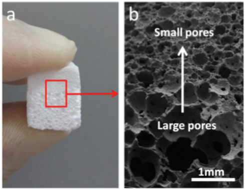
Bubble coalescence

- Fabrication of porous material under control



SEM images and pore sizes of samples with different merge time



Gradient porous scaffolds fabricated by casting foams with varied merge time.

Courtesy of Dr. Lei Yang and Changlu Xu for providing the SEM images.

Bubble coalescence

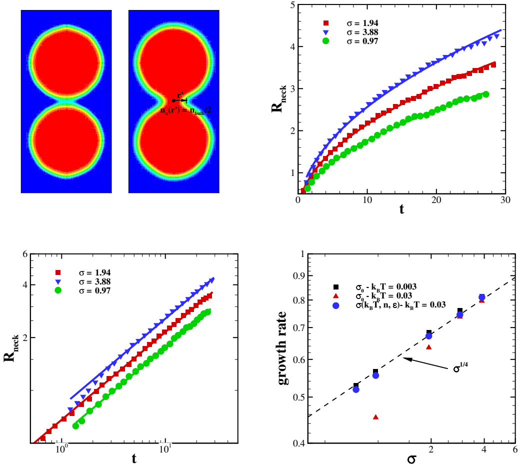


Figure: Dynamics of bubble coalescence procedure. Growth rate measured with different surface tensions.

Outline

One-component linearized hydrodynamics

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Capillary wave spectrum of fluctuating interfacial flow I

- Thermal induced interfacial fluctuation determined by surface tension
- Assume interface of the two phase fluid is given by $\eta = f(x, y)$. Change of interfacial energy (surface area) induced by thermal fluctuation is given by

$$\int \sigma \left[\sqrt{1 + f_x^2 + f_y^2} - 1\right] dxdy = \int \frac{\sigma}{2}(f_x^2 + f_y^2)dxdy \qquad (3.1)$$

- In Fourier mode $\eta(x, y) = \sum_{\mathbf{q}} \hat{\eta}(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{r}}$, change of interfacial energy of wave number $\mathbf{q}$ is

$$\Delta H(\mathbf{q}) = \frac{1}{2}\sigma\hat{\eta}(\mathbf{q})^2 q^2 L^2 \qquad (3.2)$$

Capillary wave spectrum of fluctuating interfacial flow II

- By equal-partition theorem, spectrum magnitude follows

$$\hat{\eta}(\mathbf{q})^2 = \frac{k_B T}{\sigma q^2 L^2} \tag{3.3}$$

- Spectrum of interfacial fluctuation can be dampened/amplified in the presence of gravity
- Denote two-phase fluid system with mass density ρ_L and ρ_H, increased potential energy is the energy difference by exchanging the mass density from ρ_L to ρ_H

$$\Delta H_g = \int (\rho_H - \rho_L) g \frac{\eta(x,y)}{2} \eta(x,y) dxdy, \tag{3.4}$$

Capillary wave spectrum of fluctuating interfacial flow III

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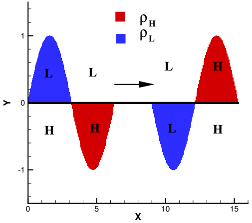
- For each $\mathbf{q}$, the contribution to potential energy difference is given by

$$\Delta H_g = \frac{1}{2} \left|\hat{\eta}(\mathbf{q})\right|^2 (\rho_H - \rho_L) g L^2 \quad (3.5)$$

- Together with interfacial energy contribution, spectrum magnitude is given by

$$\hat{\eta}(\mathbf{q})^2 = \frac{k_B T}{\sigma q^2 L^2 + \Delta\rho g L^2} \quad (3.6)$$



Sketch of the density (potential energy) exchange due to interfacial fluctuation.

Capillary wave spectrum in presence of gravity

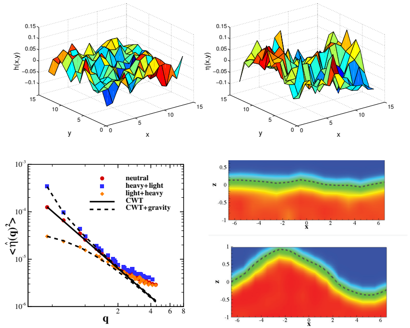


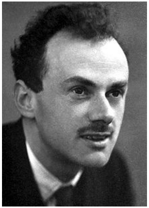
Figure: Density and fluctuation spectrum $|\hat{\eta}(\mathbf{q})|^2$ across two phase flow of different density.

H. Lei, A. Tartakovsky et al., *Phys. Rev. E*, 2016; H. Lei, G. Schenter, et al., *J. Chem. Phys*, 2015.

Concluding Remark

"The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved."

– PAUL DIRAC



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  - Alexander Tartakovsky
  - Xiaoliang Wan
  - Lei Wu