A new numerical method for the study of liquid-vapor transition

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Rare Events I

Rare events: **events that occur very infrequently**. Such as chemical reactions, conformational changes of biomolecules, nucleation events in phase transition, etc.

For instance, the following 1d stochastic differential equation describes the 1d motion of a particle in a potential force field, with thermal noise existing,

$$x_t = -\nabla_x V(x) + \sqrt{2\epsilon} W_t, \tag{1}$$

where $V(x)$ has two minima $x = 0, 1$ and a saddle point at $x = 0.5$.
The system mostly stays at $x = 0$ or $x = 1$, but has probability to hop between these two steady states, by passing through the saddle point $x = 0.5$(obviously for 1d system).

Rare Events II

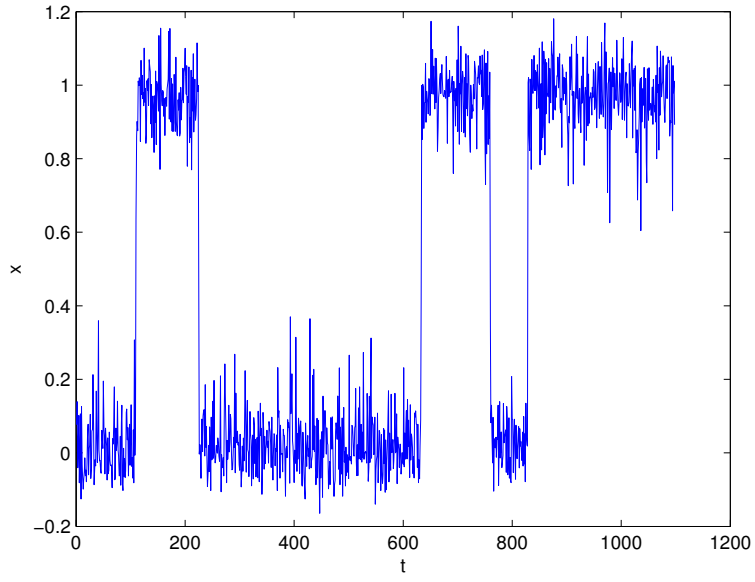

Figure 1 : Trajectory of a 1d particle whose dynamics obeys (1) simulated by Monte Carlo method.

Figure 1 shows the **difficulty** of study of rare events, that is **time scale disparity**.

Ways for Understanding Rare Events I

Based on Wentzell-Freidlin theorey, the transition from ϕ_a to ϕ_b which follows

$$\begin{cases} \phi_t = b(\phi) + \sqrt{\epsilon} W_t \\ \phi(t=0) = \phi_a, \ \phi(t=T) = \phi_b \end{cases} \tag{2}$$

has a most likely transient path $\phi^*(t)$ connecting ϕ_a and ϕ_b, $t \in [0, T]$, which minimizes

$$S_T[\phi] = \frac{1}{2} \int_0^T |\phi_t - b(\phi)|^2 \, \mathrm{d}t \tag{3}$$

Minimizer of S_T & numerical methods

1. For gradient flow, for example

$$\phi_t = -\nabla_\phi V + \sqrt{2\epsilon} W_t \tag{4}$$

ϕ^* is called the **minimum energy path(MEP)**, where

$$\dot{\phi}^*(t) = \begin{cases} \nabla_\phi V, t \in [0, T^*] \\ -\nabla_\phi V, t \in [T^*, T] \end{cases} \tag{5}$$

where $\phi^*(t = T^*)$ is the saddle point of V.
Numerical methods to search for ϕ^* in gradient flow are called as **chain-of-states based methods**, includes: nudged elastic band(NEB, Jónsson et al. 1998), the string method(E et al. 2003), etc.

2. For non-gradient flow, ϕ^* should be obtained by directly minimize the action functional S_T defined by (3) with Newton-type method.
Numerical methods such as minimum action method(MAM, E et al. 2004) can by considered.

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Model: diffuse interface + fluctuating hydrodynamics I

Diffuse interface model is one of many effective tools for depicting multi-phase flow, where noise could be introduced in via a random flux tensor $\tilde{\mathbf{\Pi}}$. Assuming the isothermal liquid-vapor system has the Helmholtz free energy

$$\mathcal{F} = \int_{\Omega} [f(\rho) + \frac{1}{2}\kappa \left|\nabla\rho\right|^2] \, \mathrm{d}\mathbf{r} \tag{6}$$

where $f(\rho)$ is a double well potential and κ is a constant. The fluctuating hydrodynamics for liquid-vapor system reads

$$\begin{aligned} \partial_t \rho + \nabla \cdot (\rho \mathbf{v}) &= 0 \\ \partial_t (\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v}\mathbf{v}) &= \nabla \cdot (\mathbf{T}(\rho, \nabla\rho) + \mathbf{\Pi} + \tilde{\mathbf{\Pi}}) \end{aligned} \tag{7}$$

where

1. ρ is the density of fluid, $\mathbf{v}$ is the velocity of fluid.

Model: diffuse interface + fluctuating hydrodynamics II

2. $\mathbf{T}$ is the capillary tensor which illustrates the interfacial effect.

$$\mathbf{T} = \left(-p(\rho) + \kappa\rho\nabla^2\rho + \frac{\kappa}{2}|\nabla\rho|^2\right) I - \kappa\nabla\rho\nabla\rho, \tag{8}$$

and $p(\rho) = \rho^2 \dfrac{\partial(f(\rho)/\rho)}{\partial\rho}$ is the thermal pressure.

3. $\mathbf{\Pi}$ is the viscous flux taking the form of

$$\mathbf{\Pi} = \eta(\rho)(\nabla\mathbf{v} + \nabla\mathbf{v}^T).$$

where $\eta(\rho)$ is the density dependent viscosity.

4. $\tilde{\mathbf{\Pi}}$ is the random flux,

$$\left\langle \tilde{\mathbf{\Pi}}_{\alpha\beta}(\mathbf{r}_1, t_1)\tilde{\mathbf{\Pi}}_{\delta\gamma}(\mathbf{r}_2, t_2)\right\rangle = 2k_B T C_{\alpha\beta\delta\gamma}\delta(t_1 - t_2)\delta(\mathbf{r}_1 - \mathbf{r}_2), \tag{9}$$

where $C_{\alpha\beta\delta\gamma} = \eta(\rho)(\delta_{\alpha\delta}\delta_{\beta\gamma} + \delta_{\alpha\gamma}\delta_{\beta\delta})$.

Metastable states I

Suppose the domain is periodic in all dimensions, where no external force and boundaries exist, the system (7) mostly stays at two typical metastable states. Except for a homogeneous vapor phase, which corresponds to one of the minima of $f(\rho)$, the other is a liquid-vapor coexist phase, as shown in Figure: 2

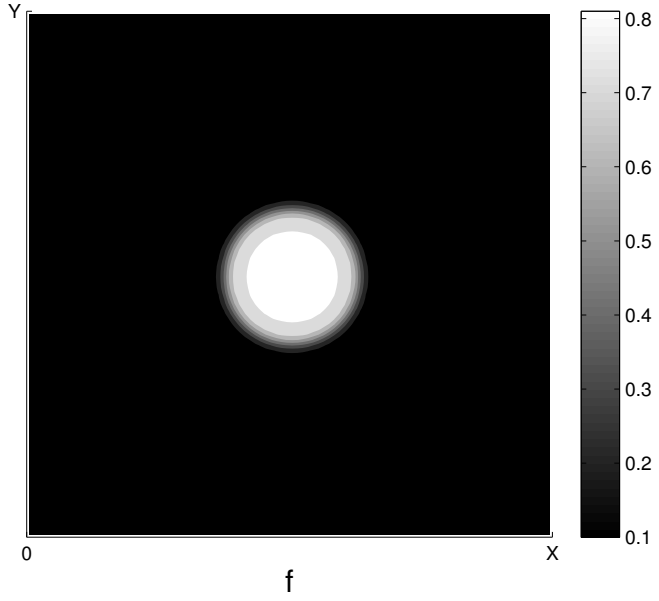

Figure 2 : Liquid-vapor coexist phase

Path searching: MAM I

As discussed before, driven by the noise term $\tilde{\mathbf{\Pi}}$, the system has probability to hop between these two metastable states.

But how ?

Due to the truth that the system (7) is non-gradient, we can minimize the action functional S_T with respect to ρ and $\mathbf{v}$ by using the minimum action method.

Precisely,

$$S_T(\lambda;\rho,\mathbf{v}) = \frac{1}{2}\int_0^T \parallel \partial_t(\rho\mathbf{v}) + \nabla\cdot(\rho\mathbf{v}\mathbf{v}) - \nabla\cdot(\mathbf{T}+\mathbf{\Pi}) \parallel_{-1}^2 \, \mathrm{d}t + \frac{1}{2\lambda}\int_0^T \parallel \partial_t\rho + \nabla\cdot(\rho\mathbf{v}) \parallel^2 \, \mathrm{d}t \tag{10}$$

on condition that $(\rho,\mathbf{v})\,|_{t=0}$ and $(\rho,\mathbf{v})\,|_{t=T}$, where $\parallel A \parallel_{-1}^2 = \left\langle A, -(\nabla\cdot(\eta(\nabla+\nabla^T)))^{-1}A\right\rangle$ and $-(\nabla\cdot(\eta(\nabla+\nabla^T)))^{-1}$ is a bounded positive self-adjoint linear operator on $\mathbb{R}^D$.

The procedure for minimization

To minimize $S_T(\lambda; \rho, \mathbf{v})$ defined in (10), we need to

1. Fix T and λ, discretize $S_T(\lambda; \rho, \mathbf{v})$ and minimize it with MAM.
2. Decrease λ and do the minimization task iteratively till steady value of S_T is achieves.
3. Increase T and do the minimization following the first two steps iteratively till a global minimizer of S_T in the space of (λ, T) is achieved.

Smoothed particle hydrodynamics I

To avoid numerous computational work of minimizing S_T, we introduce the smoothed particle hydrodynamics with fluctuations to approximate the original macroscopic fluctuating hydrodynamics (7).

The **main idea** of the smoothed particle hydrodynamics is to use smoothed particles with smoothing length on the order of $O(\sigma)$ to approximate the original field $A(\mathbf{r})$ with its interpolation A_I

$$A_I(\mathbf{r}) = \sum_{\mathbf{r}_i \in \mathcal{N}(\mathbf{r})} A_j \frac{m_j}{\rho_j} W(|\mathbf{r} - \mathbf{r}_i|, \sigma)$$

where

1. $\mathbf{r}_i$, m_i and ρ_i are the position, mass and density of smoothed particle i, and A_j is the value of A at particle j.
2. $\mathcal{N}(\mathbf{r}) = \{\mathbf{r}_j, |\mathbf{r} - \mathbf{r}_j| \leq 2\sigma\}$ which indicates the topology of the particle system.

Smoothed particle hydrodynamics II

3. $W(r,\sigma) = c\exp\left(-\frac{r^2}{\sigma^2}\right)$, where c is a normalize parameter. $\lim_{\sigma\to 0} W(r,\sigma) = \delta(x)$ and $A_I(\mathbf{r})$ is accurately $A(\mathbf{r})$.

By using smoothed particle hydrodynamics, one only needs to investigate the dynamics of N smoothed particles to approximate the dynamics of the whole macroscopic system via interpolation.

Gradient flow in particle system I

Via detailed calculation, we prove that

$$-\nabla_{\mathbf{r}_i}\mathcal{F}_h = \frac{m_i}{\rho_i}(\nabla\cdot\mathbf{T})_i, \tag{11}$$

where $\mathcal{F}_h$ is the discretization of free energy (6)

$$\mathcal{F}_h = \sum_{i=1}^{M} m_i\left(\frac{f(\rho_i)}{\rho_i} + \frac{\kappa}{2\rho_i}\left|\nabla\rho\right|_i^2\right),$$

A gradient flow is then derived for smoothed particle system in the form of following Langevin dynamics **as well as smoothed particle discretization of the continuous fluctuating hydrodynamics**

$$\begin{cases} \dot{\mathbf{r}}_i = \dfrac{\mathbf{P}_i}{m_i} \\ \dot{\mathbf{P}}_i = -\nabla_{\mathbf{r}_i}\mathcal{F}_h - \displaystyle\sum_{\mathbf{r}_j\in\mathcal{N}(\mathbf{r}_i)} \gamma_{ij}\frac{\mathbf{P}_j}{m_j} + \sum_{\mathbf{r}_j\in\mathcal{N}(\mathbf{r}_i)} \mathbf{G}_{ij} \end{cases} \tag{12}$$

Gradient flow in particle system II

where

1. m_i is the mass of smoothed particle i, which is constant vs. the dynamics by ignoring mass fluctuating flux between particles.
2. $\mathbf{P}_i$ is the momentum of particle i, where $\sum_i \mathbf{P}_i = \int_\Omega \rho \mathbf{v} \, \mathrm{d}\mathbf{r}$ will be a constant if periodic condition is used.
3. γ_{ij} is the damping effect coefficient between particle i and j due to discretization of $\nabla \cdot \mathbf{\Pi}$ on particle i.
4. $\mathbf{G}_{ij}$ is the discretization of $\tilde{\mathbf{\Pi}}$ illustrating the random force between particle i and j.

MEP in Particle System

For gradient system (12), the MEP for the transition between the interpolated metastable vapor phase and liquid-vapor coexisting phase is determined by

$$\begin{cases} \dot{\mathbf{r}} = \dfrac{\mathbf{P}}{\mathbf{m}}, \\ \dot{\mathbf{P}} = -\nabla_{\mathbf{r}}\mathcal{F}_h + \mathbf{R}\dfrac{\mathbf{P}}{\mathbf{m}}, \end{cases} \quad \text{or} \frac{\mathrm{d}}{\mathrm{d}t}\mathbf{X} = -A^T\nabla_{\mathbf{X}}H \quad \text{when } T_1 < t < T^*, \tag{13}$$

and

$$\begin{cases} \dot{\mathbf{r}} = \dfrac{\mathbf{P}}{\mathbf{m}}, \\ \dot{\mathbf{P}} = -\nabla_{\mathbf{r}}\mathcal{F}_h - \mathbf{R}\dfrac{\mathbf{P}}{\mathbf{m}}, \end{cases} \quad \text{or} \frac{\mathrm{d}}{\mathrm{d}t}\mathbf{X} = A\nabla_{\mathbf{X}}H \quad \text{when } T^* < t < T_2, \tag{14}$$

$\mathbf{r}$, $\mathbf{P}$, $\mathbf{m}$, $\mathbf{R}$ are matrix form of collection of $\mathbf{r}_i$, $\mathbf{P}_i$, m_i and γ_{ij}, and $\mathbf{X} = \begin{pmatrix} \mathbf{r} \\ \mathbf{P} \end{pmatrix}$. $H = \mathcal{F}_h + \sum_i \frac{\mathbf{P}_i^2}{2m_i}$ is the Hamiltonian of the particle system.

Numerical Method for Searching of MAP

Till now we are on the half way to obtain the MAP of liquid-vapor transition, however one can not obtain its smoothed particle configurations on the path by directly solving (13) and (14), since,

1. The potential $\mathcal{F}_h$ is determined by positions of all the smoothed particles, it is non-smooth, thus the force for evolving the path, i.e., $\nabla_{\mathbf{r}} F_h$ will change abruptly and may not lead to a convergence numerical result.
2. For problem 1, numerical method for problem with non-smooth potentials, such as finite temperature string method is unavailable, since it is impossible to determine the configuration of given N particles for the two metastable states, simultaneously.

The New Method I

By taking partial time derives of ρ_I, $\mathbf{m}_I$, which are the smoothed particle interpolations of density and momentum fields, we derive the MAP $(\rho_I^*, \mathbf{m}_I^*)$ satisfying

$$\partial_t \begin{pmatrix} \rho_I^* \\ \mathbf{m}_I^* \end{pmatrix} = \mathbf{M} \frac{\mathrm{d}X^\star}{\mathrm{d}t}, \ t \in [T_1, T_2], \tag{15}$$

where $X^\star$ is the MEP in the particle system which is governed by (13) and (14), and $\mathbf{M}$ is a matrix projecting the force exerted on particles to the interpolation fields.
Substituting the MEP (13) and (14) in (15), the MAP reads

$$\begin{cases} \partial_t \begin{pmatrix} \rho_I^* \\ \mathbf{m}_I^* \end{pmatrix} = -\mathbf{M}\mathbf{A}^T \nabla_{\mathbf{X}^\star} H, & t \in [0, T^*], \\ \partial_t \begin{pmatrix} \rho_I^* \\ \mathbf{m}_I^* \end{pmatrix} = \mathbf{M}\mathbf{A} \nabla_{\mathbf{X}^\star} H, & t \in [T^*, T]. \end{cases} \tag{16}$$

where the particle system approaches the saddle point of the Hamiltonian at $t = T^*$.

The Algorithm I

Core idea to propose the algorithm. For a given $(\rho, \mathbf{v})$, $X_1(\mathbf{r}_1)$ and $X_2(\mathbf{r}_2)$ as two sets of smoothed particles can both be used to interpolate $(\rho, \mathbf{v})$, only different at accuracy. Thus the choice of smoothed particlesat each time, which are used as interpolation functions, is free and not required to be on the trajectory of the initial selected particles.
Assume $A = (\rho_v, \mathbf{v}_v)$ and $B = (\rho_l, \mathbf{v}_l)$ are two metastable states of the fluctuating diffuse-interface liquid-vapor system, one can use the following algorithm to search for the MAP between A and B.

1. **Fix** the position of N smoothed particles. Calculate mass, density, and momentum of these particles by finite volume integration of A and B on the adapted voronoi mesh. Obtain the interpolation fields A_I and B_I and fix them as the initial and final states of the path.

The Algorithm II

2. Initialize all the intermediate state $\{(\rho_I)_i, (\mathbf{m}_I)_i\}$ of the ith image on the path as well as the particle configurations with respect to each of them by linear interpolation with two ends fixed at initial and final states.
3. For each intermediate state on the path, calculate $\mathbf{M}_i$, $\mathbf{A}_i$ and $\nabla_{\mathbf{x}_i} H$ for the construction of total force $\mathbf{M}_i \mathbf{A}_i^T \nabla_{\mathbf{x}_i} H$ and $\mathbf{M}_i \mathbf{A}_i \nabla_{\mathbf{x}_i} H$ for evolving the path.
4. Evolve the path by only using the **normal** component of the force obtained at step 3.
5. Renew the mass and momentum of particles by using finite volume integration with respect to the newly obtained interpolation fields.
6. Calculate the residual normal force exerted on all the smoothed particles and see if the iteration converges. If not, return to the third step and start a new round of iteration, where the position of particles are not changed as emphasized at the first step.

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The MAP

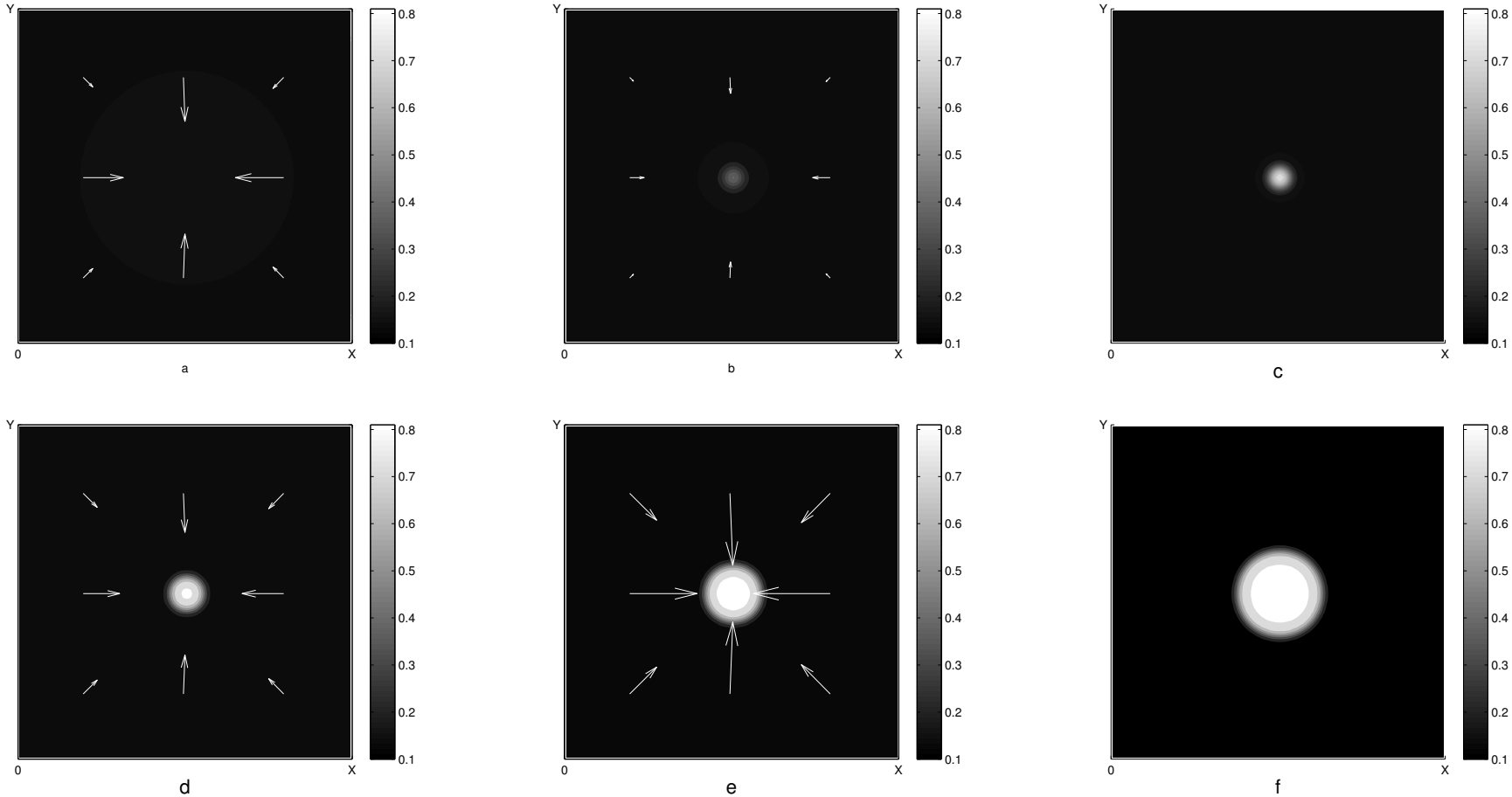


Figure 3 : Snapshots of states along the MAPs for the formation of a liquid ball, where the transition proceeds from top left to the bottom right, The velocity field of each state along the path is not zero and toward the liquid ball, but the transition state *c* and the two metastable states are zero for the reason that they correspond to the critical points of the total energy of the system.

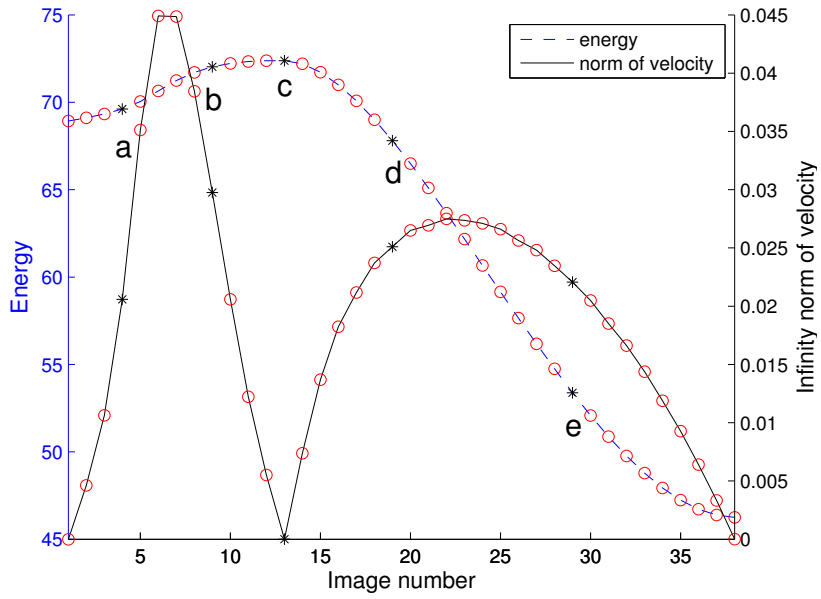


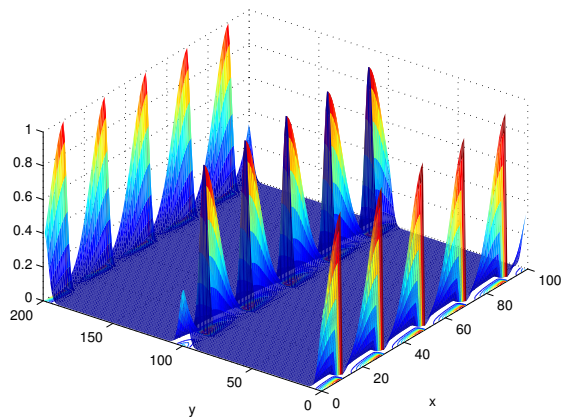
Figure 4 : Total energy H and the infinity norm of velocity of states along the MAP. The states marked with star and denoted by alphabets a, b, c, d, e in the left figure are coincident with the state given in Fig. 6. c is the transition state with zero velocity field and the largest free energy.

The Extra Potential

To generate a shear flow, we add the following potential to the periodic computational domain $[0, X] \times [0, 2Y]$

$$\mathcal{F}^{\text{ext}}(\mathbf{r}) = c \sum_{i=1}^{n_x} \exp\left(-\frac{(x - x_i)^2}{\epsilon_1^2}\right) \left[\exp\left(-\frac{(y - Y)^2}{\epsilon_2^2}\right) H(x - x_i) + \left(\exp\left(-\frac{y^2}{\epsilon_2^2}\right) + \exp\left(-\frac{(y - 2Y)^2}{\epsilon_2^2}\right)\right) H(x_i - x)\right], |\epsilon_2| \ll 1 \tag{17}$$

to the original Hamiltonian of the system, where $x_i = (i + 0.5)\frac{X}{n_x}$. The parameter c has the unit of energy, which can be adjusted to control the shear rate.



The shear flow

To see whether $\mathcal{F}^{\text{ext}}$ could generate correct shear flow, we simulate the steady homogeneous vapor phase, which is a steady Couette Flow if no slip boundary condition is imposed to velocity field.

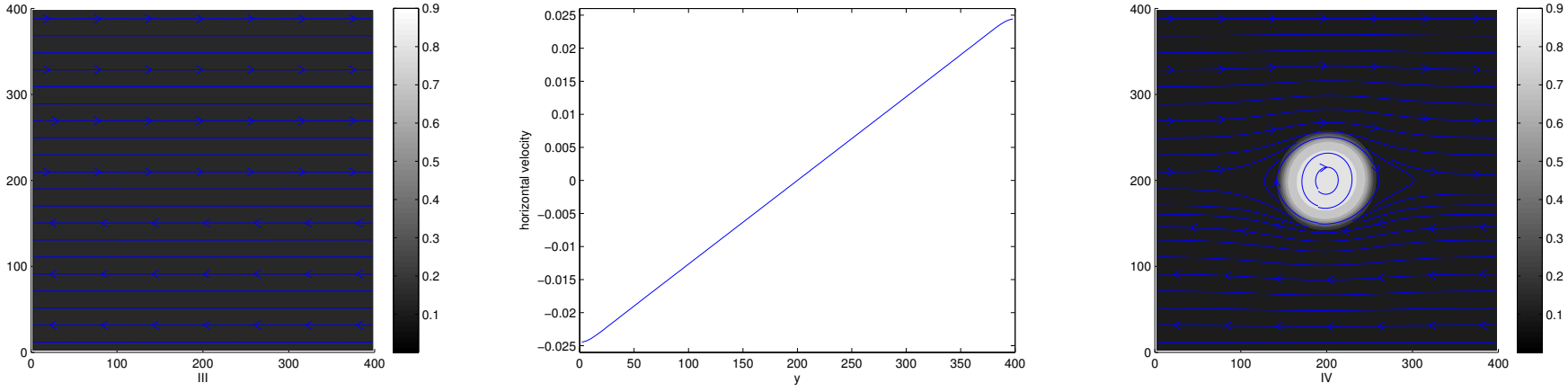


Figure 5 : Steady states when external force $F^{\text{ext}}(\mathbf{r})$ is imposed. Left : steady vapor phase. Middle : the horizontal velocity versus y-coordinate with respect to the velocity field on the left. Right : steady vapor-droplet coexist phase.

MAP in shear flow

We show some typical intermediate states on the MAP from *III* to *IV*.

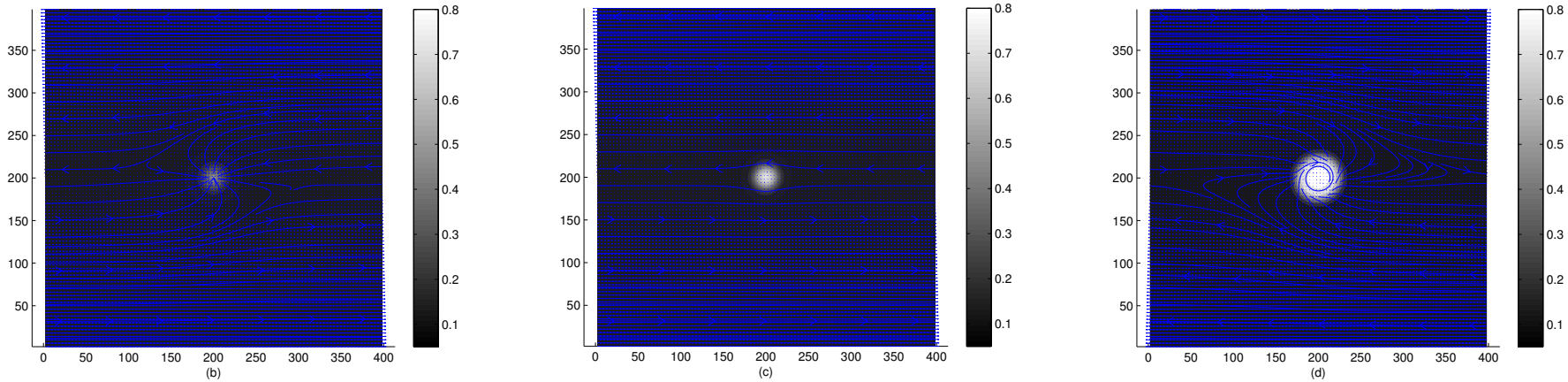


Figure 6 : Snapshots of intermediate states along the MAP from metastable state (*III*) to (*IV*), where (*c*) is the transition state.

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Conclusion

In this work, we propose a new numerical method as an alternative way to study the liquid-vapor transition. Our method doesn't require the user to minimize the full discretized action functional directly. Moreover, it can be extended to cases with external potential force exerted, which could be delicately given to approximate some typical phenomenon in fluid flows, such as shear flow and flow over patterned solid surface.

In the near future, we will use this method to study wetting transition in a shear flow over patterned solid surface by using the new proposed numerical method. By using smoothed particle hydrodynamics, the solid phase could be absorbed in our model.

Thanks!