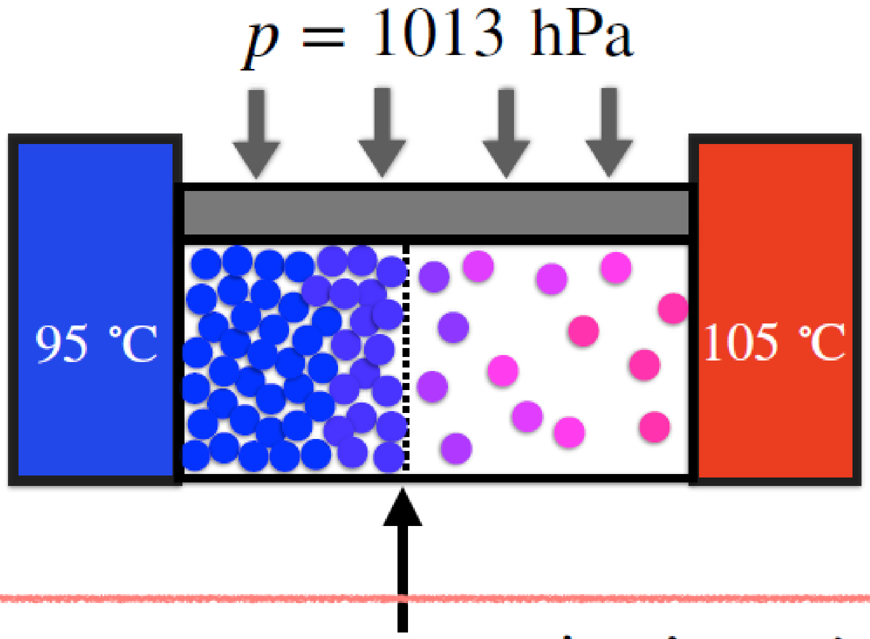
Statistical Mechanics of Non-equilibrium Phase Coexistence

Frontiers in Nonequilibrium physics
@YITP, Kyoto 26/05/11

in collaboration with Naoko Nakagawa

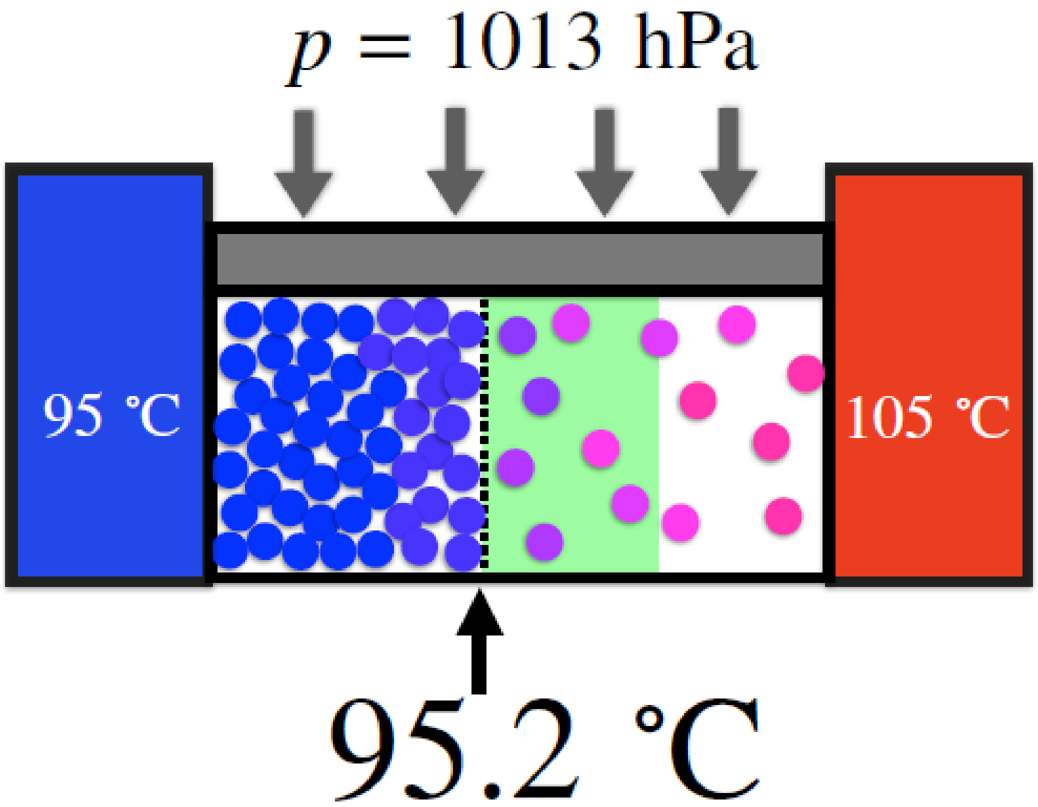
Liquid-Gas Coexistence under Weak Heat Flux

"H_2O Boiling Calmly" at atmospheric pressure



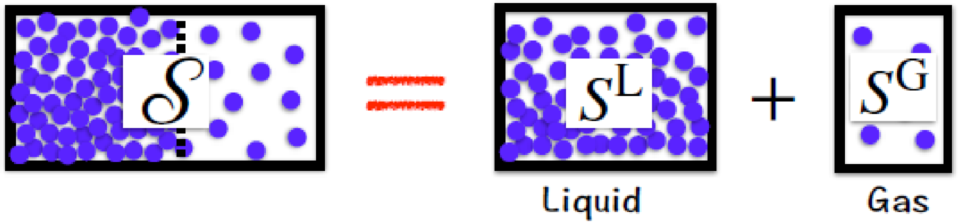
What is the temperature at the liquid-gas interface?

Global Thermodynamics Predicts



Brief Review: Coexistence in Equilibrium at fixed H, p, N

Variational function $\mathscr{S}(\mathscr{H}^{\mathrm{L}}, \mathscr{N}^{\mathrm{L}}; \underline{H, p, N}) = S^{\mathrm{L}} + S^{\mathrm{G}}$



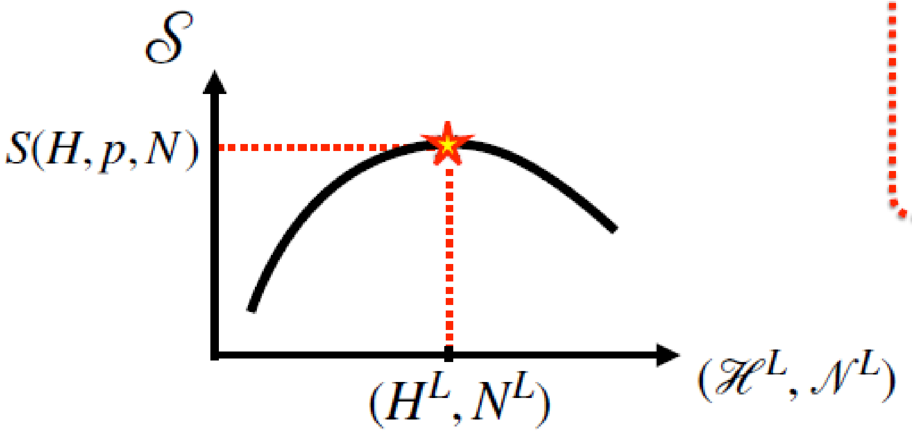
$$S^{\mathrm{L}} = S(\mathscr{H}^{\mathrm{L}}, p, \mathscr{N}^{\mathrm{L}})$$
$$S^{\mathrm{G}} = S(H - \mathscr{H}^{\mathrm{L}}, p, N - \mathscr{N}^{\mathrm{L}})$$

Maximum Entropy Principle

$$T^{\mathrm{L}} = T^{\mathrm{G}} \qquad \mu^{\mathrm{L}} = \mu^{\mathrm{G}}$$

Thermodynamic entropy

$$S(H, p, N) = \max_{\mathscr{H}^{\mathrm{L}}, \mathscr{N}^{\mathrm{L}}} \mathscr{S}(\mathscr{H}^{\mathrm{L}}, \mathscr{N}^{\mathrm{L}}; H, p, N)$$



$$dS = \frac{dH}{T} - \frac{V}{T}dp - \frac{\mu}{T}dN$$

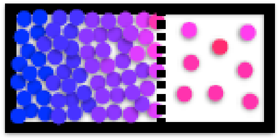
Global Temperature

$$\tilde{T} = \frac{\int d^3\boldsymbol{r}\ \rho(\boldsymbol{r})T(\boldsymbol{r})}{\int d^3\boldsymbol{r}\ \rho(\boldsymbol{r})}$$

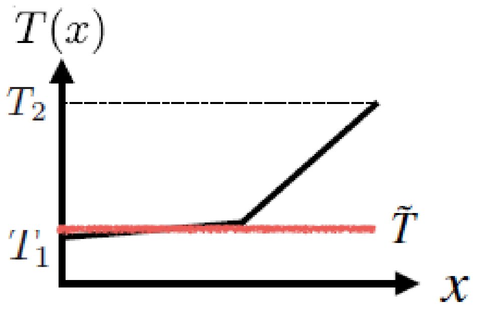
$$\langle K \rangle = \frac{3N}{2}\tilde{T}$$

mean kinetic energy of the system

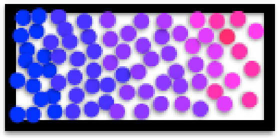
Liquid-gas coexistence



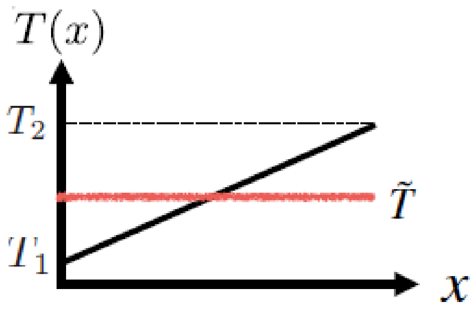
$$\tilde{T} \neq \frac{T_1 + T_2}{2} + O(\epsilon^2)$$



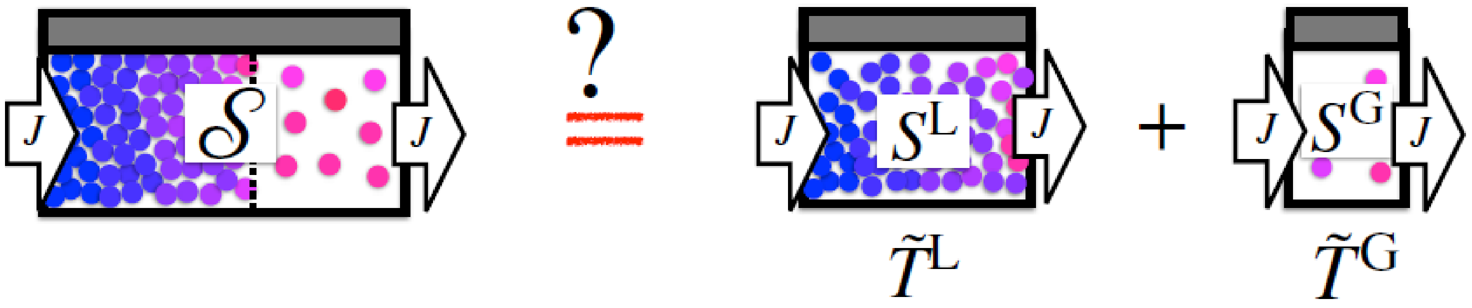
Single-phase state



$$\tilde{T} = \frac{T_1 + T_2}{2} + O(\epsilon^2)$$



Question variational entropy $\mathcal{S} = S^{\mathrm{L}} + S^{\mathrm{G}}$? fixed H, p, N



$\mathcal{S} = S^{\mathrm{L}} + S^{\mathrm{G}}$ leads to $\tilde{T}^{\mathrm{L}} = \tilde{T}^{\mathrm{G}}$

should be $\tilde{T}^{\mathrm{L}} \neq \tilde{T}^{\mathrm{G}}$

need extension

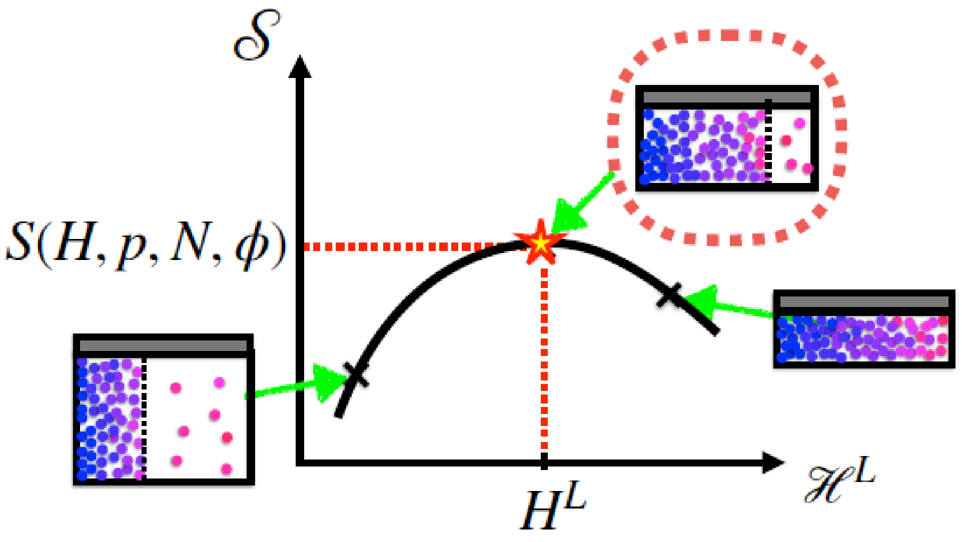
$\mathcal{S} = S^L + S^G + \phi\Psi$ degree of nonequilibrium $\phi \propto J$

Our Guiding Principle:

Simultaneous Extension of Thermodynamic and Variational Entropies

$$\mathcal{S}(\mathscr{H}^{\mathrm{L}}, \mathscr{N}^{\mathrm{L}}; H, p, N, \phi) = S(\mathscr{H}^{\mathrm{L}}, p, \mathscr{N}^{\mathrm{L}}) + S(H - \mathscr{H}^{\mathrm{L}}, p, N - \mathscr{N}^{\mathrm{L}}) + \phi\Psi$$

$$S(H, p, N, \phi) = \max_{\mathscr{H}^{\mathrm{L}},\, \mathscr{N}^{\mathrm{L}}} \mathcal{S}(\mathscr{H}^{\mathrm{L}}, \mathscr{N}^{\mathrm{L}}; H, p, N, \phi)$$



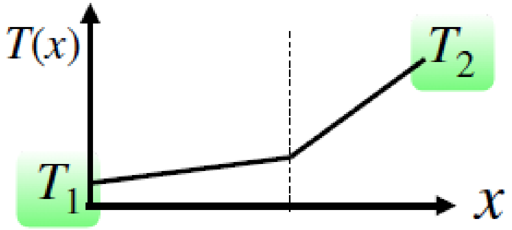
$$dS = \frac{dH}{\tilde{T}} - \frac{V}{\tilde{T}}dp - \frac{\tilde{\mu}}{\tilde{T}}dN + \Psi d\phi$$

$$\tilde{T} = \frac{\int d^3\mathbf{r}\ \rho(\mathbf{r})T(\mathbf{r})}{\int d^3\mathbf{r}\ \rho(\mathbf{r})}$$

Result Unique extension of Entropy

Phys. Rev. Res., 4, 033155 (2022)

Degree of nonequilibrium $$\phi = \frac{T_2 - T_1}{\tilde{T}}$$



Variational function

$$\mathcal{S}(\mathscr{H}^{\mathrm{L}}, \mathscr{N}^{\mathrm{L}}; H, p, N, \phi) = S(\mathscr{H}^{\mathrm{L}}, p, \mathscr{N}^{\mathrm{L}}) + S(H - \mathscr{H}^{\mathrm{L}}, p, N - \mathscr{N}^{\mathrm{L}}) + \frac{\phi}{2}\frac{H}{T_c(p)}\left(\frac{\mathscr{N}^{L}}{N} - \frac{\mathscr{H}^{L}}{H}\right)$$

$T_c(p)$: equilibrium transition temperature

maximize

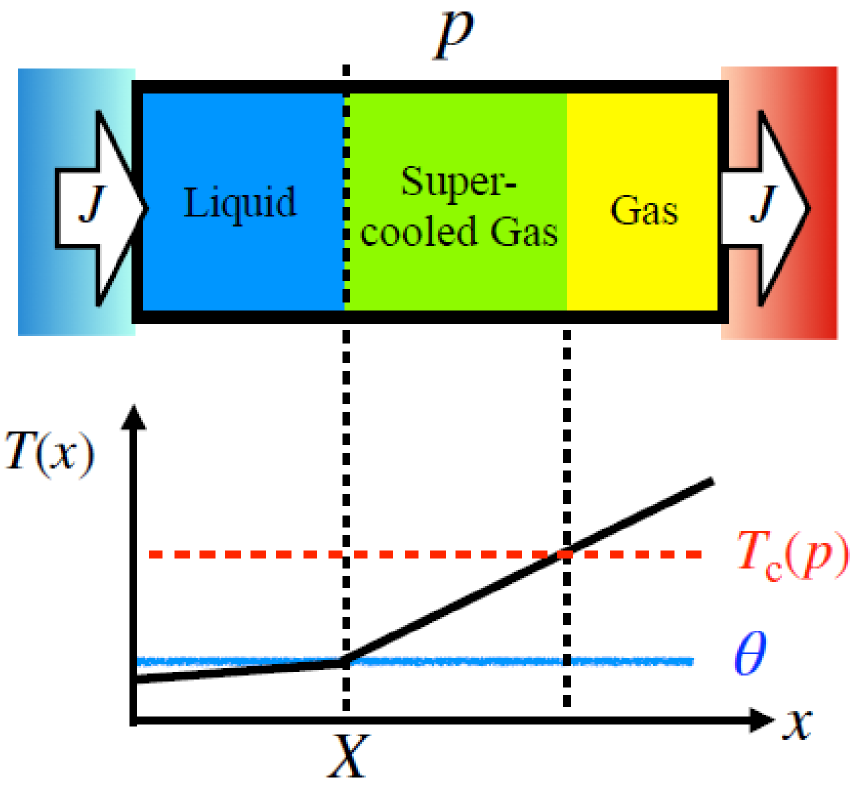
$$S(H, p, N, \phi) = S^L + S^G + \phi\Psi$$

$$\Psi = \frac{\hat{q}(p)}{T_c(p)}\frac{N^L N^G}{2N}$$

$\hat{q}(p)$: latent heat

Interface temperature θ deviates from Tc(p)

$$\theta - T_c(p) = \left[|J| \left(\frac{1}{\kappa^G} - \frac{1}{\kappa^L} \right) - \frac{|T_2 - T_1|}{L} \frac{V}{N} (\rho^L - \rho^G) \right] \frac{X(L-X)}{2L}$$



X : width of liquid region

J heat flux

$\kappa^{L/G}$ heat conductivity of liquid or gas

$\rho^{L/G}$ density of liquid or gas

Heat flow stabilizes meta-stable local states.

Nakagawa and Sasa, J. Stat. Phys., 177, 825 (2019)

Non-equilibrium phase coexistence

Prediction

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

Stabilization of meta-stable states
by non-equilibrium current

Meso-scale dynamics

- Numerical simulations
- Theoretical analysis

Derivation

Global thermodynamics

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).
N. N and S. S, PRL, **136**, 057101 (2026).

Derivation

Derivation

Micro-scale dynamics

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

Main message

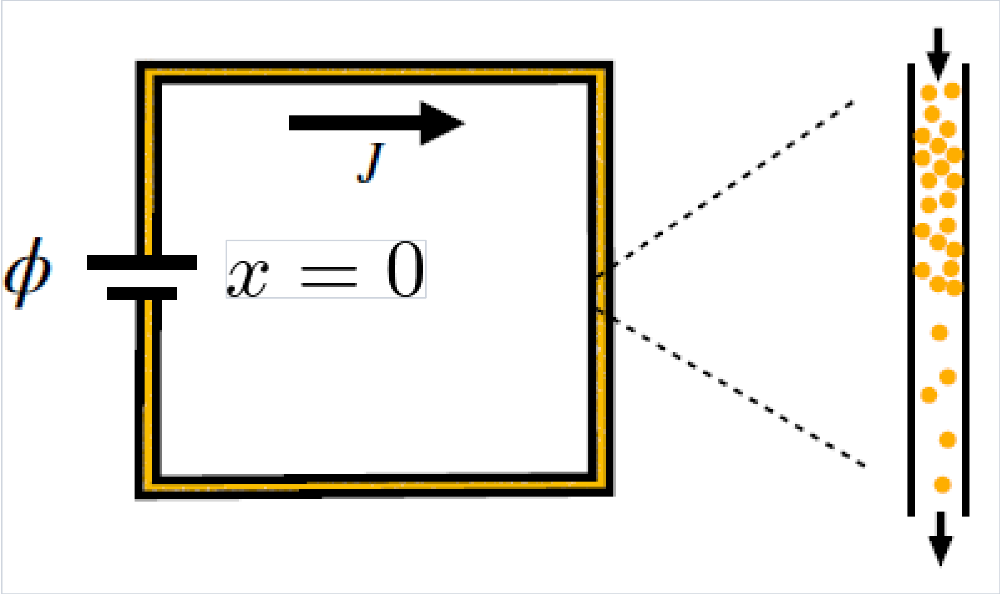
We propose **discrete fluctuating dynamics** (model B) that exhibits liquid-gas **phase coexistence** under driving

By analyzing this model, we derive the formula in **Global thermodynamics,** which claims that **metastable states stably appear** near the interface in the non-equilibrium liquid-gas phase coexistence.

Outline of my talk

1. Main message (8min)
2. Mesoscopic models
3. Phase coexistence conditions
4. Analysis
5. Results
6. Summary and remarks

Particle diffusion driven by a battery



One-dimensional model

Phase coexistence

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

A the area of the cross-section of the tube

Key assumption

Spatially discrete model

✓ (standard) continuum description is not obviously valid for very thin interfaces

(Number) density is the only locally conserved quantity.

✓ momenta and energy are not conserved.
(physical example: particle flow in a porous medium)

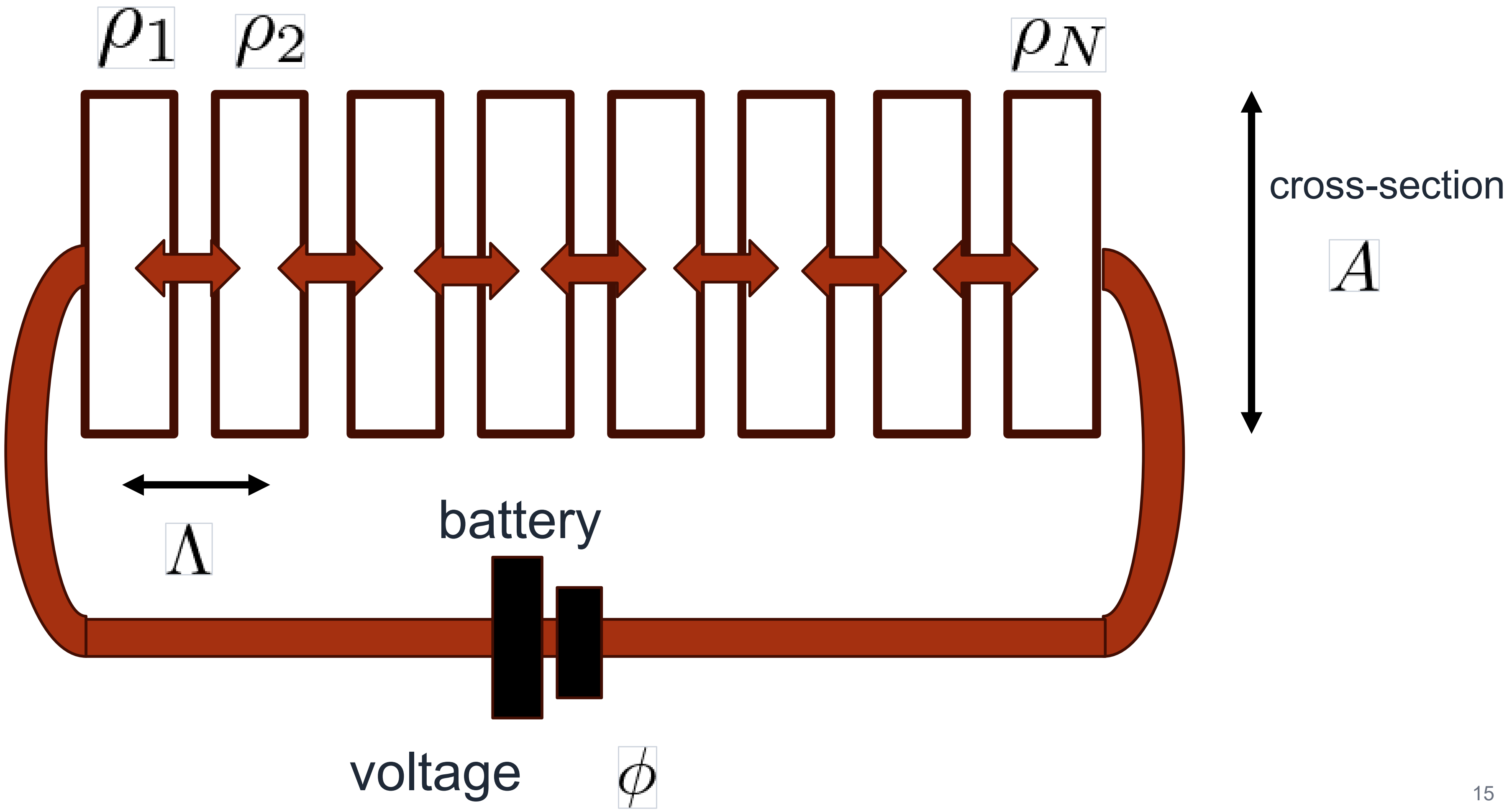
Setup - discrete Model B -

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

Periodic boundary

$$\rho_0 = \rho_N$$

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



Thermodynamics $\phi = 0$

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

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

(Generalized) chemical potential

$$\begin{aligned} \tilde{\mu}_i &\equiv \frac{1}{\Lambda}\frac{\partial \mathcal{F}}{\partial \rho_i} \\ &= \mu(\rho_i) - \frac{\kappa}{\Lambda^2}(\rho_{i+1} + \rho_{i-1} - 2\rho_i) \end{aligned}$$

Non-equilibrium stochastic 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)

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

→ **Steady state**

$N \to \infty$ $T_{\mathrm{eff}} \to 0$

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

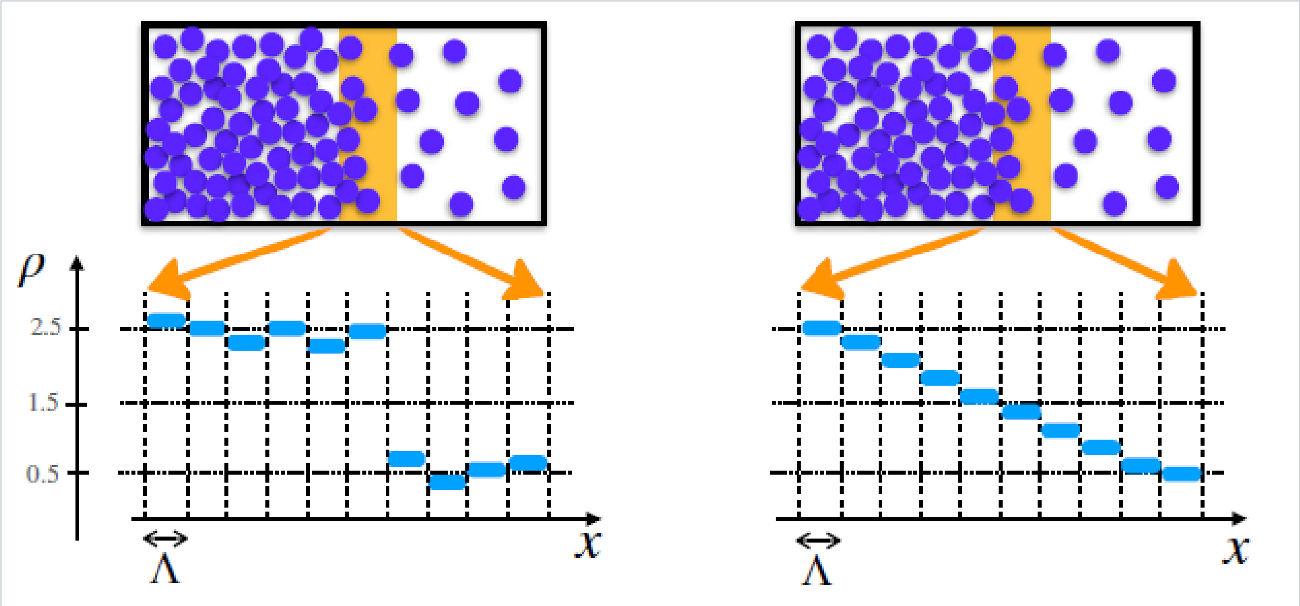
Two limiting cases

singular interface limit

$$\kappa_\Lambda \ll 1$$

Continuum limit

$$\kappa_\Lambda \gg 1$$



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

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

“standard”
fluctuating hydrodynamics

Fluctuating hydrodynamics (Model B)

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

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

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

$$\boldsymbol{\rho} = (\rho(x))_{0 \le x \le L}$$

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

Outline of my talk

1. Main message
2. Mesoscopic models (15min)
3. Phase coexistence conditions
4. Analysis
5. Results
6. Summary and remarks

Equilibrium Thermodynamics

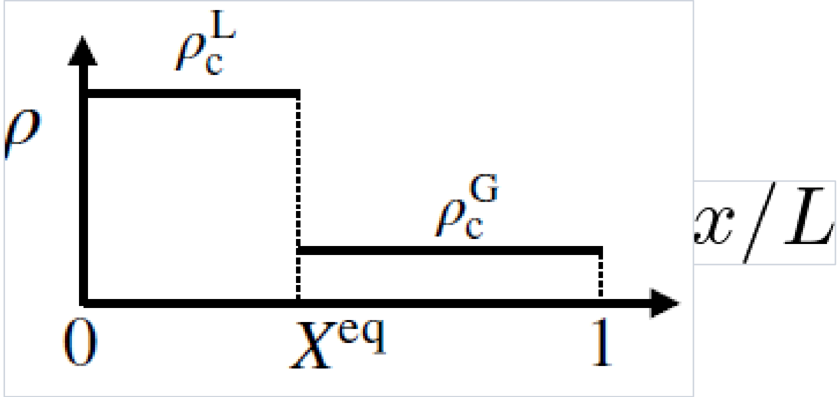
Phase coexistence occurs when $\bar{\rho}$ satisfies $\rho_c^G \le \bar{\rho} \le \rho_c^L$

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

$\mu(\rho_c^L) = \mu(\rho_c^G)$ and $p(\rho_c^L) = p(\rho_c^G)$

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

μ_c



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

Non-equilibrium cases:
Specific model for numerical simulations

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

$\rho_c^{\mathrm{L}} = 2.5$ $\rho_c^{\mathrm{G}} = 0.5$ $\mu_c = 0$

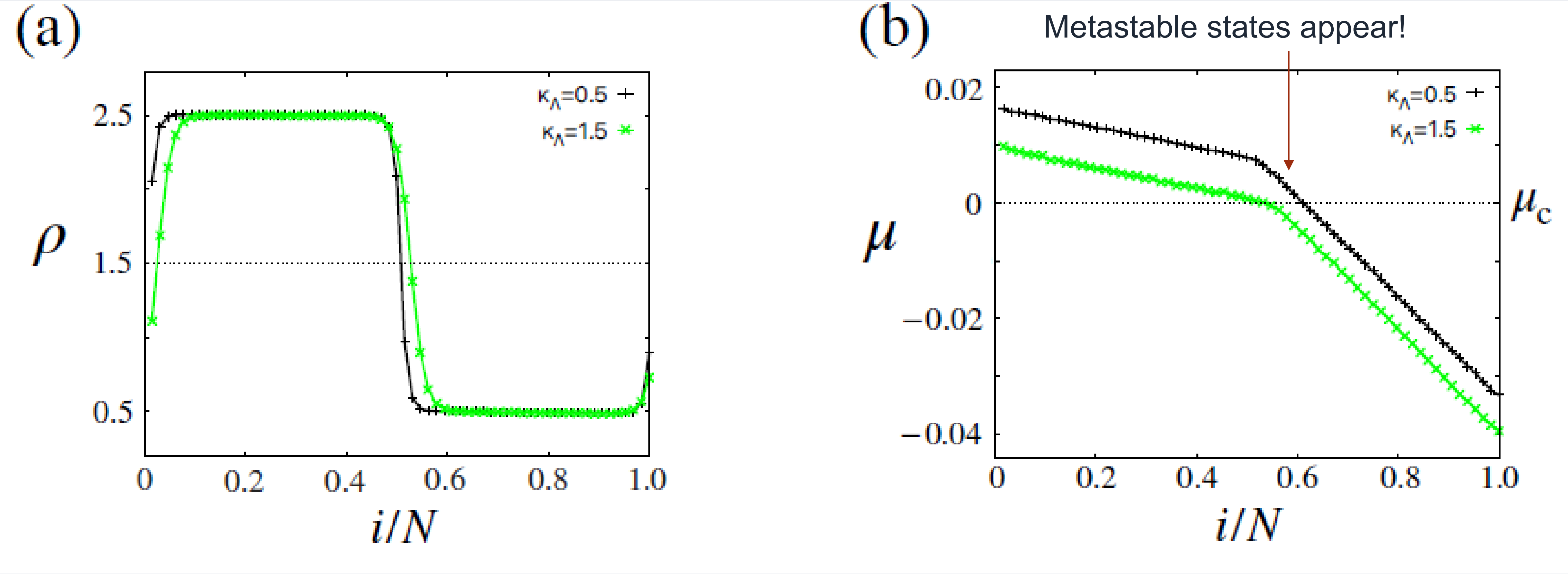
$\sigma(\rho) = \rho$

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

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

Unfixed parameter κ_Λ

Numerical result



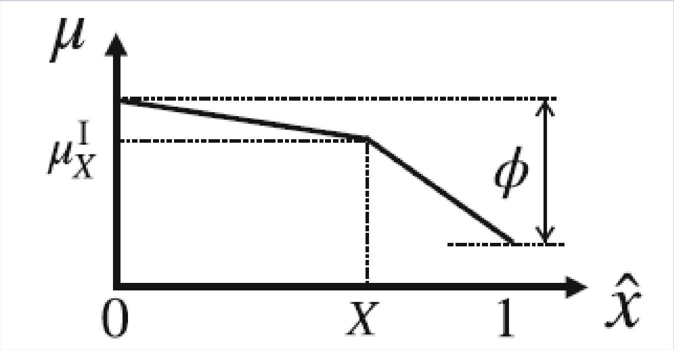
Non-equilibrium system

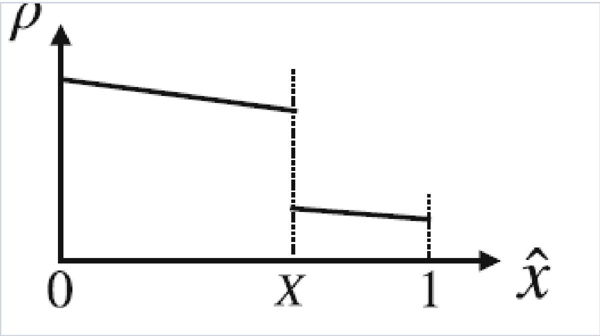
$\kappa_\Lambda \ll 1$

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

Many solutions (corresponding to metastable states)

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





$\hat{x} = i/N$

Question

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

↓

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

Outline of my talk

1. Main message
2. Mesoscopic models
3. Phase coexistence conditions (21min)
4. Analysis
5. Results
6. Summary and remarks

Steady-state distribution

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

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

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

- ✓ Zubarav-Mclennan representation (See Maes, Nectony, JMP 2010)
- ✓ Calculate the correction term with the time integration

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

Variational function for determining

$$
\begin{aligned}
L\mathcal{V}_{\mathrm{ss}}(X) \equiv \mathcal{F}_{\mathrm{ss}}(\rho_X^\phi) &= \mathcal{F}(\boldsymbol{\rho}_X^\phi) + \phi \, \langle Q \rangle^{\mathrm{eq}}_{\boldsymbol{\rho}_X^\phi} + O(\phi^2) \\
&= \mathcal{F}(\boldsymbol{\rho}_X^\phi) + \phi \, \langle Q \rangle^{\mathrm{eq}}_{\boldsymbol{\rho}_X^{\phi=0}} + O(\phi^2)
\end{aligned}
$$

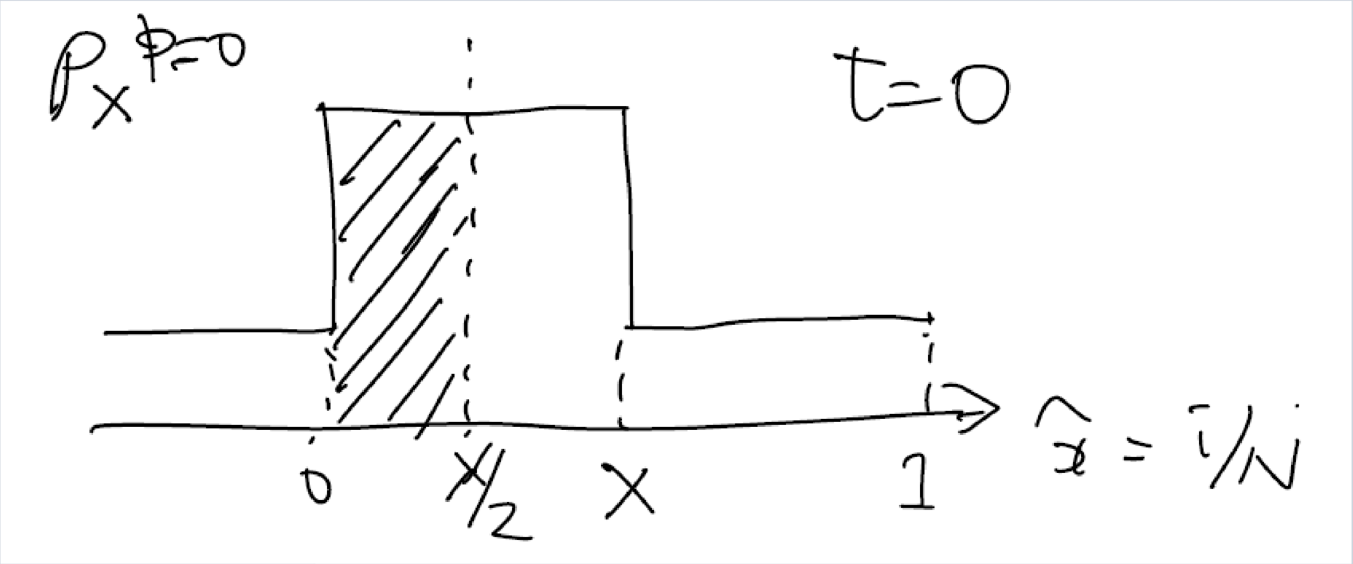
Variational principle $\mathcal{V}_{\mathrm{ss}}(X_*) = \min_X \mathcal{V}_{\mathrm{ss}}(X)$

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

→ μ^{I} Chemical potential at the interface

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

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



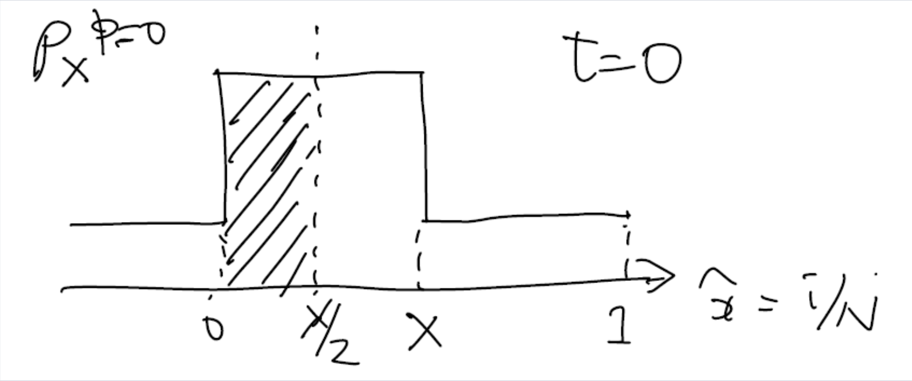
Particle conservation law

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

Time-integration

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

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



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

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

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

Variational function (Main result)

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

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

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

Outline of my talk

1. Main message
2. Mesoscopic models
3. Phase coexistence conditions
4. Analysis (25min)
5. Results
6. Summary and remarks

Result for $\kappa_\Lambda \ll 1$

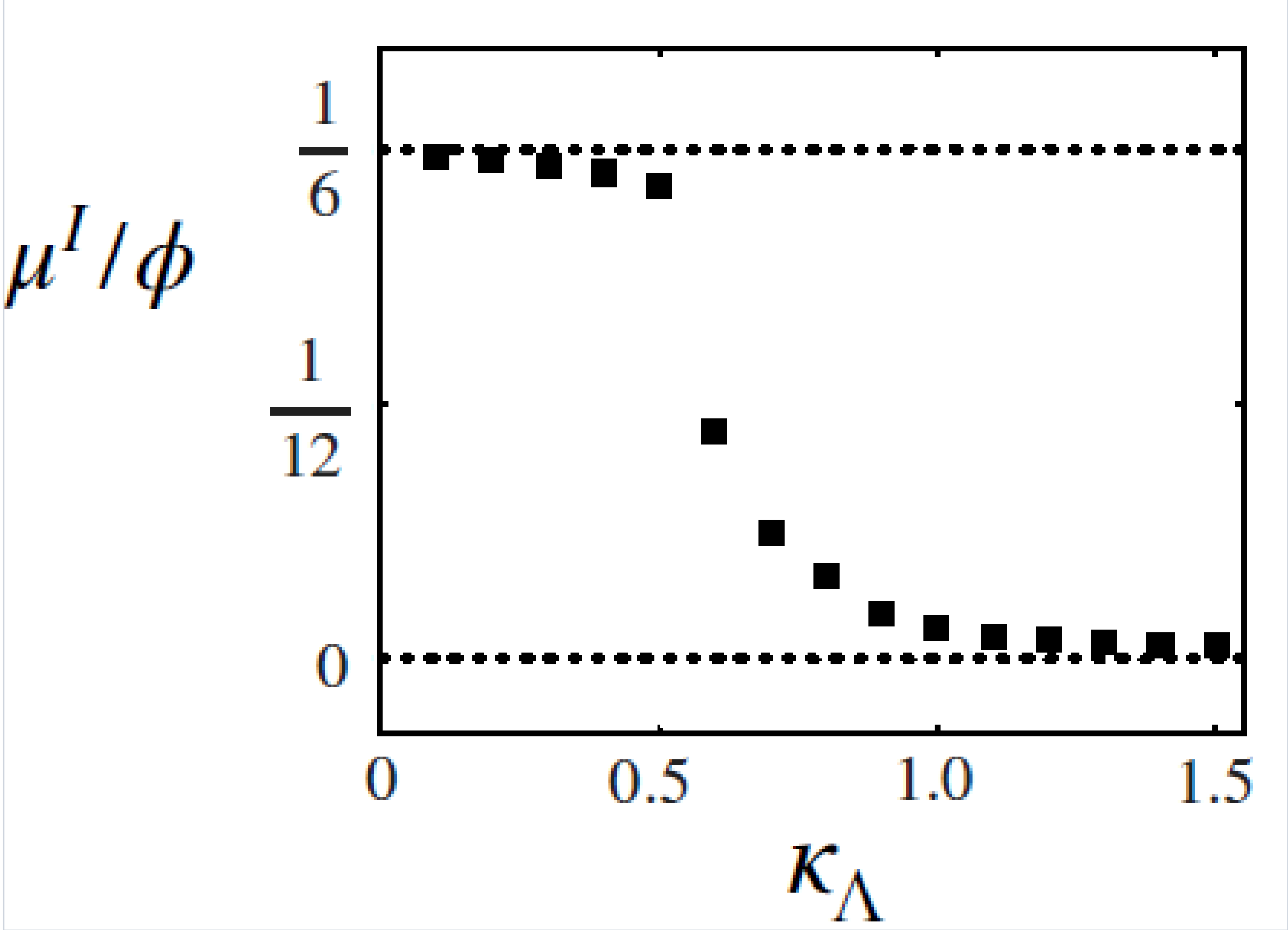
$$\mu^{\mathrm{I}} = \mu_{\mathrm{c}} + \frac{\phi}{2} \frac{(\sigma^{\mathrm{L}} - \sigma^{\mathrm{G}}) X^{\mathrm{eq}} (1 - X^{\mathrm{eq}})}{\sigma^{\mathrm{G}} X^{\mathrm{eq}} + \sigma^{\mathrm{L}} (1 - X^{\mathrm{eq}})}$$

Perfect agreement with the prediction by global thermodynamics!

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

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

Numerical result II



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

$\mu_{\mathrm{c}} = 0$

$\sigma^{\mathrm{L}} = 2.5$

$\sigma^{\mathrm{G}} = 0.5$

$X^{\mathrm{eq}} = 1/2$

Outline of my talk

1. Main message
2. Mesoscopic models
3. Phase coexistence conditions
4. Analysis
5. Results (27min)
6. Summary and remarks

Summary

Discrete fluctuating dynamics (model B) under external driving

Metastable states stably appear near the interface in the liquid-gas phase coexistence!

The formula of Global thermodynamics has been derived!

Next problems

Discrete fluctuating dynamics (model B) with open boundary conditions [particle reservoirs are attached at the both ends]

We are studying the Zubarev-Mclennan term (with the aid of AI).
(work in progress)

Analysis of a stochastic model for the liquid-gas coexistence of the simple liquid under heat conduction

Non-equilibrium phase coexistence

Experiments!

Prediction

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

Stabilization of meta-stable states
by non-equilibrium current

Meso-scale dynamics

- Numerical simulations
- Theoretical analysis

Derivation

Global thermodynamics

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).
N. N and S. S, PRL, **136**, 057101 (2026).

Derivation

Derivation

Micro-scale dynamics

M. Kobayashi, N. N and S. S PRL **130**, 247102 (2023)

Supplement

Non-equilibrium system $\kappa_\Lambda \gg 1$

Stationary solutions of the deterministic equation

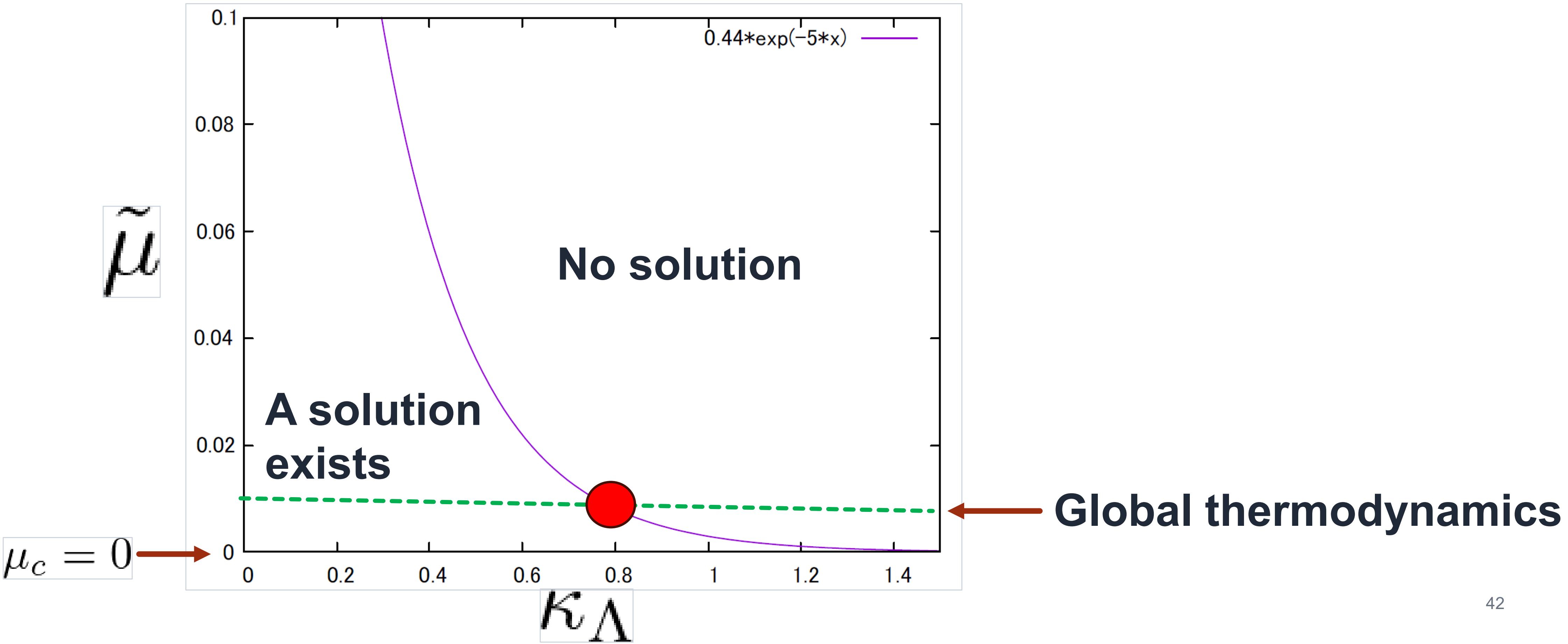
$$\partial_x[f'(\rho) - \kappa\partial_x^2\rho] = -\frac{J}{\sigma(\rho(x))}$$

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

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

Phase coexistence solutions at equilibrium with finite κ_Λ

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



Result with finite κ_Λ

$0 < \kappa_\Lambda \leq \kappa_\Lambda^c$ **Global thermodynamic phase**

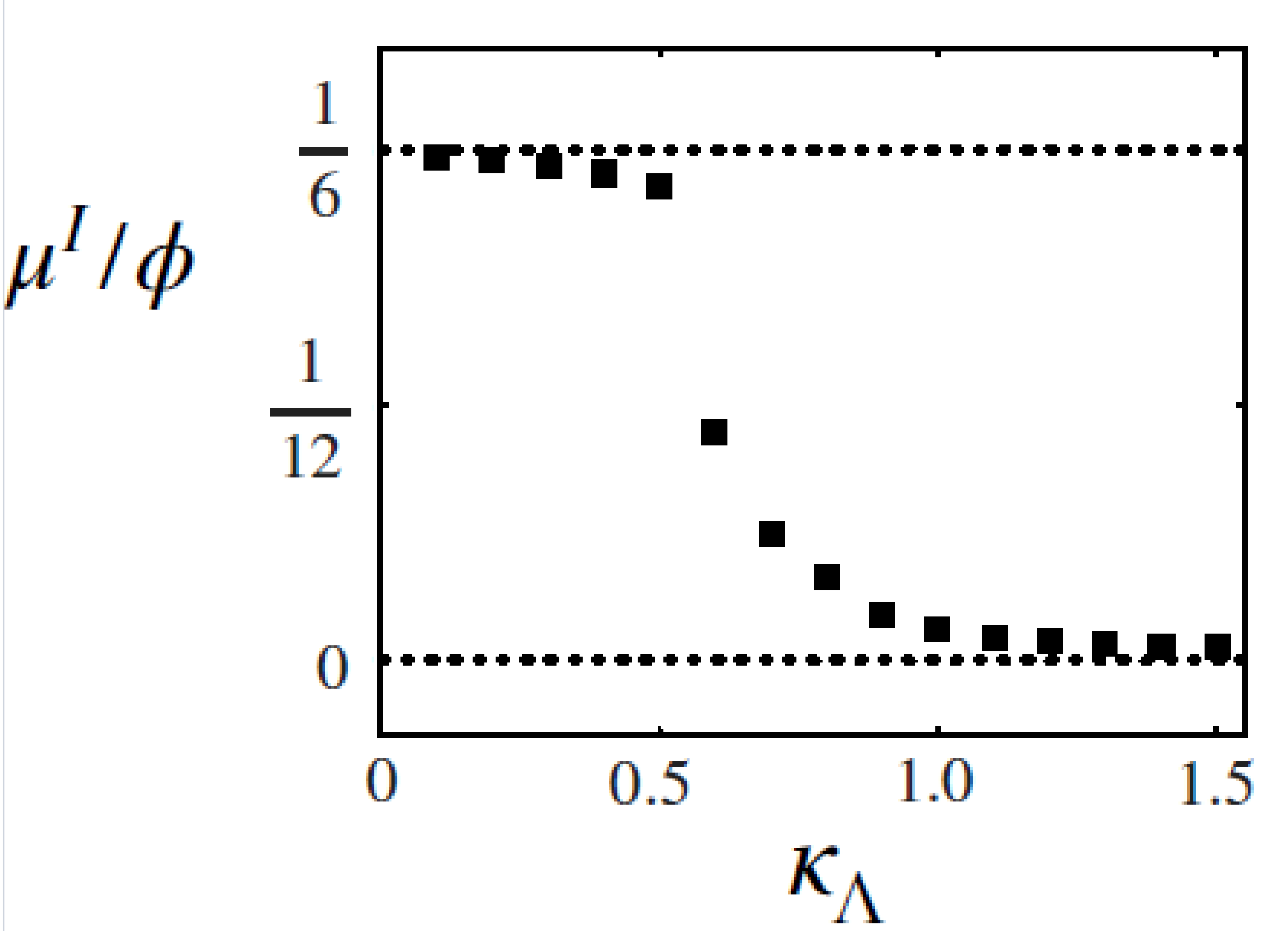
$$\mu^{\mathrm{I}} = \mu_{\mathrm{c}} + \frac{\phi}{2} \frac{(\sigma^{\mathrm{L}} - \sigma^{\mathrm{G}}) X^{\mathrm{eq}} (1 - X^{\mathrm{eq}})}{\sigma^{\mathrm{G}} X^{\mathrm{eq}} + \sigma^{\mathrm{L}} (1 - X^{\mathrm{eq}})}$$

$\kappa_\Lambda \to \infty$ **Local equilibrium state** $\mu^{\mathrm{I}} = \mu_{\mathrm{c}}$

$\kappa_\Lambda \geq \kappa_\Lambda^c$ **Cross-over** $\mu_I = \mu_c + \mathrm{e}^{-a(\kappa_\Lambda - \kappa_\Lambda^c)}$

$$\kappa_\Lambda^c = A - B \log \phi$$

Numerical result II



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

$$\mu_{\mathrm{c}} = 0$$

$$\sigma^{\mathrm{L}} = 2.5$$

$$\sigma^{\mathrm{G}} = 0.5$$

$$X^{\mathrm{eq}} = 1/2$$