Nonadditivity in the quasi-equilibrium state of a short-range interacting system

Takashi Mori (Univ. Tokyo)

Conference on Long-Range-Interacting Many Body Systems: from Atomic to Astrophysical Scales

Outline

1. **Introduction**
   additivity and nonadditivity
   No-go theorem in equilibrium state
   Quasi-equilibrium states
2. **Model**
3. **Numerical result**
   non-additivity in the quasi-equilibrium state
4. **Discussion and Summary**

additivity and nonadditivity

Rough meaning:

If the system can be regarded as a collection of independent subsystems, the system is said to be additive.

Expression in terms of the energy

$$H = H_A + H_B + H_{AB}$$

$$H_A, H_B \gg H_{AB}$$

? The value of the Hamiltonian depends on the microscopic state

Interaction between subsystems

$\langle H_A \rangle_{\mathrm{eq}}, \langle H_B \rangle_{\mathrm{eq}} \gg \langle H_{AB} \rangle_{\mathrm{eq}}$

✖ Not sufficient

There is a model in which this condition is satisfied but the two subsystems are not independent

$H_A, H_B \gg H_{AB}$ for ***any*** microscopic state

✖ Not necessary

There is a model in which this condition is violated but the two subsystems are almost independent

Definition of additivity *in this talk*

T. Mori, J. Stat. Phys. 159, 172 (2015)

$$H_i = H_A + H_B + H_{AB}$$

$$H_f = H_A + H_B$$

$$H(t) = H_A + H_B + \lambda H_{AB}$$

λ: $1 \to 0$ very slowly

Amount of work performed by the system: $W = E - E'$

If $W = o(V)$, the system is said to be additive

Consequence of additivity 1

$W = o(V)$

T. Mori, J. Stat. Phys. 159, 172 (2015)

Entropy is conserved during a quasi-static adiabatic process

$$S_{A+B}(E) = \max_{E'=E_A+E_B} [S_A(E_A) + S_B(E_B)]$$

$E' = E - W$: the internal energy after the thermodynamic process

$$W = o(V) \to E' = E + o(V)$$

Additivity of entropy:

$$S_{A+B}(E) = \max_{E=E_A+E_B} [S_A(E_A) + S_B(E_B)] + o(V)$$

Consequence of additivity 2

$W = o(V)$

T. Mori, J. Stat. Phys. 159, 172 (2015)

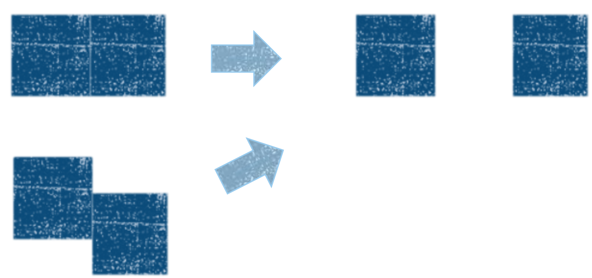
Additivity of entropy:

$$S_{A+B}(E) = \max_{E=E_A+E_B} [S_A(E_A) + S_B(E_B)] + o(V)$$

Shape-independence of entropy

S_{A+B}

$S_{A+B'}$



$S_A + S_B$

Consequence of additivity 3

$W = o(V)$ T. Mori, J. Stat. Phys. 159, 172 (2015)

→ Additivity of entropy:

$$S_{A+B}(E) = \max_{E=E_A+E_B} [S_A(E_A) + S_B(E_B)] + o(V)$$

→ Shape-independence of entropy

$$s_A(\varepsilon) = s_B(\varepsilon) = s_{A+B}(\varepsilon) = s(\varepsilon)$$

→ Concavity of entropy

$$\frac{V_A}{V} = x, \frac{V_B}{V} = 1 - x \qquad s(\varepsilon) \geq xs(\varepsilon_A) + (1-x)s(\varepsilon_B)$$

for any ε_A and ε_B with $\varepsilon = x\varepsilon_A + (1-x)\varepsilon_B$

Consequence of additivity 4

$W = o(V)$

T. Mori, J. Stat. Phys. 159, 172 (2015)

- Additivity of entropy:

$$S_{A+B}(E) = \max_{E=E_A+E_B} [S_A(E_A) + S_B(E_B)] + o(V)$$

- Shape-independence of entropy

$$s_A(\varepsilon) = s_B(\varepsilon) = s_{A+B}(\varepsilon) = s(\varepsilon)$$

- Concavity of entropy

$$s(\lambda\varepsilon_A + (1-\lambda)\varepsilon_B) \geq \lambda s(\varepsilon_A) + (1-\lambda)s(\varepsilon_B)$$

- Ensemble equivalence, non-negativity of the specific heat,…

All the desired properties of additive systems are derived from the single condition!

Nonadditive systems

Entropy may depend on the shape of the system
Entropy may be non-concave
Ensemble equivalence may be violated
Specific heat may be negative in the microcanonical ensemble
etc…

Unscreened long-range interactions make the system nonadditive

Rigorous results in equilibrium statistical mechanics

Short-range interaction $V(r) \lesssim \dfrac{1}{r^{d+\epsilon}}$ with some $\epsilon > 0$

Any short-range interacting particle or spin systems with sufficiently strong short-range repulsions are additive

D. Ruelle, “statistical mechanics”

Nonadditivity cannot be realized in an equilibrium state of a short-range interacting macroscopic system

No-Go theorem in equilibrium stat. mech.

Possible ways towards long-range effective Hamiltonian

Small systems

Interaction range ~ system size

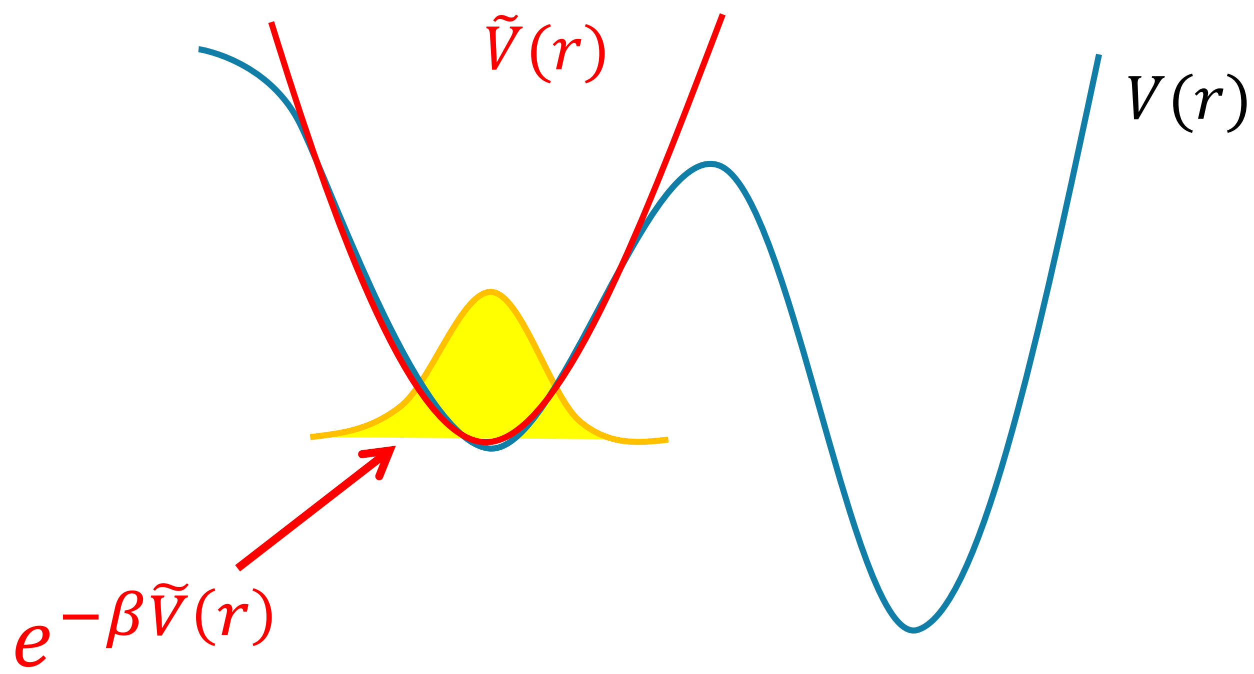
Macroscopic systems

Non-neutral Coulomb system
Dipolar systems

Non-equilibrium states

Nonequilibrium steady states (NESS): broken detailed balance condition
Quasi-equilibrium states (metastable equilibrium): detailed balance satisfied

Quasi-equilibrium state (metastable equilibrium)



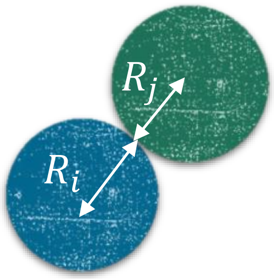
Quasi-equilibrium state is described by the equilibrium distribution of an effective Hamiltonian

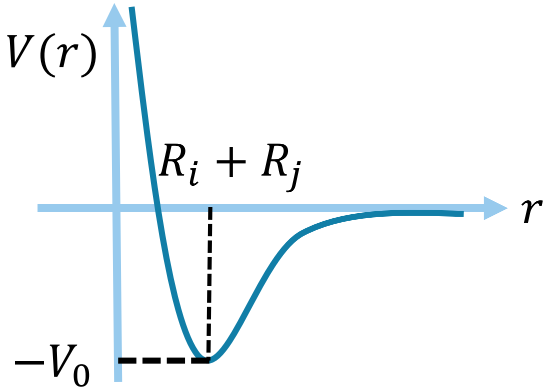
Model

Classical particle systems in the two or three dimensional space
(In this talk: two-dimensional system)

Pair interactions: $V(r)$

Atomic radius R
Potential depth V_0





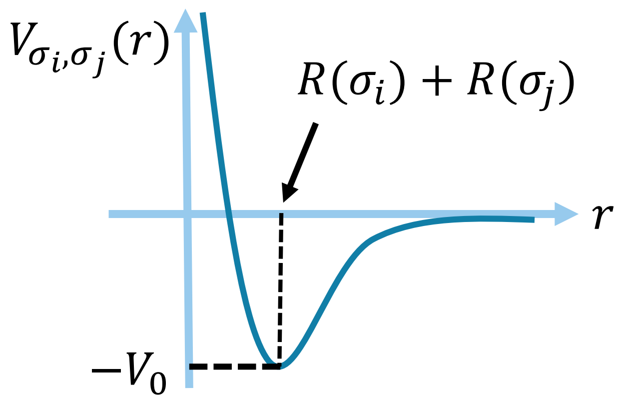
Each particle has an internal degree of freedom $\sigma = \pm 1$

Depending on σ, the radius of the particle changes

$R = R(\sigma)$, $R(-1) < R(+1)$ $\qquad$ $R_i = R(\sigma_i), R_j = R(\sigma_j)$

Hamiltonian

$$H = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} + \sum_{i<j}^{N} V_{\sigma_i,\sigma_j}(\boldsymbol{q}_i - \boldsymbol{q}_j) - h \sum_{i=1}^{N} \sigma_i$$



<u>dynamics</u>

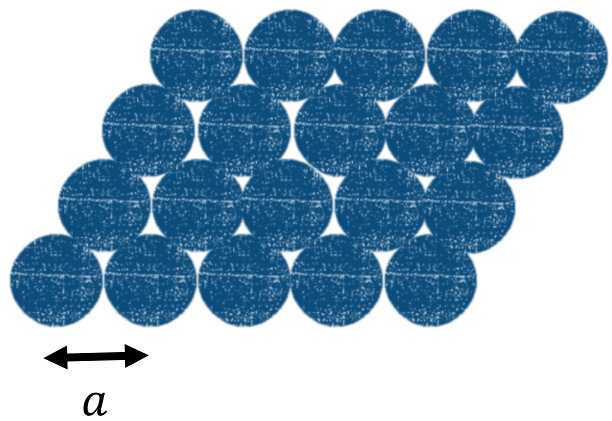
$\{\boldsymbol{q}_i, \boldsymbol{p}_i\}$: Hamilton dynamics
$\{\sigma_i\}$: Monte-Carlo dynamics

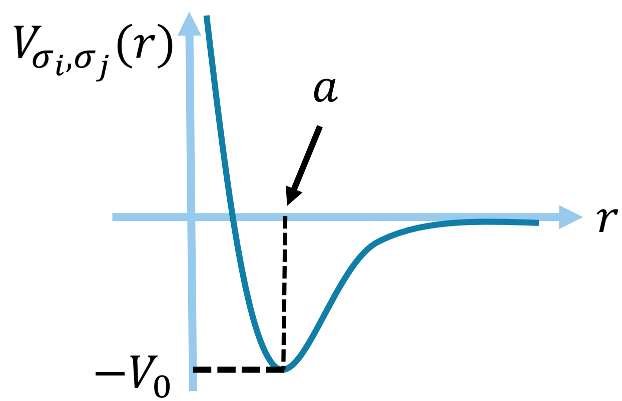
Canonical: Metropolis
Microcanonical: Creutz

A model for Spin-Crossover material: P. Gütlich, et.al., Angew. Chem., Int. Ed. Engl. 33, 2024 (1994)
$\sigma = 1$ High-Spin state
$\sigma = -1$ Low-Spin state
The size difference between HS and LS molecules is an experimental fact

Initial state

triangular lattice structure put in the infinitely extended space



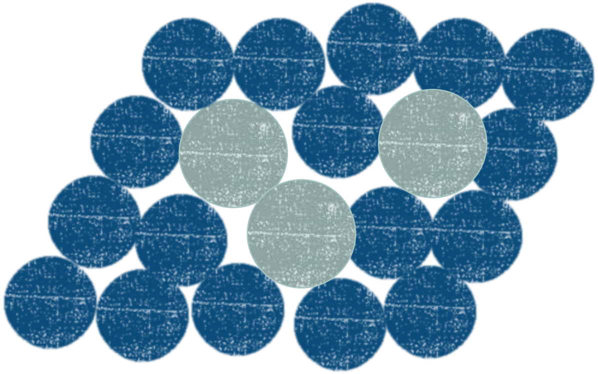


$k_B T \ll V_0$ This lattice structure is stable up to the time $\tau \sim e^{\frac{V_0}{k_B T}}$

The system will reach the quasi-equilibrium state with this lattice structure held kept

Intermediate state 1

triangular lattice structure put in the infinitely extended space

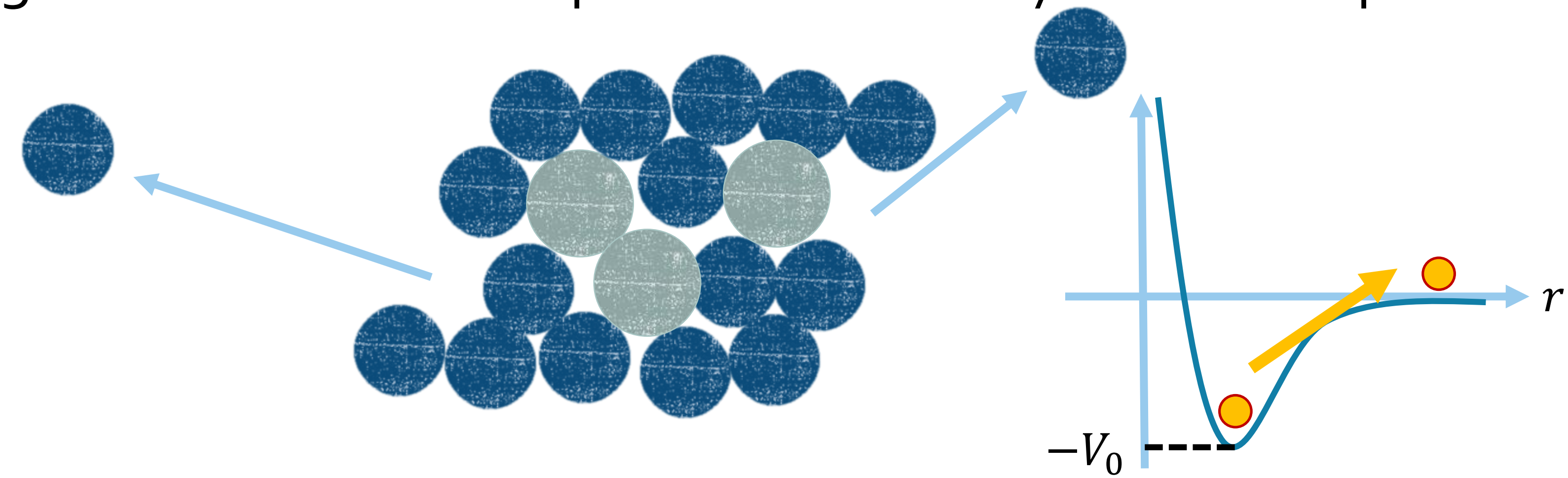


$k_B T \ll V_0$ This lattice structure is stable up to the time $\tau \sim e^{\frac{V_0}{k_B T}}$

The system will reach the quasi-equilibrium state with this lattice structure held kept

Intermediate state 2

triangular lattice structure put in the infinitely extended space

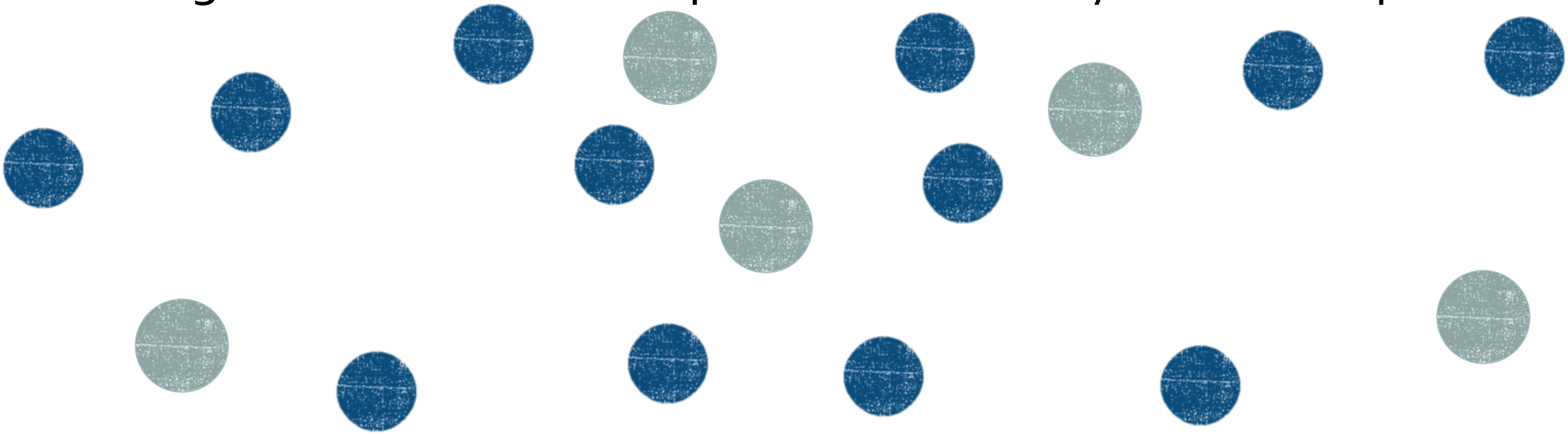


$\color{red}{k_B T \ll V_0}$ This lattice structure is stable up to the time $\tau \sim e^{\frac{V_0}{k_B T}}$

The system will reach the quasi-equilibrium state with this lattice structure held kept

Final state

triangular lattice structure put in the infinitely extended space



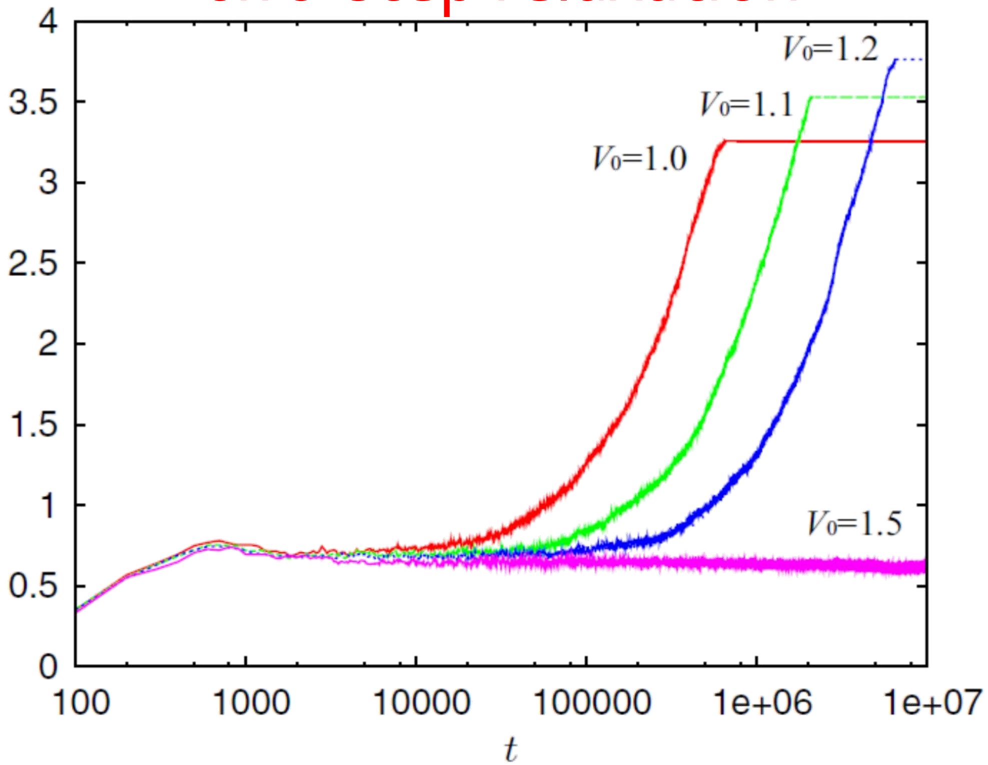
The particles finally go somewhere far away

Numerical simulation

$m = 1, k_B T = 0.26, h = 0, R(-1) = 1, R(1) = 1.1$

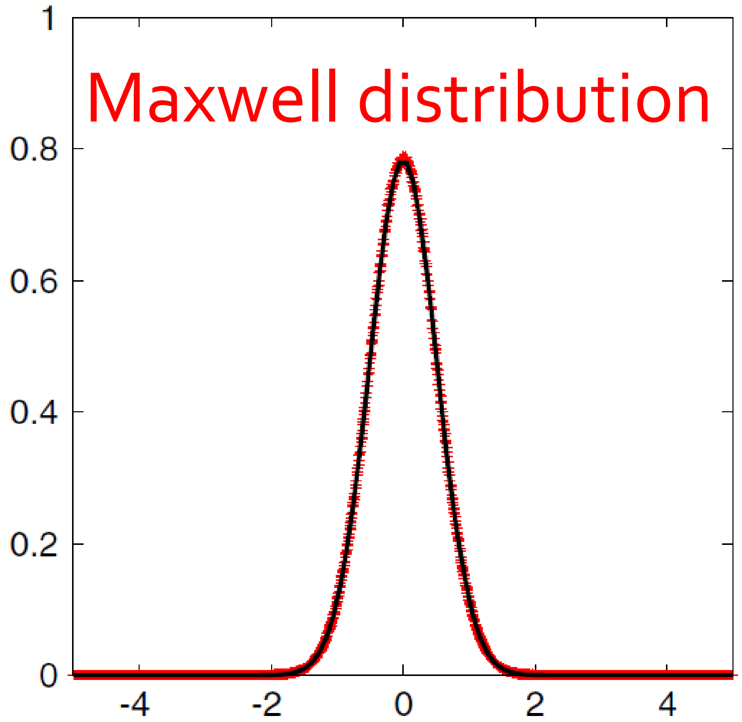
two-step relaxation

E/N



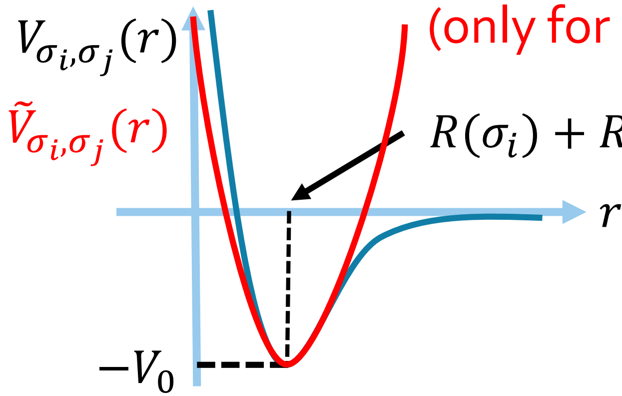
Quasi-equilibrium state

Momentum distribution in the quasi-equilibrium state



Effective Hamiltonian

In the quasi-equilibrium state, the lattice structure is maintained.
→ We can approximate the interaction potential between the nearest neighbor pair by the quadratic one



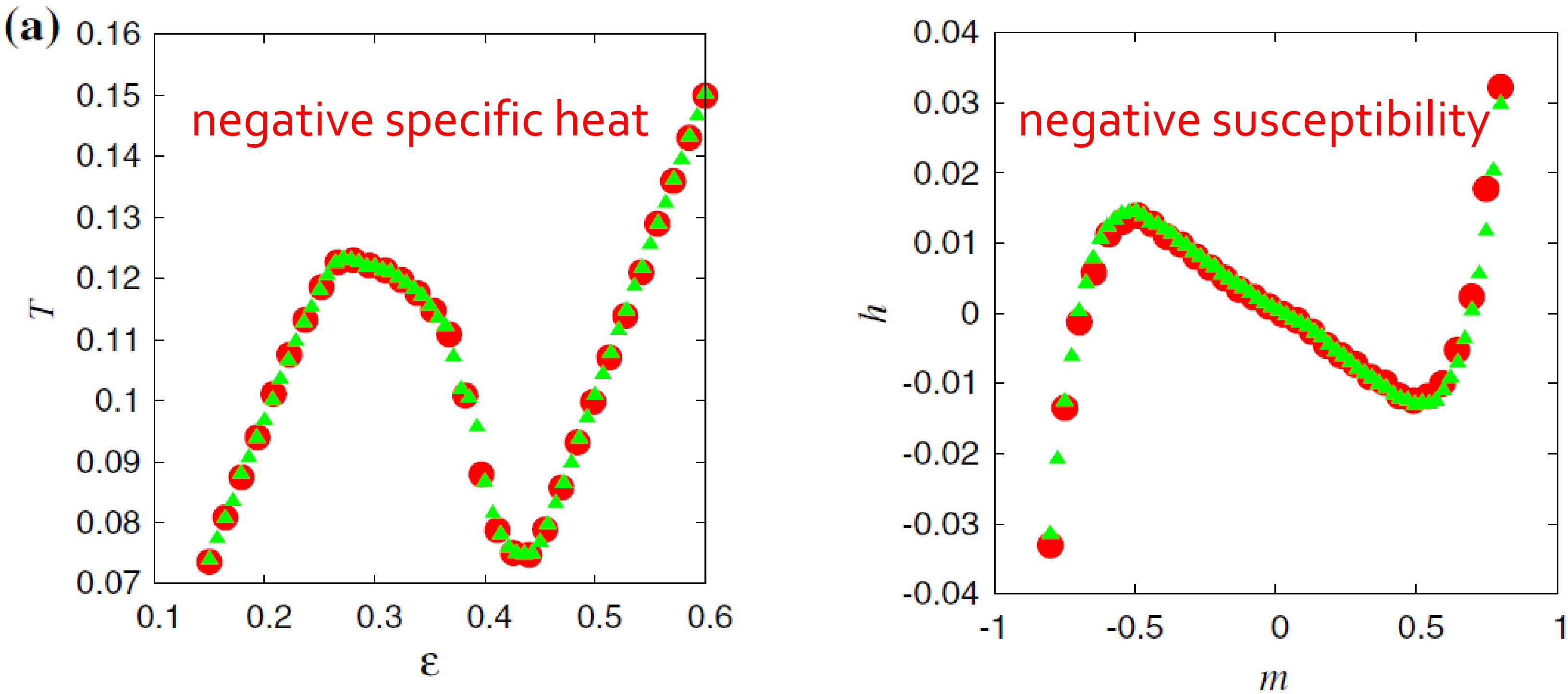
only the nearest neighbors

$$\tilde{H} = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} + \sum_{<i,j>}^{N} \frac{k}{2}\left(|\boldsymbol{q}_i - \boldsymbol{q}_j| - R(\sigma_i) - R(\sigma_j)\right)^2 - h \sum_{i=1}^{N} \sigma_i$$

Thermodynamic properties

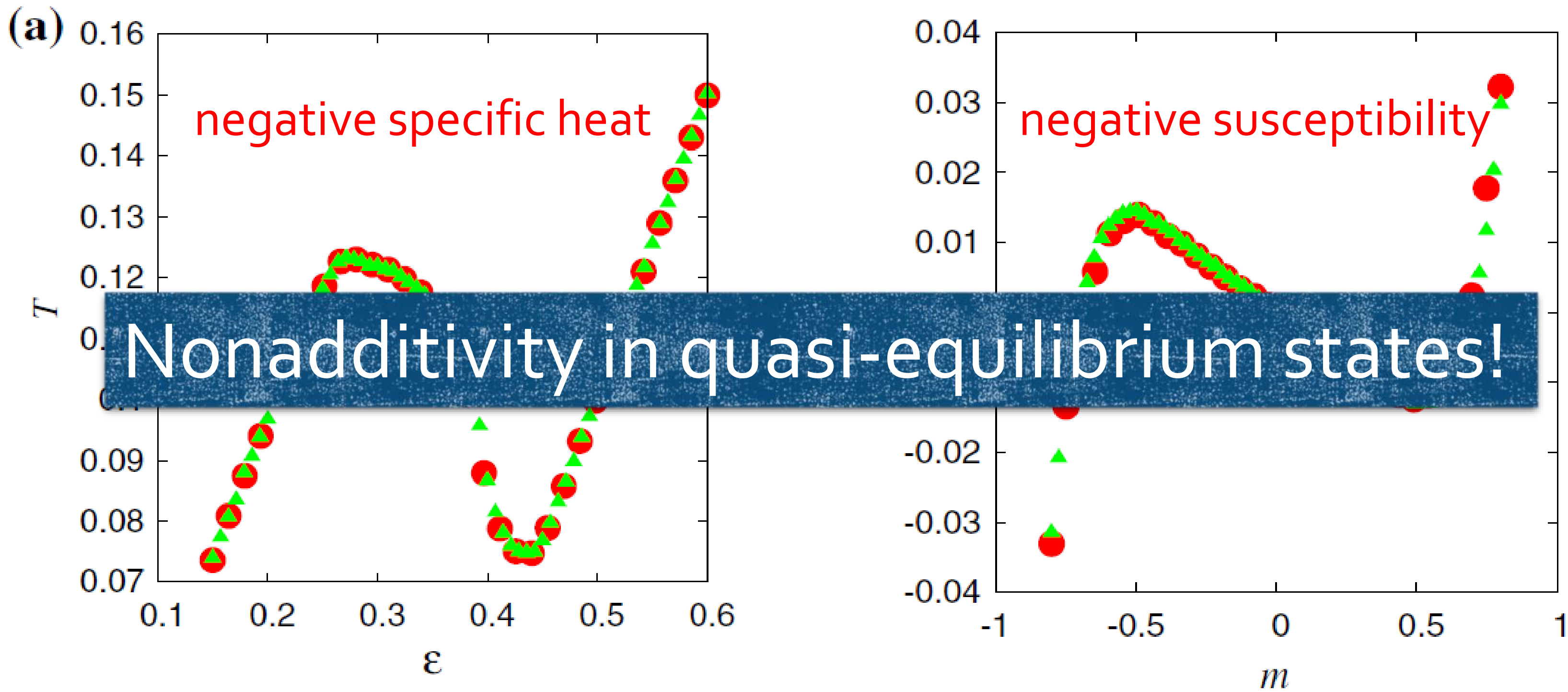
Red: average in the quasi-equilibrium state

Green: average in the equilibrium state of $\widetilde{H}$



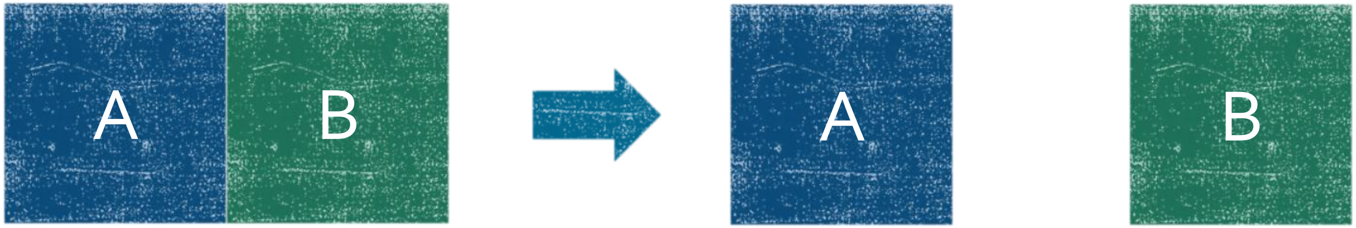
Thermodynamic properties

Red: average in the quasi-equilibrium state
Green: average in the equilibrium state of $\tilde{H}$

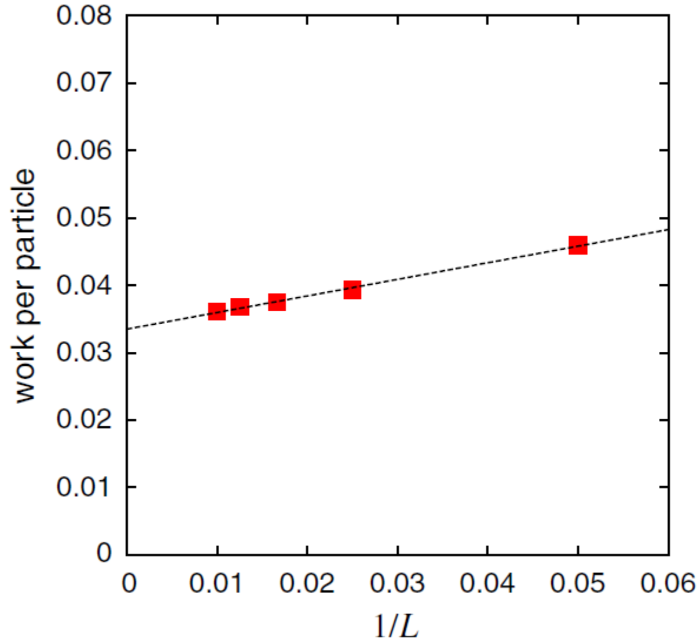


Nonadditivity in quasi-equilibrium states!

Direct evidence of nonadditivity



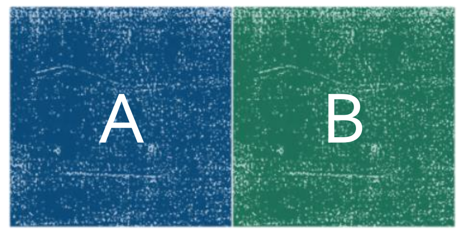
Hamiltonian: $\widetilde{H}$



$W = \mathcal{O}(N)$

Macroscopic amount of work is necessary

Thermal average of the interaction energy is negligible



$$\widetilde{H} = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} + \sum_{<i,j>}^{N} \frac{k}{2}\left(\left|\boldsymbol{q}_i - \boldsymbol{q}_j\right| - R(\sigma_i) - R(\sigma_j)\right)^2 - h \sum_{i=1}^{N} \sigma_i$$

Only nearest-neighbor interactions

$$\langle H_A \rangle_{\mathrm{eq}}, \langle H_B \rangle_{\mathrm{eq}} \gg \langle H_{AB} \rangle_{\mathrm{eq}}$$

Effective spin-spin interactions

The degrees of freedom $\{\boldsymbol{q}_i, \boldsymbol{p}_i, \sigma_i\}$

integrate out over $\{\boldsymbol{q}_i, \boldsymbol{p}_i\}$ ➡ Effective spin-spin interaction

$\widetilde{H}(\{\boldsymbol{q}_i, \boldsymbol{p}_i, \sigma_i\}) \to H_{\text{eff}}(\{\sigma_i\})$

$e^{-\beta H_{\text{eff}}} \sim \int d\boldsymbol{q} \int d\boldsymbol{p} e^{-\beta \widetilde{H}}$

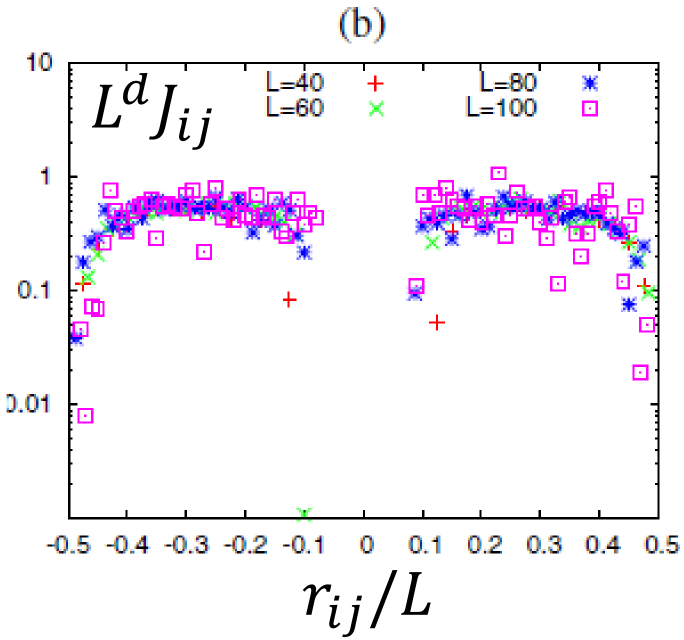
It is difficult to obtain H_{eff}
→ guess the interaction potential under the ansatz

$$H_{\text{eff}} = \sum_{i<j} J_{ij} \sigma_i \sigma_j - h \sum_{i=1}^{N} \sigma_i$$

Effective spin-spin interactions

The data of correlation functions: $C_{ij} = \langle \sigma_i \sigma_j \rangle$

$$\beta J_{ij} \simeq \delta_{ij} - (C^{-1})_{ij}$$



It is found that J_{ij} obeys the scaling

$$J_{ij} = \frac{1}{L^d} \phi\left(\frac{\boldsymbol{r}_i - \boldsymbol{r}_j}{L}\right)$$

J_{ij} is independent of the temperature (energetic origin, not entropic origin)

Meaning of the scaling

$$J_{ij} = \frac{1}{L^d}\phi\left(\frac{\boldsymbol{r}_i - \boldsymbol{r}_j}{L}\right)$$

The interaction range is comparable with the system size
The interaction between two particles is very weak
→ The interaction energy per particle is independent of the system size

Long-range interactions with Kac's prescription
extensive but nonadditive

Discussion: Kac's prescription

The spin degrees of freedom of the model is described by the effective Hamiltonian with pair interactions

$$J_{ij} = \frac{1}{L^d} \phi\left(\frac{\boldsymbol{r}_i - \boldsymbol{r}_j}{L}\right)$$

Kac's prescription naturally appears

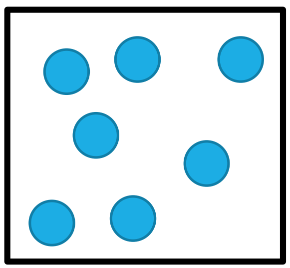
Originally short-range interacting systems

$$\widetilde{H} = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} + \sum_{<i,j>}^{N} \frac{k}{2}\left(\left|\boldsymbol{q}_i - \boldsymbol{q}_j\right| - R(\sigma_i) - R(\sigma_j)\right)^2 - h\sum_{i=1}^{N} \sigma_i$$

Long-range force → nonadditivity
Nearest neighbor interaction → extensivity

"Equilibrium" depends on timescale

Practically, we cannot distinguish equilibrium and quasi-equilibrium.

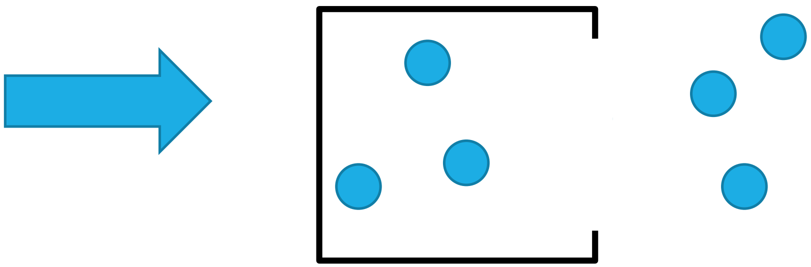


$$H = \sum_i \left[\frac{\boldsymbol{p}_i^2}{2m} + U(\boldsymbol{q}_i) \right] + \sum_{i \neq j} V(\boldsymbol{q}_i - \boldsymbol{q}_j)$$

Container is modeled by potential barrier

Quasi-equilibrium state

If we consider the Hamiltonian of all the atoms of the gas and the container, this state is not the true equilibrium state



Container is eroded and broken

“Equilibrium” depends on timescale

Feynman in “Statistical Mechanics”

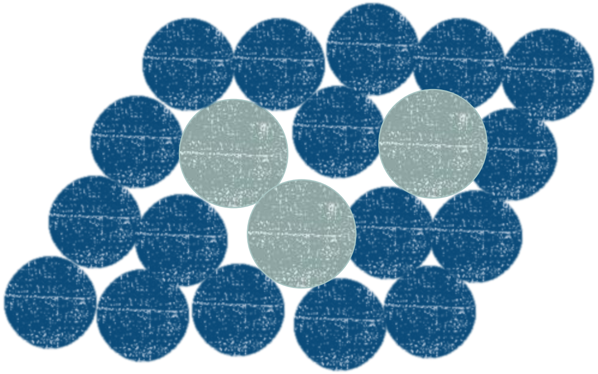
If all the “fast” things have happened and all the “slow” things not, the system is said to be in thermal equilibrium.

In this sense, practically we cannot distinguish equilibrium and quasi-equilibrium.
The concept of “equilibrium” depends on the timescale!

In a certain (not infinitely long) timescale, short-range systems can exhibit nonadditivity.

Dynamics

Spin-spin effective interaction is long-ranged,
But the interactions spread with finite speed.



In short-time dynamics, the system behaves as a short-range interacting system.

It is expected that the dynamical phenomena in this system differ from those in usual long-range interacting systems.

Summary

- Short-range interacting macroscopic systems can exhibit nonadditivity in their quasi-equilibrium states
- Such quasi-equilibrium states do not depend on the detail of the dynamical rule
- Effective Hamiltonian contains long-range interactions
- Kac's prescription is not necessary (the size-dependent scaling naturally appears in the effective potential)
- Distinction between quasi-equilibrium and equilibrium is rather subtle.

T. Mori, J. Stat. Phys. 159, 172 (2015)
T. Mori, Phys. Rev. Lett. 111, 020601 (2013)