大域熱力学の統計力学に向けて

京大理　佐々真一
統計物理学懇談会
25/03/24

S.-i. Sasa and N. Nakagawa
JSP. **192** (2), 1-33 (2025).

in collaboration with Naoko Nakagawa

Phase coexistence in nature

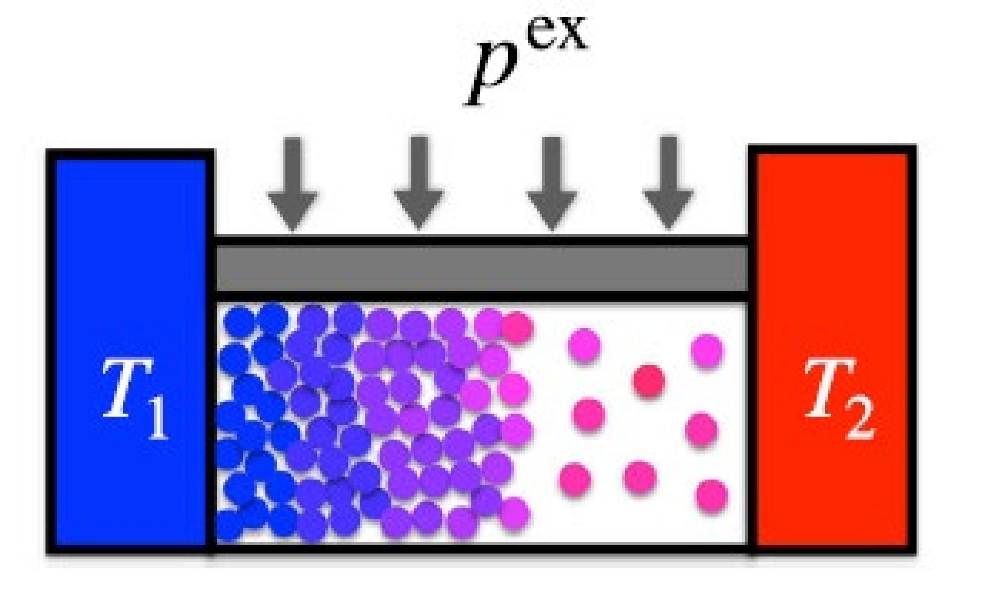
Boiling

Crystal growth

Cloud

Dynamic and complex

Phase coexistence in heat conduction



Example: Water at $p^{\mathrm{ex}} = 1\ \mathrm{atm}$

$$T_1 = 95\ ^\circ\mathrm{C}$$

$$T_2 = 105\ ^\circ\mathrm{C}$$

Temperature at the interface: θ ?

What is your guess ?

Phase coexistence condition at equilibrium

✓ Maxwell construction

✓ Continuity of pressure and chemical potential

✓ Variational principle for determining the equilibrium state

Well-established, but not so popular in textbooks

Phase coexistence condition at NESS ?

✓ Continuity of pressure and chemical potential

Standard assumption, local equilibrium at the interface

✓ Variational principle for determining the NESS

No well-established thermodynamic framework….

⇒ consistent and unique extension
of the thermodynamic relation and the variational principle

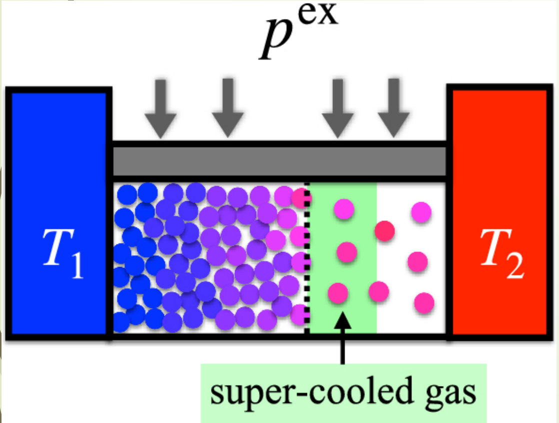
Global thermodynamics

A thermodynamic framework describing non-uniform local thermodynamic states of out of equilibrium systems in terms "global quantities"

Predict **stabilization of metastable states due to heat flux**: Linear response regime

$$\theta - T_c = \left[|J| \left(\frac{1}{\kappa^G} - \frac{1}{\kappa^L} \right) - |\nabla T| \frac{\rho^L - \rho^G}{\bar{\rho}} \right] \frac{X(L-X)}{2L}$$

N. N and S. S, PRL. **119**, 260602 (2017).
N. N and S. S, JSP. **177**, 825-888 (2019).
N. N and S. S, PRR. **4**, 033155 (2022).



Example: Water at $p^{ex} = 1 \text{ atm}$

$T_1 = 95\ ^\circ\mathrm{C}$ $T_2 = 105\ ^\circ\mathrm{C}$

Temperature at the interface: θ ?

$\theta = 95.3\ ^\circ\mathrm{C}$

Many questions may arise……

What about experimental results ?

What about molecular dynamic simulations ?

What about hydrodynamic descriptions ?

What about other types of phase coexistence ?

What about the linear response theory ?

What about a simple stochastic model ?

Non-equilibrium phase coexistence

Prediction

S. S and N. N,
JSP, **192**, 1-33 (2025).

Derivation

Stabilization of meta-stable states
by non-equilibrium current

Meso-scale dynamics

- Numerical simulations
- Theoretical analysis

Global thermodynamics

N. N and S. S, PRL. **119**, 260602 (2017).
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Derivation

Derivation

Micro-scale dynamics

M. Kobayashi et al PRL **130**, 247102 (2023)

Outline of my talk

1. Introduction
2. Basic issue on a technical side
3. Mesoscopic models
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Zubarev-Mclennan distribution

A collection of microscopic or mesoscopic variables Γ

Equilibrium distribution (e.g. canonical distribution) $\rho_{\mathrm{eq}}(\Gamma) = \frac{1}{Z} e^{-\beta H(\Gamma)}$

Steady-state distribution in the linear response regime $\rho_{\mathrm{ss}}(\Gamma) = \frac{1}{Z} e^{-\beta H_{\mathrm{ss}}(\Gamma)}$

$$H_{\mathrm{ss}}(\Gamma) = H(\Gamma) + T \int_0^{\infty} dt \langle \sigma(\Gamma_t) \rangle^{\mathrm{eq}}_{\Gamma_0 = \Gamma}$$

$\sigma(\Gamma_t)$: Entropy production rate at Γ_t

Γ_t : phase space point at time t

How to use it

The expectation of $A(\Gamma)$ in the linear response regime is given by the time integration of the time correlation function between $A(\Gamma)$ and the entropy production rate

⇒ linear response formula (such as the Green-Kubo formula)

Choose "density fields" as Γ .

"The variational function" is given by the Hamiltonian

⇒ fluctuating hydrodynamics; macroscopic fluctuation theory

↓

Derivation of the "variational principle" for determining thermodynamic quantities in the linear response regime

Points of the argument

- ✓ Explicitly calculate the correction term with the time integration
- ✓ Study the simplest example as the first-step trial
- ✓ Consider a new class of "discrete fluctuating hydrodynamics"

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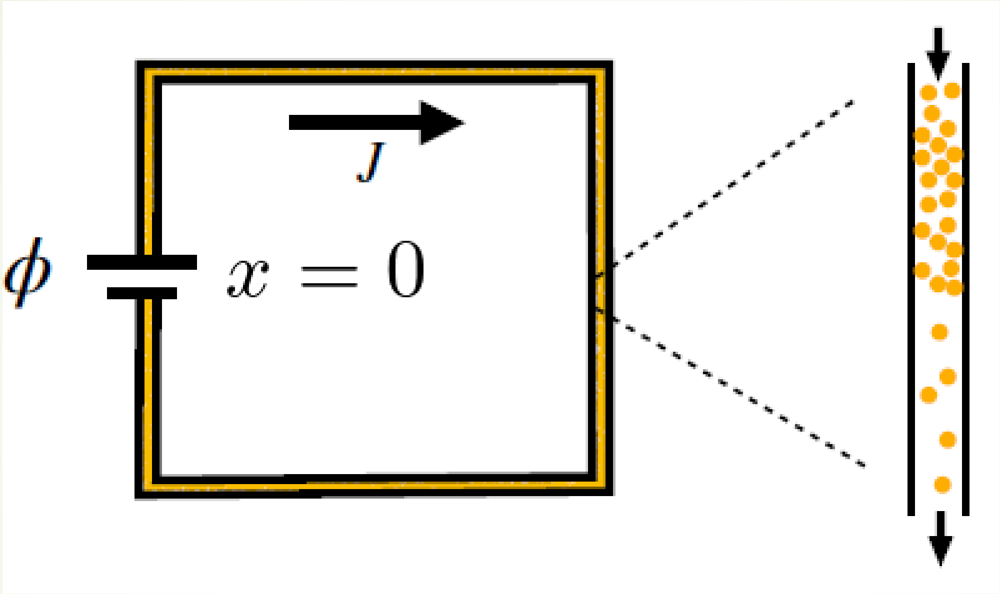
Particle diffusion driven by a battery



$$\rho(x) = \frac{1}{A} \int dydz\ \rho(x, y, z)$$

A **the area of the cross-section of the tube**

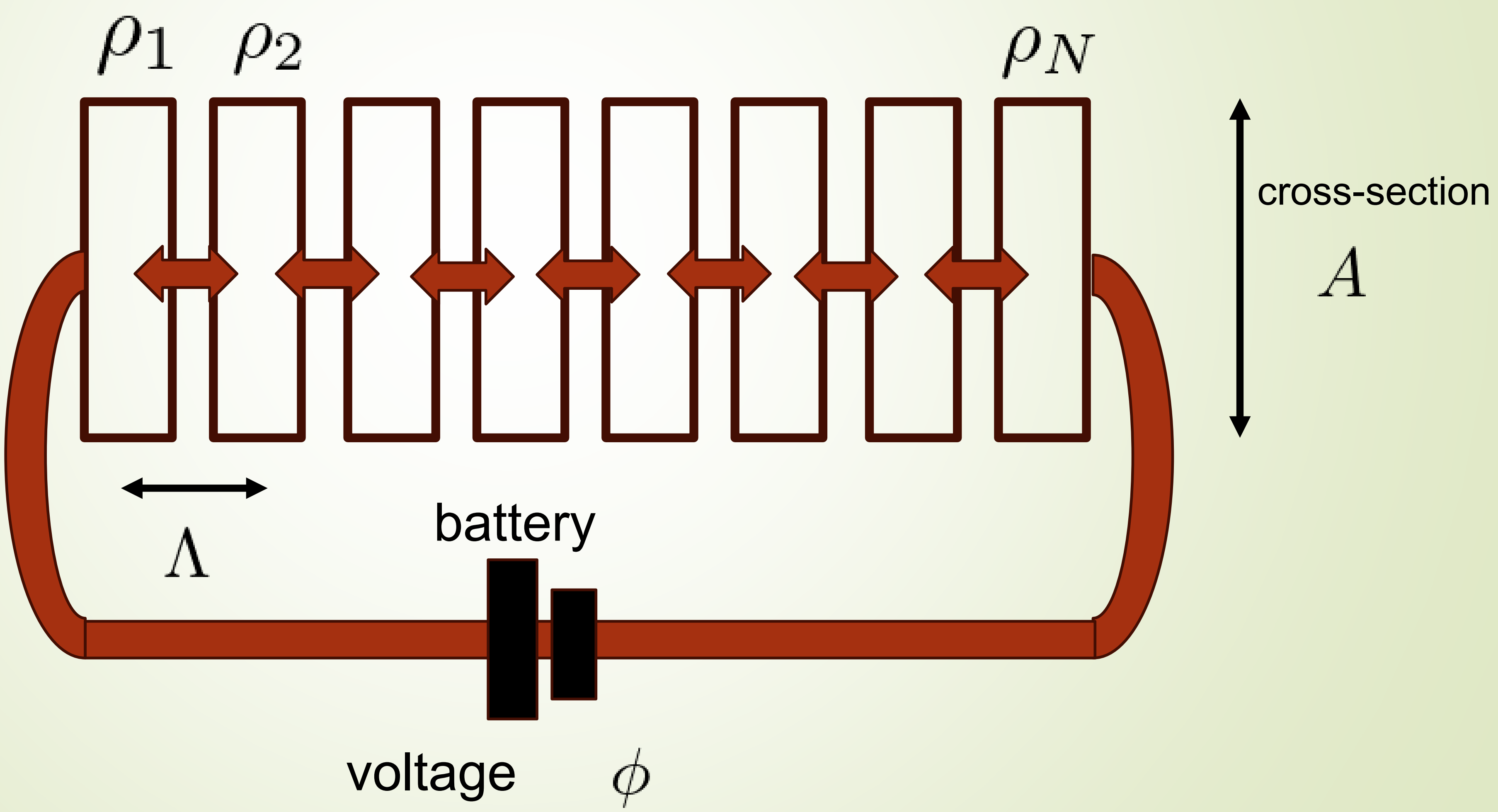
Setup - discrete Model B -

$$\boldsymbol{\rho} = (\rho_i)_{i=1}^{N}$$

Periodic boundary

$$\rho_0 = \rho_N$$

$$\rho_{N+1} = \rho_1$$



Thermodynamics $\quad \phi = 0$

Free energy functional

$$\mathcal{F}(\boldsymbol{\rho}) = \Lambda \sum_{i=1}^{N} \left[f(\rho_i) + \frac{\kappa}{2\Lambda^2} (\rho_{i+1} - \rho_i)^2 \right]$$

Equilibrium distribution

$$\mathcal{P}_{\text{eq}}(\boldsymbol{\rho}) = \frac{1}{Z} e^{-\beta A \mathcal{F}(\boldsymbol{\rho})} \delta \left(\sum_i \rho_i - \bar{\rho} N \right)$$

(Generalized) chemical potential

$$\tilde{\mu}_i \equiv \frac{1}{\Lambda} \frac{\partial \mathcal{F}}{\partial \rho_i}$$

$$= \mu(\rho_i) - \frac{\kappa}{\Lambda^2} (\rho_{i+1} + \rho_{i-1} - 2\rho_i)$$

Non-equilibrium dynamics

$$\frac{d\rho_i}{dt} + \frac{j_i - j_{i-1}}{\Lambda} = 0$$

$$j_i(t) = -\frac{\sigma(\rho_i^{\mathrm{m}})}{\Lambda}(\tilde{\mu}_{i+1} - \tilde{\mu}_i - \phi\delta_{i,N}) + \sqrt{\frac{2\sigma(\rho_i^{\mathrm{m}})T}{A\Lambda}} \cdot \xi_i(t)$$

$$\rho_i^{\mathrm{m}} = (\rho_i + \rho_{i+1})/2$$

Detailed balance condition when $\phi = 0$

Non-equilibrium nature comes from only through the boundary condition

Independent parameters

Independent parameters (with $f(\rho)$ and $\sigma(\rho)$ fixed)

$$(\kappa_\Lambda, T_{\rm eff}, \phi, \bar{\rho}, N) \qquad \kappa_\Lambda \equiv \frac{\kappa}{\Lambda^2} \qquad T_{\rm eff} \equiv \frac{T}{A} \qquad \phi \geq 0$$

→ **Steady state**

$$N \to \infty \qquad T_{\rm eff} \to 0$$

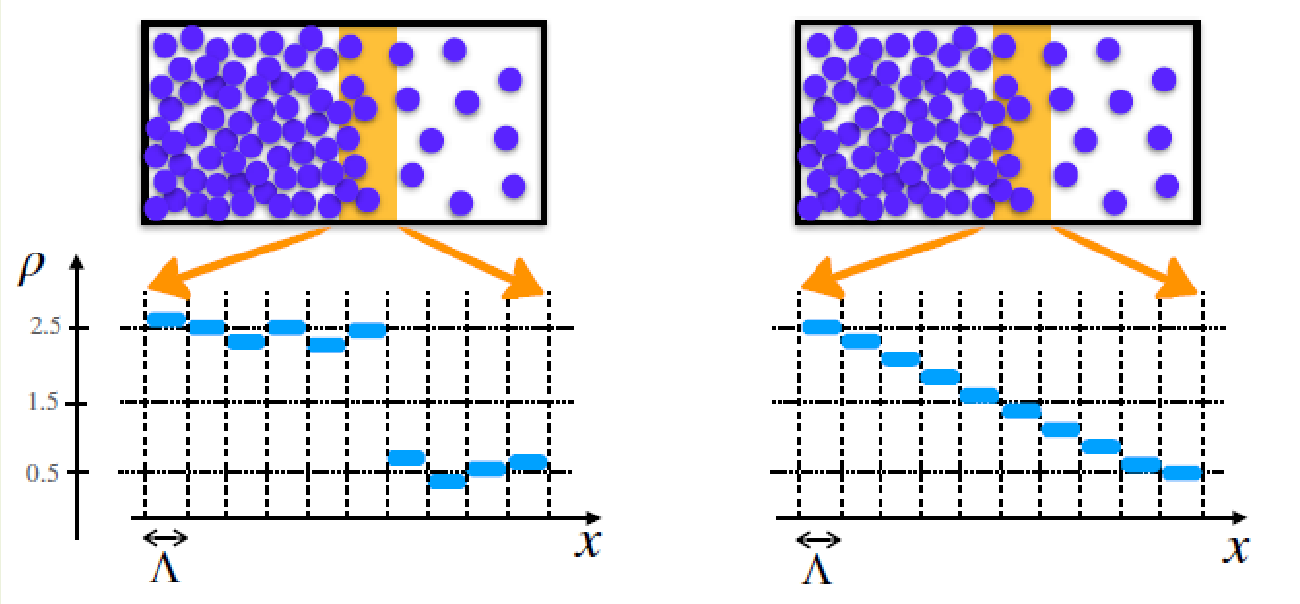
The length unit, energy unit, and time unit are fixed to be microscales in the forms of $f(\rho)$ and $\sigma(\rho)$

Two limiting cases

$\kappa_\Lambda \ll 1$

$\kappa_\Lambda \gg 1$

(蔵本条件　1974)
“ゆらぎとの決別”



$$\sqrt{\kappa} \ll \Lambda \ll L \equiv N\Lambda$$

$$\Lambda \ll \sqrt{\kappa} \ll L \equiv N\Lambda$$

“standard”
fluctuating hydrodynamics

Fluctuating hydrodynamics (Model B)

$$\partial_t \rho + \partial_x j = 0$$

$$j(x,t) = -\sigma(\rho(x)) \left[\partial_x \frac{\delta \mathcal{F}}{\delta \rho(x)} - \phi \delta(x) \right] + \sqrt{\frac{2\sigma(\rho(x))T}{A}} \cdot \xi(x,t)$$

$$\mathcal{F}(\boldsymbol{\rho}) = \int_0^L dx \left[f(\rho(x)) + \frac{\kappa}{2} (\partial_x \rho)^2 \right] \qquad \boldsymbol{\rho} = (\rho(x))_{0 \le x \le L}$$

$$\langle \xi(x,t) \xi(x',t') \rangle = \delta(x-x') \delta(t-t')$$

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Equilibrium Thermodynamics

Phase coexistence occurs when $\bar{\rho}$ satisfies $\rho_c^G \le \bar{\rho} \le \rho_c^L$

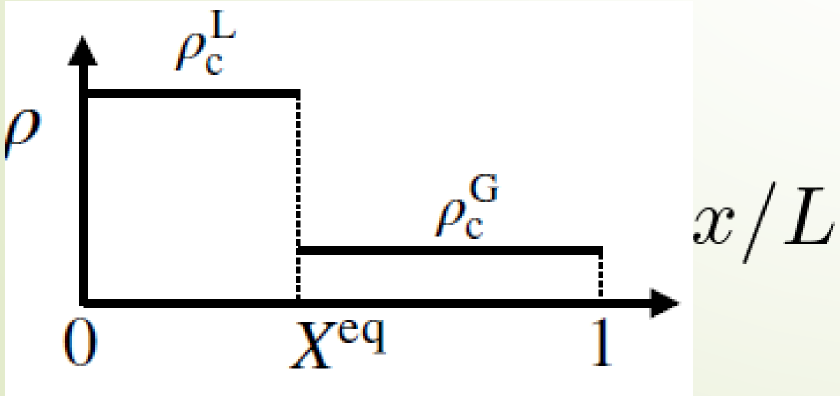
ρ_c^L and ρ_c^G determined by (equivalent to Maxwell's construction)

$$\mu(\rho_c^L) = \mu(\rho_c^G) \quad \text{and} \quad p(\rho_c^L) = p(\rho_c^G)$$

$$\downarrow$$

$$\mu_c$$

$$p(\rho) \equiv \rho\mu(\rho) - f(\rho)$$



$$\rho_c^L X^{eq} + \rho_c^G (1 - X^{eq}) = \bar{\rho}$$

Non-equilibrium system

$\kappa_\Lambda \gg 1$

Stationary solutions of the deterministic equation

$$\partial_x [f'(\rho) - \kappa \partial_x^2 \rho] = -\frac{J}{\sigma(\rho(x))}$$

Unique existence of the phase coexistence solution when $\rho_{\rm c}^{\rm G} \le \bar{\rho} \le \rho_{\rm c}^{\rm L}$

$\Rightarrow$ $\mu^{\rm I} = \mu_{\rm c}$

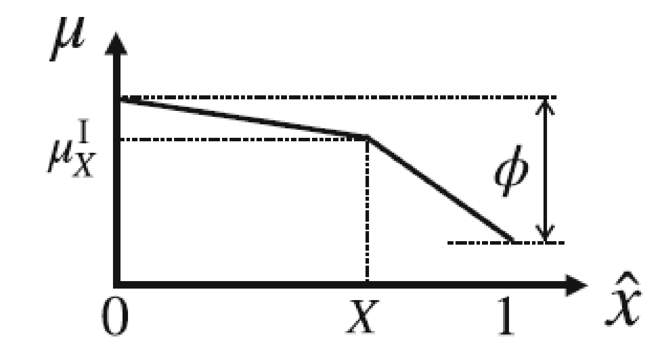
Non-equilibrium system

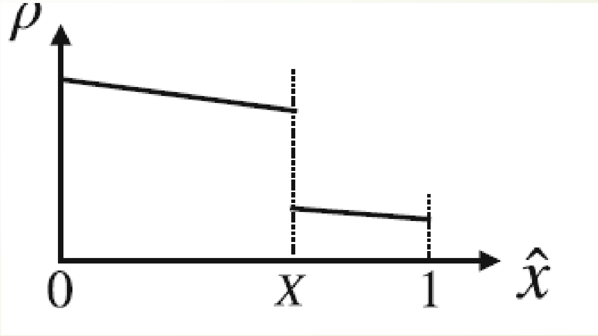
$\kappa_\Lambda \ll 1$

$$\frac{1}{\Lambda}(\mu_{i+1} - \mu_i + \phi\delta_{i,N}) = -\frac{J}{\sigma(\rho_i^{\mathrm{m}})}$$

Many solutions (corresponding to metastable states)

$\boldsymbol{\rho}_X^\phi$ $\quad X$ interface position in the scaled coordinate

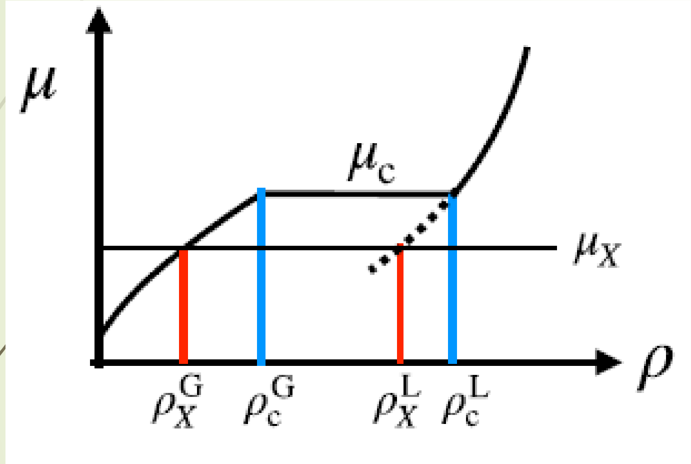


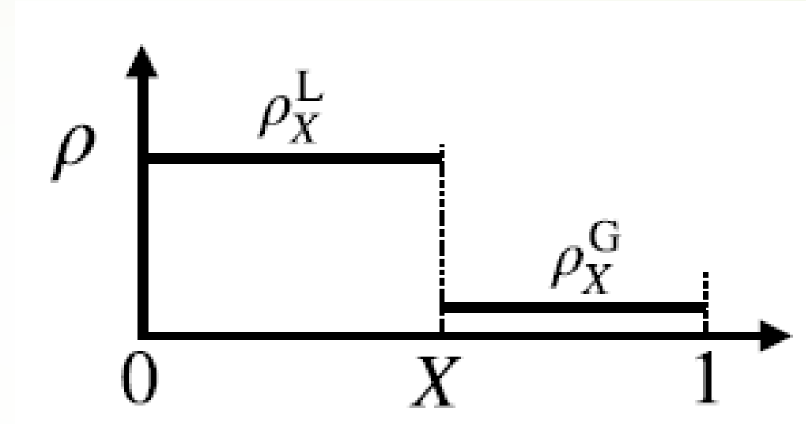


$\hat{x} = i/N$

Why do many solutions appear?

$$\phi = 0$$





$$\hat{x} = i/N$$

Non-equilibrium cases:
Deformation from these meta-stable solutions

Question

Determine the **most probable solution** among $\boldsymbol{\rho}_X^{\phi}$

Phase coexistence condition for $\kappa_\Lambda \ll 1$

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Steady-state distribution

$$\mathcal{P}_{\mathrm{ss}}(\boldsymbol{\rho}) = \frac{1}{Z_{\mathrm{ss}}} e^{-\beta A \mathcal{F}_{\mathrm{ss}}(\boldsymbol{\rho})} \delta\left(\sum_i \rho_i - \bar{\rho} N\right)$$

$$\mathcal{F}_{\mathrm{ss}}(\boldsymbol{\rho}) = \mathcal{F}(\boldsymbol{\rho}) + \phi \langle Q \rangle_{\boldsymbol{\rho}}^{\mathrm{eq}} + O(\phi^2)$$

$$Q = \int_0^\infty dt \; j_N(t)$$

Variational principle for $\kappa_\Lambda \ll 1$

Variational function for determining

$$L\mathcal{V}_{\rm ss}(X) \equiv \mathcal{F}_{\rm ss}(\rho_X^\phi) = \mathcal{F}(\boldsymbol{\rho}_X^\phi) + \phi \langle Q \rangle^{\rm eq}_{\boldsymbol{\rho}_X^\phi} + O(\phi^2)$$

$$= \mathcal{F}(\boldsymbol{\rho}_X^\phi) + \phi \langle Q \rangle^{\rm eq}_{\boldsymbol{\rho}_X^{\phi=0}} + O(\phi^2)$$

Variational principle $\mathcal{V}_{\rm ss}(X_*) = \min_X \mathcal{V}_{\rm ss}(X)$

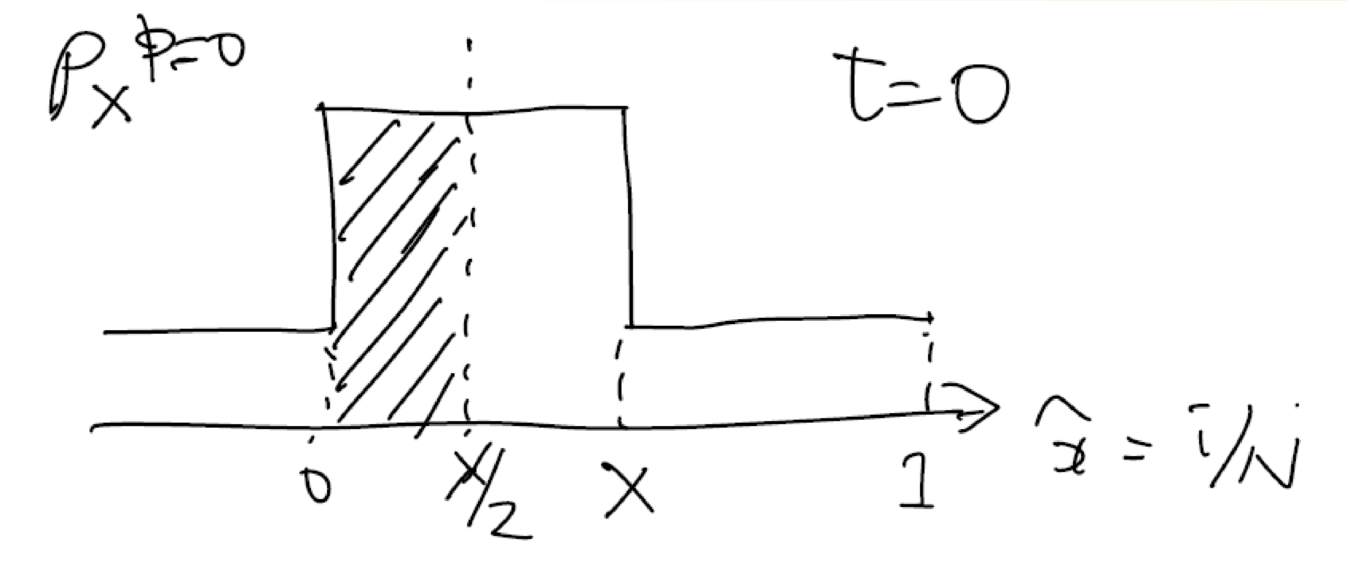
Steady state profile $\boldsymbol{\rho}_{X_*}^\phi$

→ $\mu^{\rm I}$ Chemical potential at the interface

Calculation of $\langle Q \rangle^{\text{eq}}_{\boldsymbol{\rho}_X^{\phi=0}}$

(by H. Tasaki, 24/12/16)

Equilibrium stochastic dynamics $\boldsymbol{\rho}_X^{\phi=0} \to \boldsymbol{\rho}(t)$



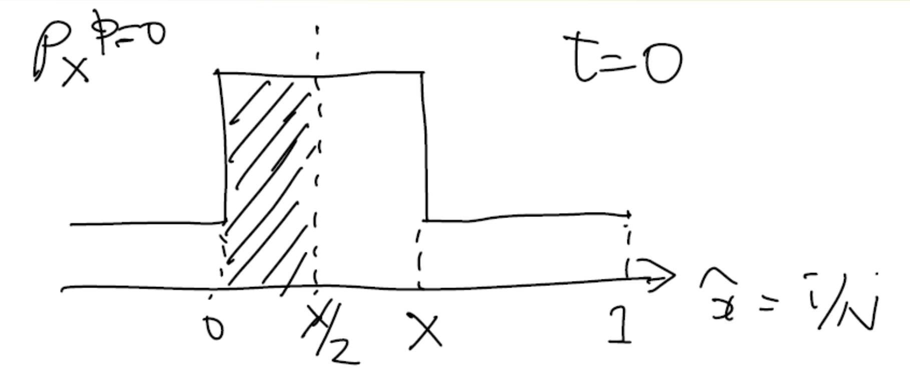
Continuity equation

$$\Lambda \frac{d}{dt} \sum_{i=1}^{NX/2} \rho_i(t) = -j_{NX/2} + j_0$$

Time-integration

$$\Lambda \sum_{i=1}^{NX/2} (\rho_i(\infty) - \rho_i(0)) = -\int_0^\infty dt j_{NX/2}(t) + \int_0^\infty dt j_0(t)$$

$$\int_0^\infty dt \, \langle j_{NX/2}(t) \rangle^{\mathrm{eq}}_{\boldsymbol{\rho}_X^{\phi=0}} = 0$$



$$\langle Q \rangle^{\mathrm{eq}}_{\boldsymbol{\rho}_X^{\phi=0}} = \Lambda(\bar{\rho} - \rho_X^{\mathrm{L}}) \frac{NX}{2}$$

$$= -L(\rho_X^{\mathrm{L}} - \rho_X^{\mathrm{G}}) \frac{X(1-X)}{2}$$

Variational function (Main result)

$$\mathcal{V}_{\mathrm{ss}}(X) = Xf\left(\bar{\rho}_X^{\mathrm{L}}\right) + (1-X)f\left(\bar{\rho}_X^{\mathrm{G}}\right) - \frac{\phi}{2}\left(\bar{\rho}_X^{\mathrm{L}} - \bar{\rho}_X^{\mathrm{G}}\right)X(1-X)$$

$$\bar{\rho}_X^{\mathrm{L}} = \frac{1}{NX}\sum_{i=1}^{NX}\rho_{X;i}^{\phi} \qquad \bar{\rho}_X^{\mathrm{G}} = \frac{1}{N(1-X)}\sum_{i=NX+1}^{N}\rho_{X;i}^{\phi}$$

This variational function was first calculated by using a method of global thermodynamics.

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Result for $\kappa_\Lambda \ll 1$

$$\mu^{\mathrm{I}} = \mu_{\mathrm{c}} + \frac{\phi}{2} \frac{(\sigma^{\mathrm{L}} - \sigma^{\mathrm{G}}) X^{\mathrm{eq}} (1 - X^{\mathrm{eq}})}{\sigma^{\mathrm{G}} X^{\mathrm{eq}} + \sigma^{\mathrm{L}} (1 - X^{\mathrm{eq}})}$$

Perfect agreement with the prediction by global thermodynamics!

$$\sigma^{\mathrm{L}} = \sigma(\rho_{\mathrm{c}}^{\mathrm{L}}) \quad \sigma^{\mathrm{G}} = \sigma(\rho_{\mathrm{c}}^{\mathrm{G}})$$

$$\mu^{\mathrm{I}} = \mu_{\mathrm{c}} - \frac{JLX^{\mathrm{eq}}(1 - X^{\mathrm{eq}})}{2} \left(\frac{1}{\sigma^{\mathrm{L}}} - \frac{1}{\sigma^{\mathrm{G}}} \right)$$

The pressure is **discontinuous** at the interface

Specific model for numerical simulations

$$f(\rho) = -\frac{1}{2}(\rho - 1.5)^2 + \frac{1}{4}(\rho - 1.5)^4$$

$$\rho_{\mathrm{c}}^{\mathrm{L}} = 2.5 \qquad \rho_{\mathrm{c}}^{\mathrm{G}} = 0.5 \qquad \mu_{\mathrm{c}} = 0$$

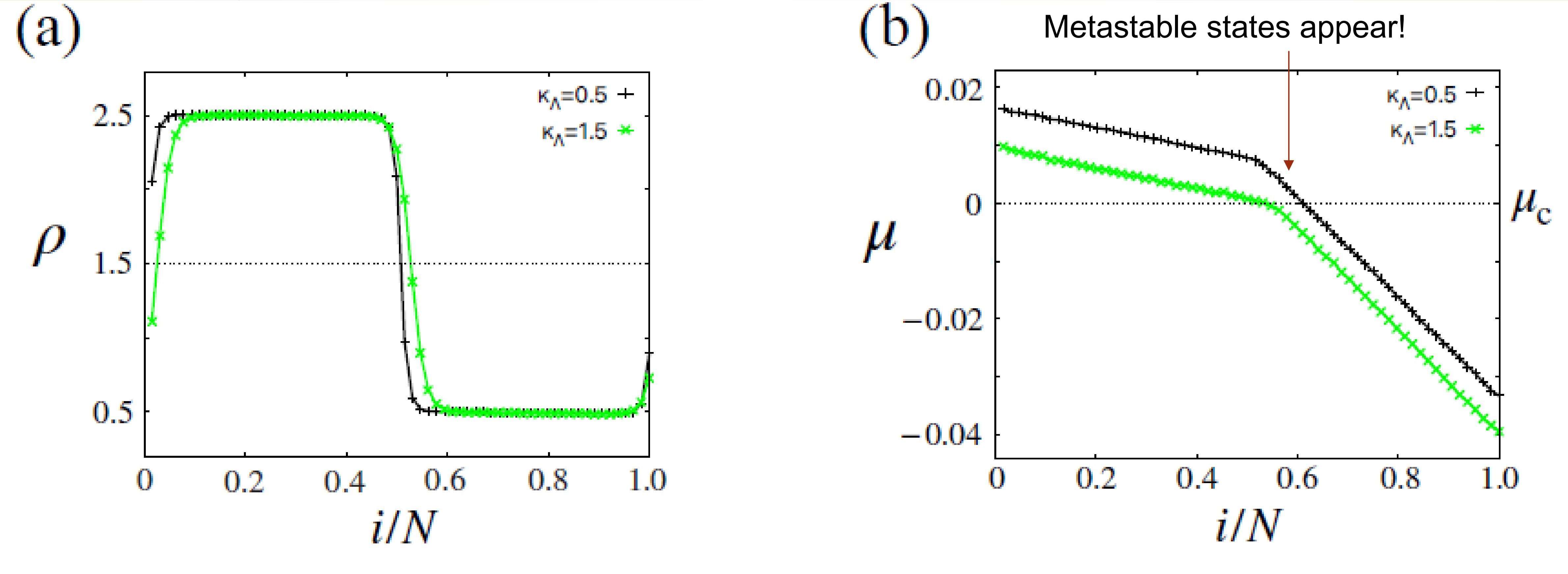
$$\sigma(\rho) = \rho$$

$$\sigma^{\mathrm{L}} = 2.5 \qquad \sigma^{\mathrm{G}} = 0.5$$

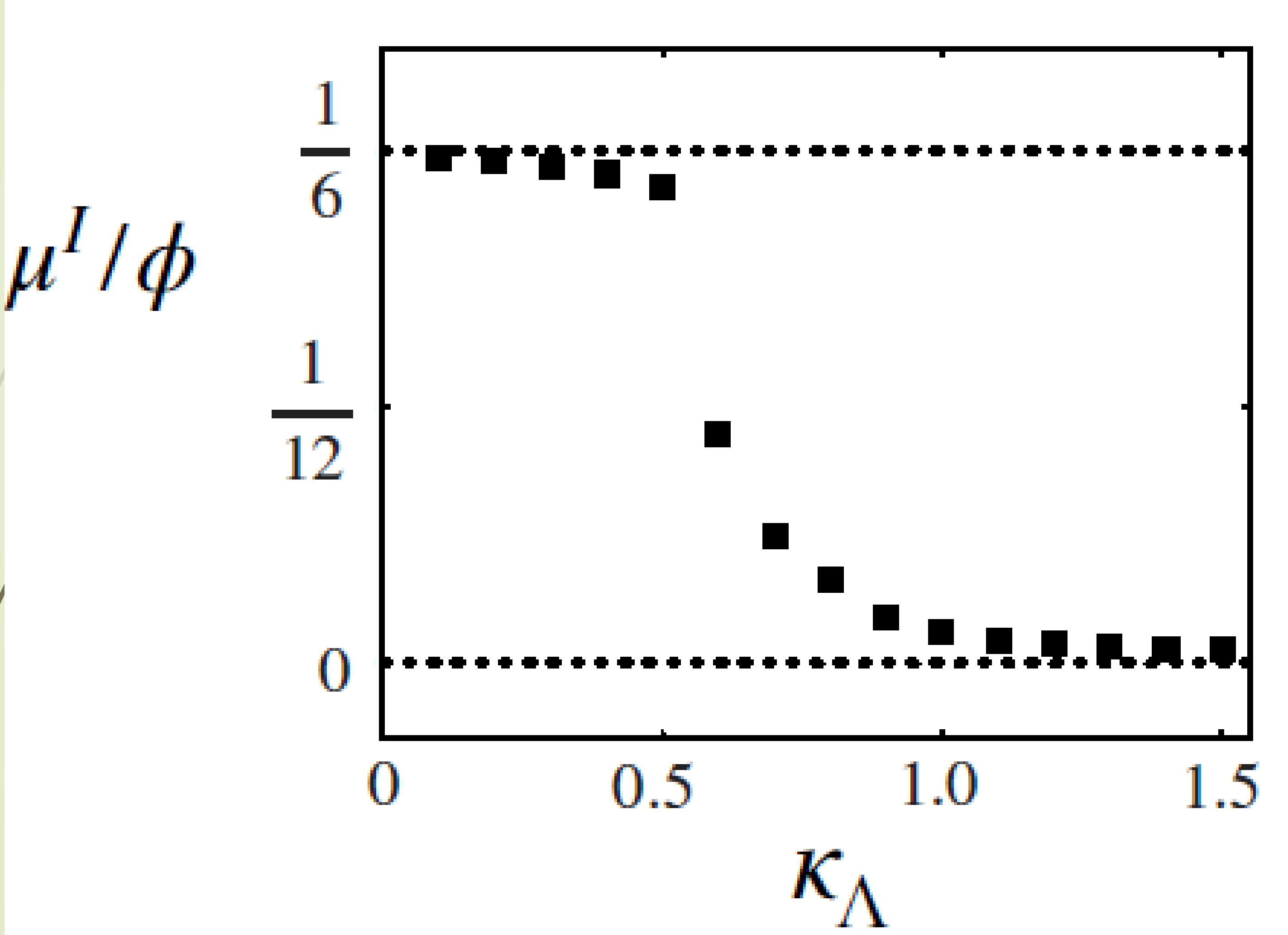
$$(T_{\mathrm{eff}}, \phi, \bar{\rho}, N) = (0.002, 0.05, 1.5, 64) \Rightarrow X^{\mathrm{eq}} = 1/2$$

Unfixed parameter κ_Λ

Numerical result I



Numerical result II



$$\mu^{\mathrm{I}} = \mu_{\mathrm{c}} + \frac{\phi}{2}\frac{(\sigma^{\mathrm{L}} - \sigma^{\mathrm{G}})X^{\mathrm{eq}}(1 - X^{\mathrm{eq}})}{\sigma^{\mathrm{G}}X^{\mathrm{eq}} + \sigma^{\mathrm{L}}(1 - X^{\mathrm{eq}})}$$

$$\mu_{\mathrm{c}} = 0$$
$$\sigma^{\mathrm{L}} = 2.5$$
$$\sigma^{\mathrm{G}} = 0.5$$
$$X^{\mathrm{eq}} = 1/2$$

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Summary

Liquid-gas phase coexistence in boundary-driven diffusion systems

Discrete fluctuating dynamics (model B)

When the interface width is smaller than the cut-off length,
the chemical potential at the interface deviates from the equilibrium

$$\mu^{\mathrm{I}} = \mu_{\mathrm{c}} + \frac{\phi}{2} \frac{(\sigma^{\mathrm{L}} - \sigma^{\mathrm{G}}) X^{\mathrm{eq}} (1 - X^{\mathrm{eq}})}{\sigma^{\mathrm{G}} X^{\mathrm{eq}} + \sigma^{\mathrm{L}} (1 - X^{\mathrm{eq}})}$$

Metastable states stably appear near the interface !

Global thermodynamics predicts the same formula
without analyzing stochastic models

Remarks

Analysis of the system with finite κ_Λ

$\Rightarrow$ Phase transition or not ?

Microscopic view of “discrete” fluctuating hydrodynamics?

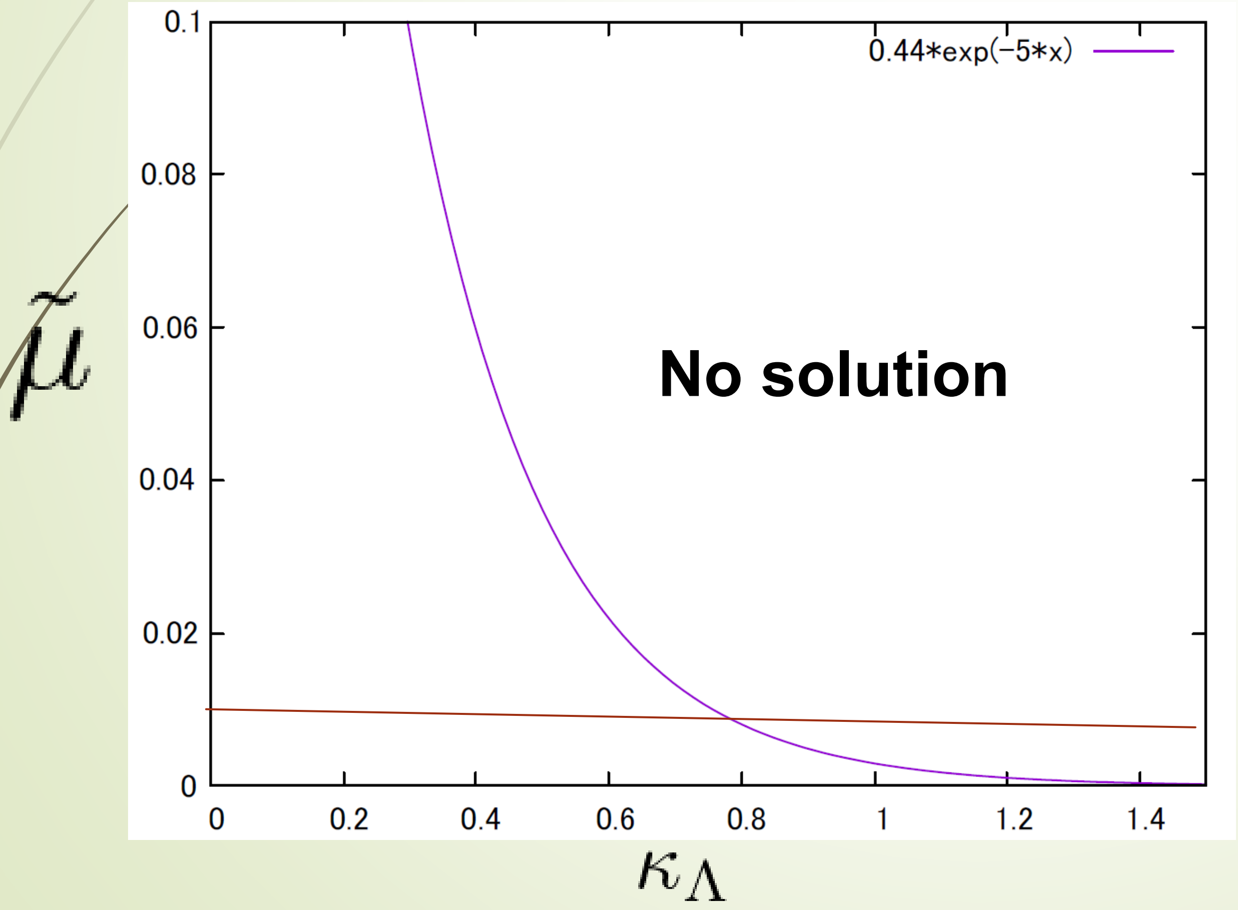
Liquid-gas coexistence in heat conduction?

Theoretical understanding of (entropic) dynamics?

cf. “Attractor crowding” (1989)

Phase coexistence solutions at equilibrium with finite κ_Λ

$$\mu(\rho_i) - \kappa_\Lambda(\rho_{i+1} + \rho_{i-1} - 2\rho_i) = \tilde{\mu}(= \mathrm{const})$$



Global thermodynamics

Liquid-gas coexistence in heat conduction

"discrete fluctuating hydrodynamics" for energy density, momentum density, and mass density

Too hard to have a consistent and robust model ・・・・,
Recently, we have fixed troubles….
(A. Yoshida et al, in preparation)

Numerical simulation and theoretical analysis show similar behavior to Model B