Thermodynamic concepts out of equilibrium: from classical to quantum

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Boltzmann Lecture, SISSA, Italia, 2021

Statistical physics

Advantage

No need to solve the dynamic equations!

Under the *ergodic hypothesis*, after some *equilibration time* t_{eq}, *macroscopic observables* can be, on average, obtained with a *static* calculation, as an average over all configurations in phase space weighted with a probability distribution function $\boldsymbol{P(\{\vec{p}_i, \vec{x}_i\})}$

$$\langle A \rangle = \int \prod_i d\vec{p}_i d\vec{x}_i \, \boldsymbol{P(\{\vec{p}_i, \vec{x}_i\})} \, A(\{\vec{p}_i, \vec{x}_i\})$$

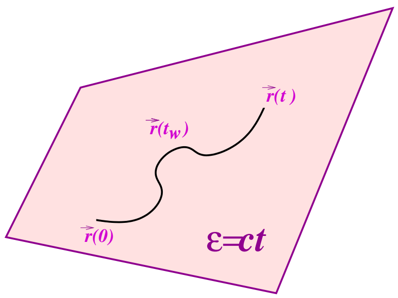
$\langle A \rangle$ should coincide with $\overline{A} \equiv \lim_{\tau \to \infty} \frac{1}{\tau} \int_{t_{\mathrm{eq}}}^{t_{\mathrm{eq}}+\tau} dt' \, A(\{\vec{p}_i(t'), \vec{x}_i(t')\})$

the *time average* typically measured experimentally

Boltzmann, late XIX

Statistical Physics

Ensembles: recipes for $P(\vec{p}_i, \vec{x}_i)$ according to circumstances



Isolated system

$$\mathcal{E} = \mathcal{H}(\{\vec{p}_i, \vec{x}_i\}) = ct$$

Microcanonical distribution

$$\boxed{P(\{\vec{p}_i, \vec{x}_i\}) \propto \delta(\mathcal{H}(\{\vec{p}_i, \vec{x}_i\}) - \mathcal{E})}$$

Flat probability density

$$S_{\mathcal{E}} = k_B \ln g(\mathcal{E}) \qquad \beta \equiv \frac{1}{k_B T} = \left.\frac{\partial S_{\mathcal{E}}}{\partial \mathcal{E}}\right|_{\mathcal{E}}$$

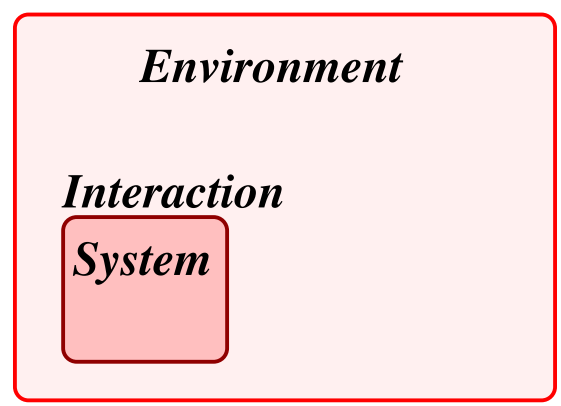
Entropy — Temperature

$$\mathcal{E} = \mathcal{E}_{syst} + \mathcal{E}_{env} + \mathcal{E}_{int}$$

Neglect $\mathcal{E}_{int}$ (short-range interact.)

$$\mathcal{E}_{syst} \ll \mathcal{E}_{env} \qquad \beta = \frac{\partial S_{\mathcal{E}_{env}}}{\partial \mathcal{E}_{env}}$$

$$\boxed{P(\{\vec{p}_i, \vec{x}_i\}) \propto e^{-\beta \mathcal{H}(\{\vec{p}_i, \vec{x}_i\})}}$$



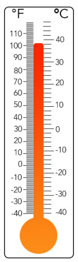
Canonical ensemble

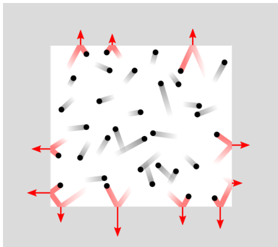
Statistical physics

Accomplishments

- Microscopic definition & derivation of thermodynamic concepts

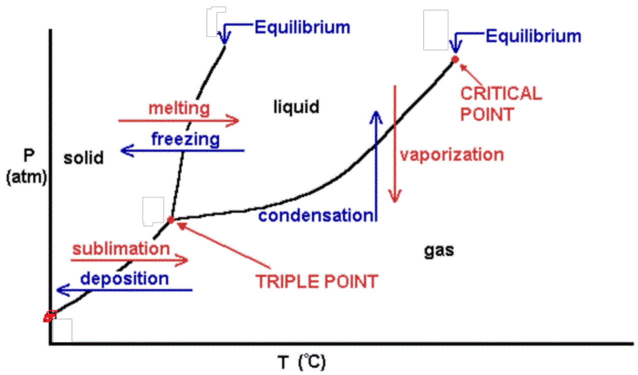
  (temperature, pressure, *etc.*) and laws (equations of state, *etc.*)





$$PV = nRT$$

- Theoretical understanding of collective effects $\Rightarrow$ phase diagrams



Phase transitions : sharp changes in the macroscopic behavior when an external (*e.g.* the temperature of the environment) or an internal (*e.g.* the interaction potential) parameter is changed

- Calculations can be difficult but the theoretical frame is set beyond doubt

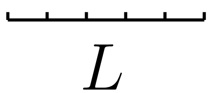
Statistical physics

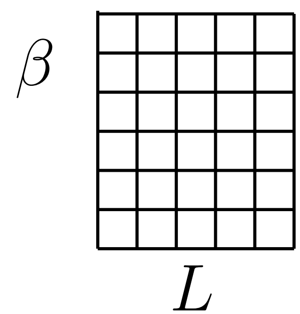
Classical $\Leftrightarrow$ Quantum

Partition function correspondence

Quantum d dimensional $\equiv$ Classical $d+1$ dimensional

$$\mathcal{Z}(\beta) = \text{Tr}\, e^{-\beta \hat{H}} \qquad \mathcal{Z}(\beta) = \sum_{conf} e^{-\beta \mathcal{H}(conf)}$$





β-periodic imaginary time direction

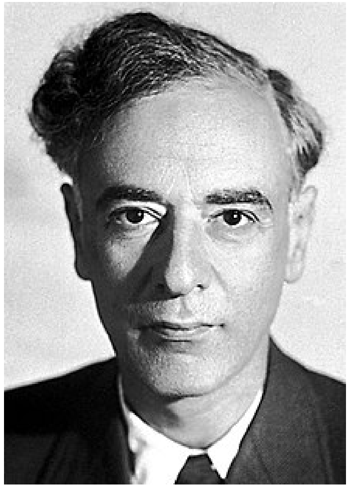
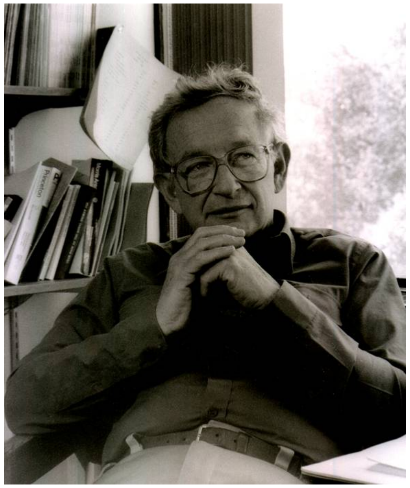
$$\phi(\vec{x}) \qquad \phi(\tau, \vec{x}) = \phi(\tau + \beta, \vec{x})$$

Feynman-Hibbs 65, Trotter & Suzuki 76, Matsubara

Quantum Phase transitions, Quantum Monte Carlo methods, *etc.*

Statistical Physics

Four very important players

L. D. Landau	P. W. Anderson	K. Wilson	D. J. Thouless
			
Phase transitions	Higgs Mechanism	Renormalization	Topology
Symmetry breaking	Glassiness, Localization	Universality	Disorder, Localization

Theoretical description of phase transitions
Importance of randomness
More is different

Beyond equilibrium

Out of equilibrium

Possible reasons

- The equilibration time goes beyond the experimentally accessible times in **macroscopic systems** in which t_{eq} grows with the system size,

$$\lim_{N\gg 1} t_{eq}(N) \gg t$$

e.g., **Critical slowing down, coarsening, glassy physics**

- **Driven systems** Energy injection

$$\vec{F}_{\rm ext} \neq -\vec{\nabla} V(\vec{x})$$

e.g., **active matter**

- **Integrability**

$$I_\mu(\{\vec{p}_i, \vec{x}_i\}) = ct, \qquad \mu = 1, \dots, N$$

Too many constants of motion inhibit equilibration to the Gibbs ensembles.

e.g., **1d bosonic gases**

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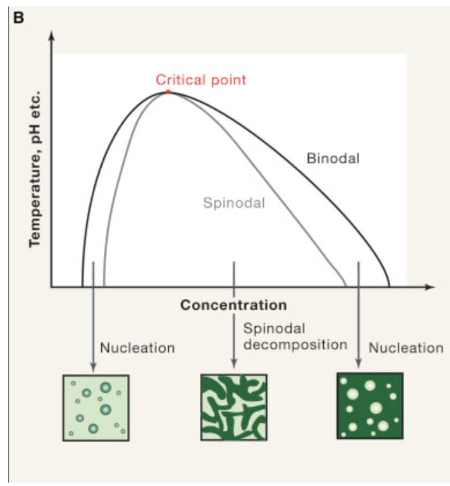
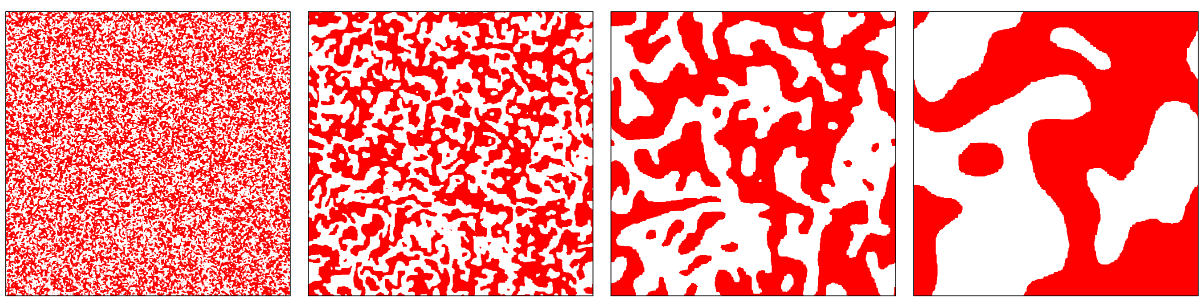
Phase separation

Quench below the binodal : remnant interfaces



$t_1 \quad < \quad t_2 \quad < \quad t_3 \quad < \quad t_4 \quad < \quad \dots$

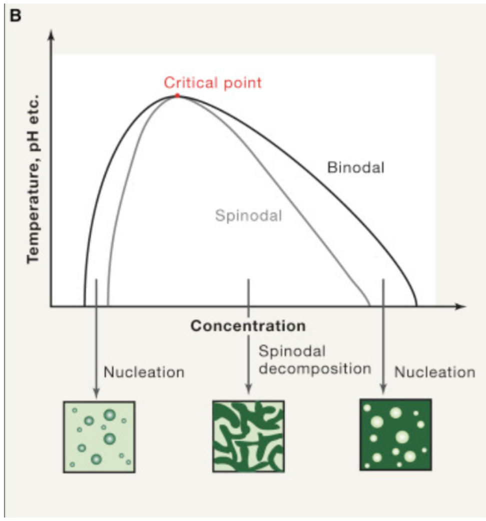


Coarsening process with growing length $\mathcal{R}(t) \simeq t^{1/z} \implies \boxed{t_{eq} \sim L^z}$

Equilibration time diverges with the system size

Phase separation

Quench below the binodal : universality



Microscopic details are irrelevant

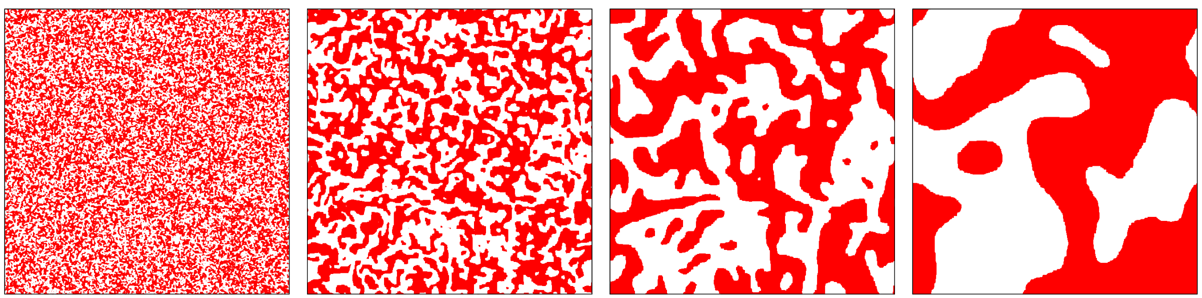
but conservation laws and

dimension of order parameter fix the

$\Longrightarrow$

Dynamic universality class

$$t_1 \quad < \quad t_2 \quad < \quad t_3 \quad < \quad t_4 \quad < \quad \ldots$$



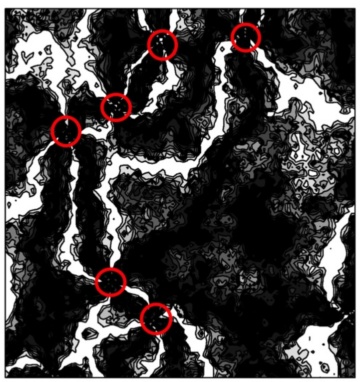
Coarsening process classified according to $\mathcal{R}(t) \simeq t^{1/z}$

Topological phase transitions

Vortices in the $2d$ XY model - O(2) field theory

$$\mathcal{H} = -\frac{J}{2}\sum_{\langle ij\rangle} \vec{s}_i\cdot\vec{s}_j \quad \Longrightarrow \int d^2x \, \left[\frac{1}{2}(\vec{\nabla}\vec{\phi}(\vec{x}))^2 - \frac{r}{2}\phi^2(\vec{x}) + \frac{\lambda}{4}\phi^4(\vec{x})\right]$$

Unbinding of vortex pairs $\rho_v^{\rm free}(T > T_{KT}) > 0$ **Kosterlitz & Thouless 70s**



After a quench to $T < T_{KT}$

Free vortex annihilation

Schlieren pattern

gray scale

$\sin^2(2\vec{s}_i \cdot \hat{e}_x)$

Jelić & LFC 12

Growing length scale $\mathcal{R}(t) \simeq (t/\ln t)^{1/z}$ & free vortex density $\rho_v^{\rm free}(t) \sim \mathcal{R}^{-2}(t)$

$$\Longrightarrow \boxed{t_{eq} \sim L^z \ln L}$$

In boson gases, polaritons, *etc.* **Blakie, Capusotto, Davis, Proukakis, Symanska, ...**

numerics & **Beugnon-Dalibard, ... Popovic et al., ...** experiments. Last 10 years

Rugged free-energy landscapes

Glassy physics: beyond the $\lambda\phi^4$ Ginzburg-Landau Questions!

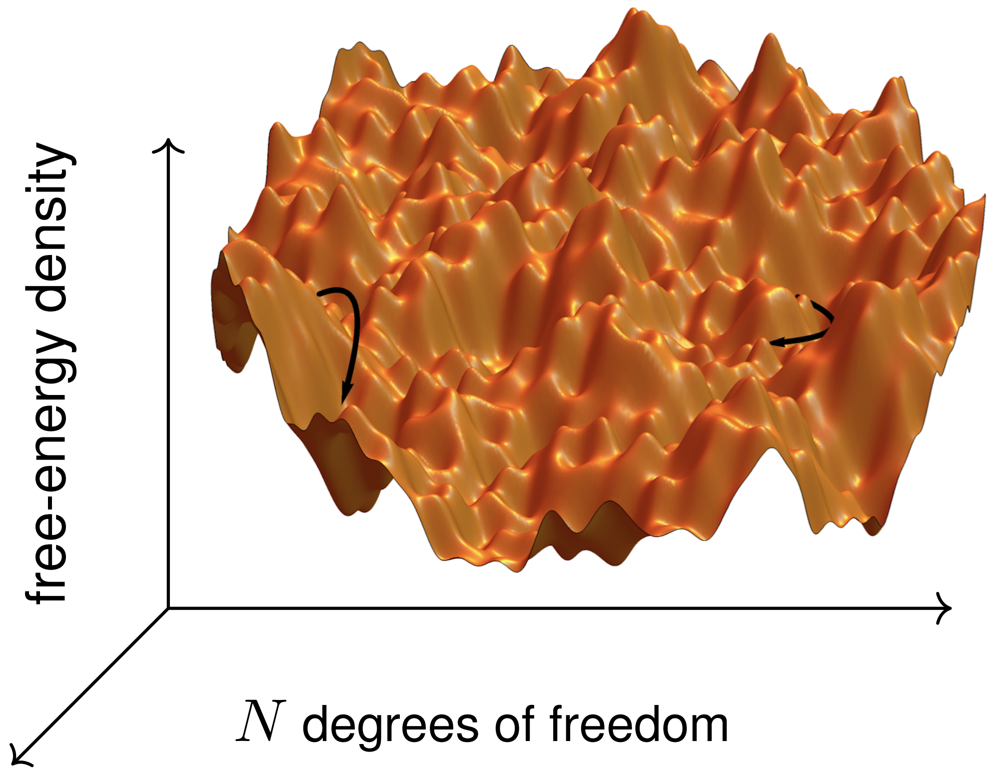


Figure adapted from a picture by **C. Cammarota**

Topography of the landscape on the N-dimensional substrate made by the order parameters?

Numerous studies by **theoretical physicists** and **probabilists**

Rugged free-energy landscapes

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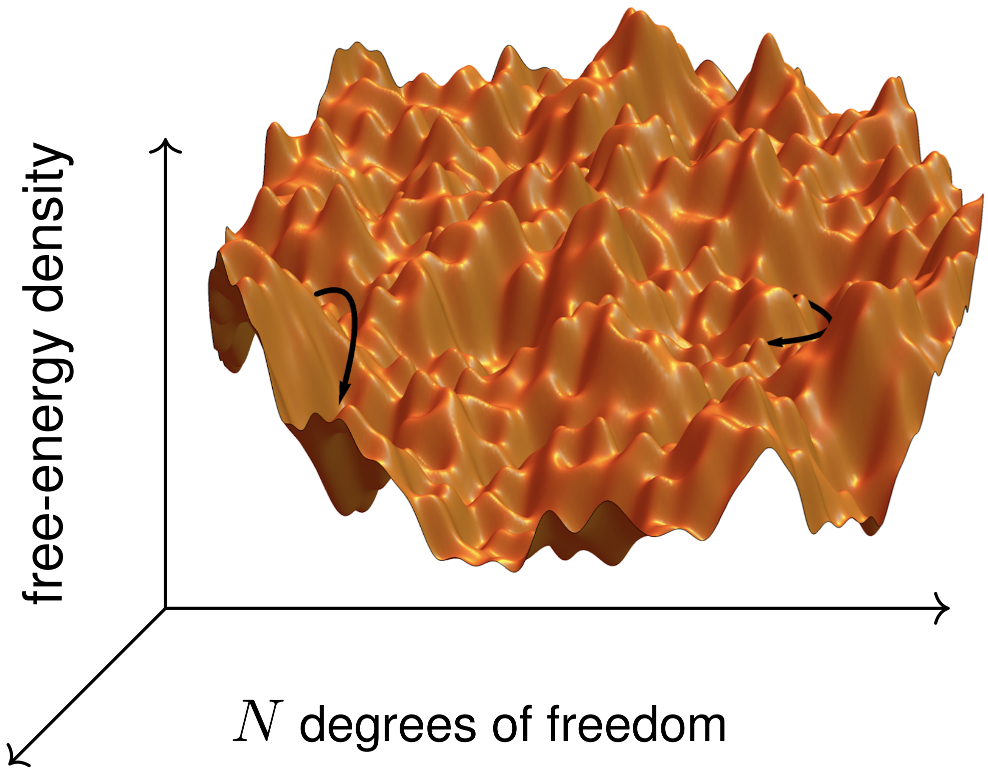


Figure adapted from a picture by **C. Cammarota**

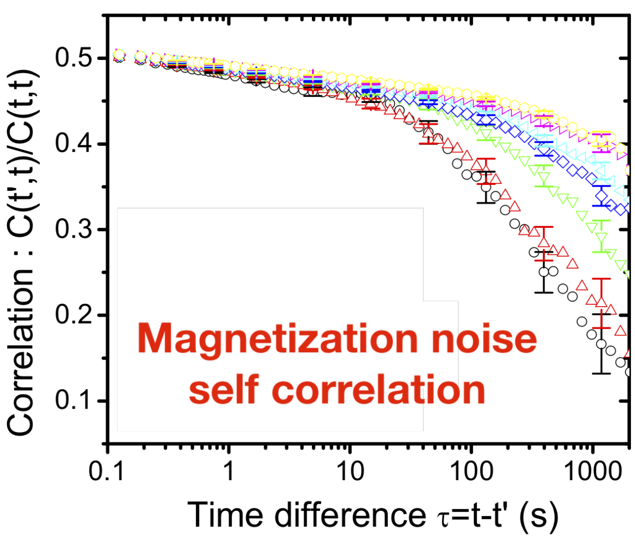
How to reach the absolute minimum ?

Thermal activation, surfing over tilted regions, quantum tunneling ?

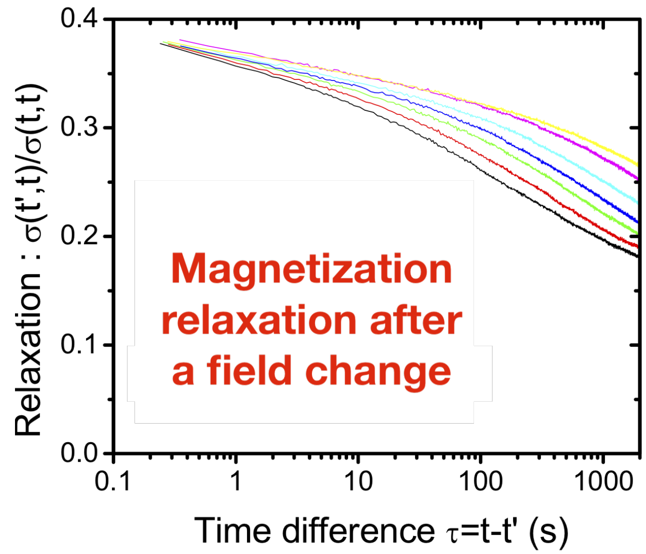
Optimisation problem Smart algorithms ? Computer sc - applied math

Rugged free-energy landscapes

Glassy physics : slow relaxation & loss of stationarity (aging)



Correlation



Linear response

Different curves are measured after different reference times t' after the quench:

breakdown of stationarity $\Longrightarrow$ far from equilibrium

No identifiable growing length $\mathcal{R}(t)$: **microscopic mechanisms ?**

Spin-glass experiments **Hérisson & Ocio 02-04**

Out of equilibrium

Possible reasons

- The equilibration time goes beyond the experimentally accessible times in **macroscopic systems** in which t_{eq} grows with the system size,

$$\lim_{N\gg 1} t_{eq}(N) \gg t$$

e.g., **Critical slowing down, coarsening, glassy physics**

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$$\vec{F}_{\mathrm{ext}} \neq -\vec{\nabla} V(\vec{x})$$

e.g., **active matter**

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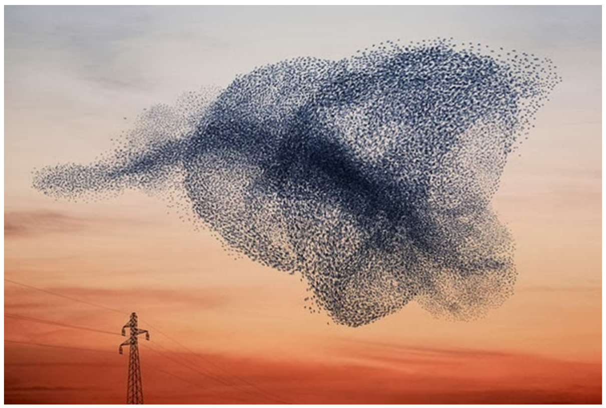
$$I_\mu(\{\vec{p}_i, \vec{x}_i\}) = ct, \qquad \mu = 1, \dots, N$$

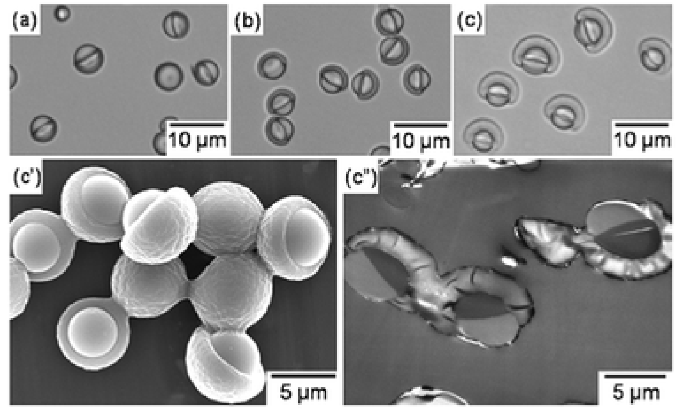
Too many constants of motion inhibit equilibration to the Gibbs ensembles.

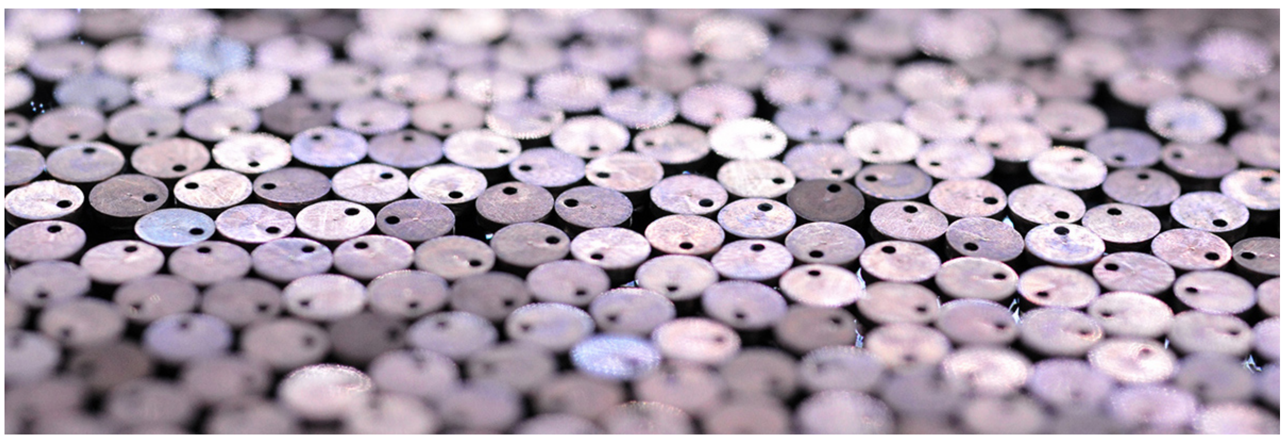
e.g., **1d bosonic gases**

Active matter

Natural & artificial systems





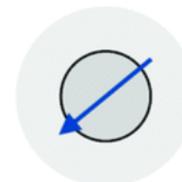


Experiments & observations **Bartolo** *et al.* Lyon, **Bocquet** *et al.* Paris, **Cavagna** *et al.* Roma, **di Leonardo** *et al.* Roma, **Dauchot** *et al.* Paris, just to mention some Europeans

Active Brownian particles

The standard model – ABPs

Spherical particles with diameter σ_d



Environment $\Longrightarrow$ Langevin dynamics

Scales $\Longrightarrow$ over-damped motion

Self-propulsion $\Longrightarrow$ active force $\vec{F}_{\rm act}$ along $\vec{n}_i = (\cos\theta_i(t), \sin\theta_i(t))$

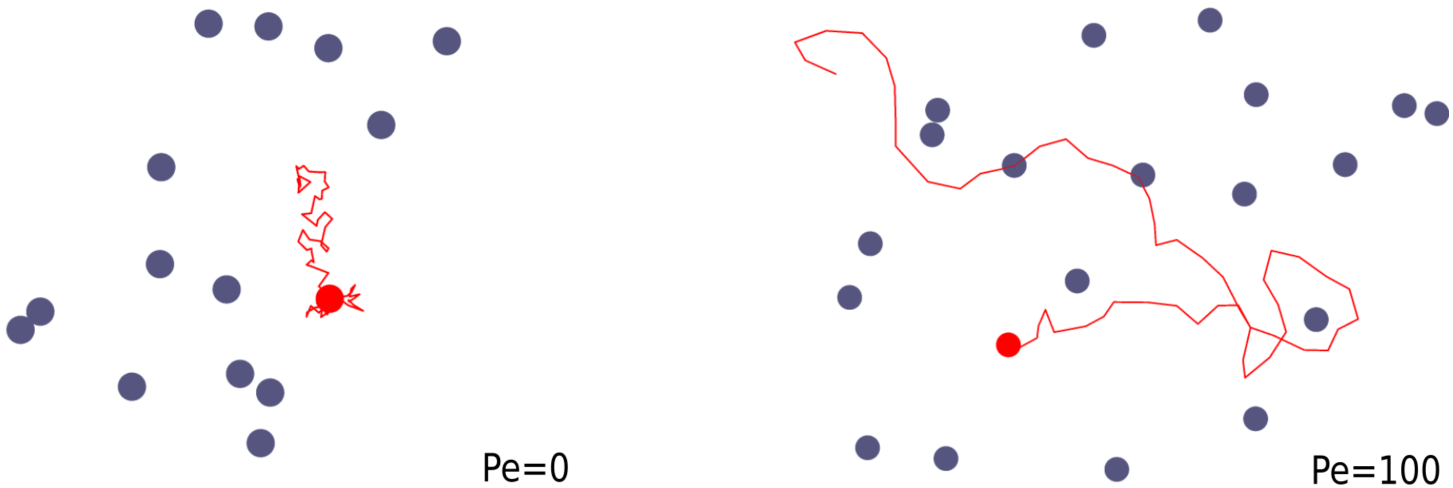
$$\underbrace{\gamma\dot{\vec{r}}_i}_{\text{friction}} = \underbrace{F_{\rm act}\vec{n}_i}_{\text{propulsion}} - \underbrace{\vec{\nabla}_i \sum_{j(\neq i)} U(r_{ij})}_{\text{inter-particle interactions}} + \underbrace{\vec{\xi}_i}_{\text{translational white noise}} \qquad \underbrace{\dot{\theta}_i = \eta_i}_{\text{rotational white noise}}$$

$2d$ packing fraction $\boxed{\phi = \pi\sigma_d^2 N/(4S)}$ Péclet number $\boxed{\text{Pe} = F_{\rm act}\sigma_{\rm d}/(k_B T)}$

Bialké, Speck & Löwen, Fily & Marchetti 12

Active Brownian particles

Typical motion of ABPs in interaction



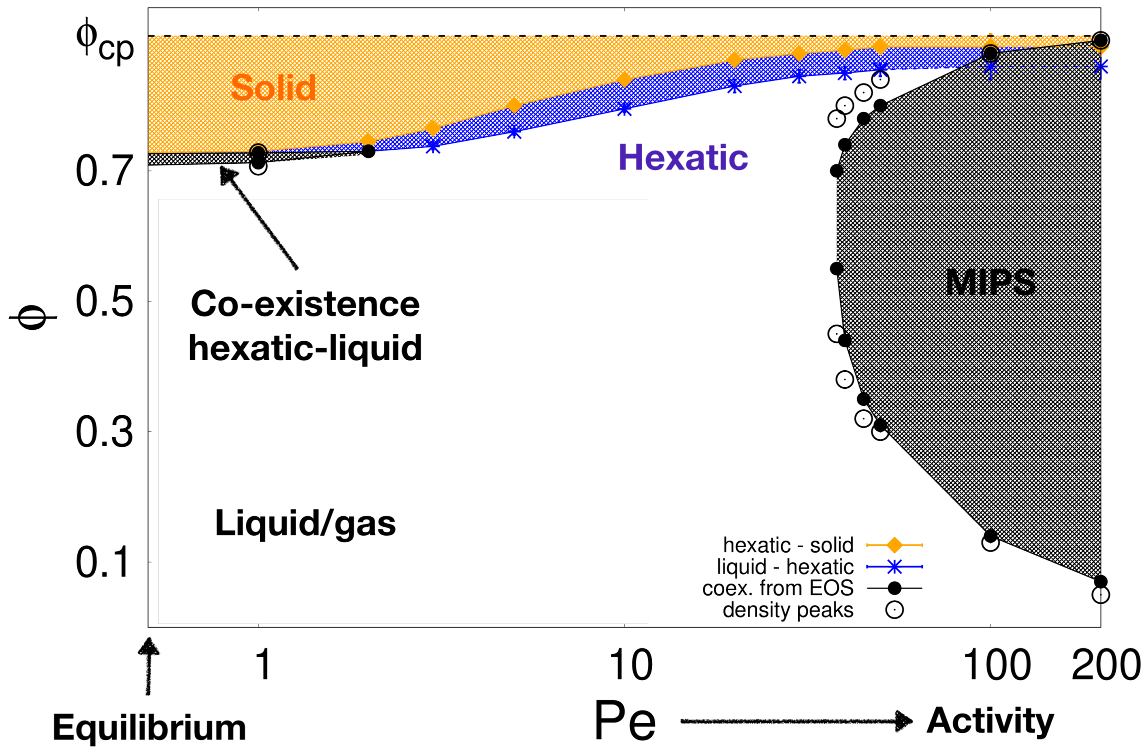
The activity induces a persistent random motion

Long running periods and

sudden changes in direction

Active Brownian particles

Complex out of equilibrium phase diagram



Motility induced phase separation (MIPS)

gas & dense droplet

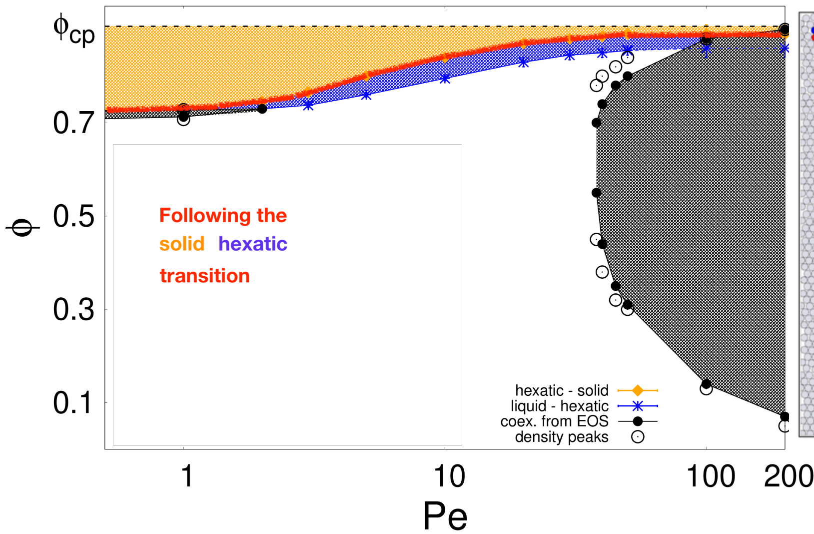
Cates & Tailleur 12

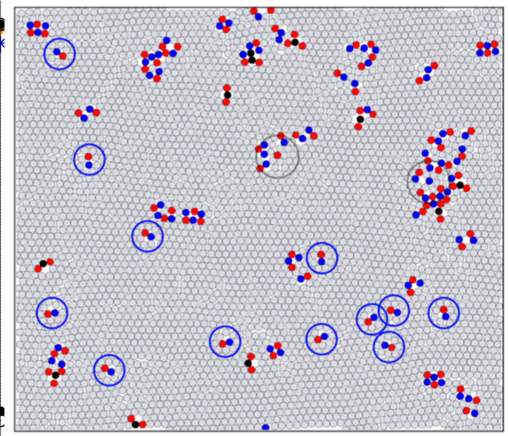
From virial pressure $P(\phi)$, translational and orientational correlations G_T and G_6, distributions of local density and hexatic order ϕ_i and ψ_{6i}, at fixed $k_BT = 0.05$

Digregorio, Levis, Suma, LFC, Gonnella & Pagonabarraga 18

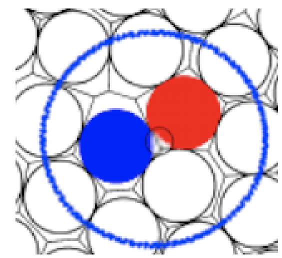
Active Brownian particles

Out of equilibrium phase diagram **First question (out of many !)**





Free dislocation:
a 7-5 neighbor



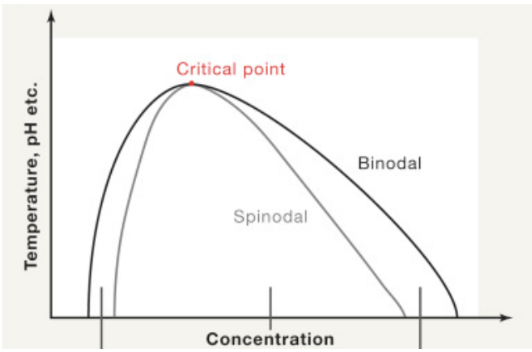
Solid - **Hexatic** transition, **driven by unbinding of dislocation pairs**

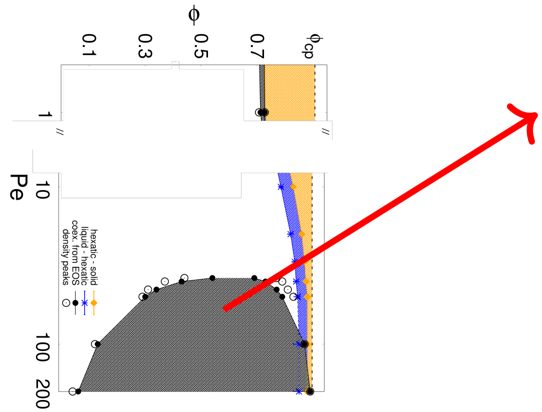
as in Berezinskii-Kosterlitz-Thouless-Halperin-Nelson-Young universality ?

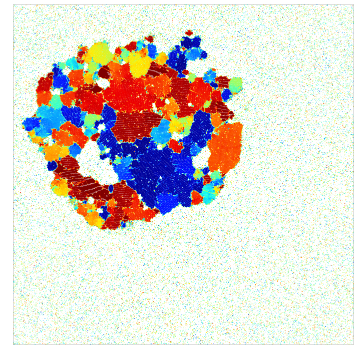
$$\rho_{disloc} \simeq a \exp\left[-b\left(\frac{\phi_{sh}}{\phi_{sh}-\phi}\right)^{\nu}\right] \qquad \nu \sim 0.37 \quad \forall \text{Pe ?}$$

Active Brownian particles

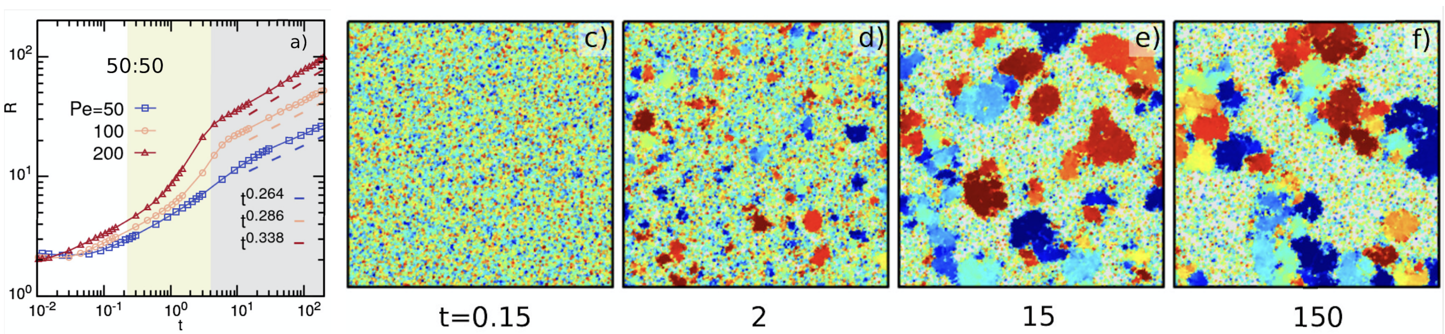
Out of equilibrium phase diagram **So many questions !**







Dynamics of formation of the dense phase ? but bubbles, hexatic order, ...



Universality with the Lifshitz-Slyozov law $\mathcal{R}(t) \simeq t^{1/3}$? Geometry ?

Redner ***et al*** **13, Stenhammar** ***et al*** **14, ... , Caporusso** ***et al*** **20, Caprini** ***et al*** **20, ...**

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e.g., **Critical slowing down, coarsening, glassy physics**

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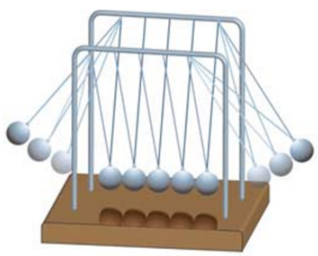
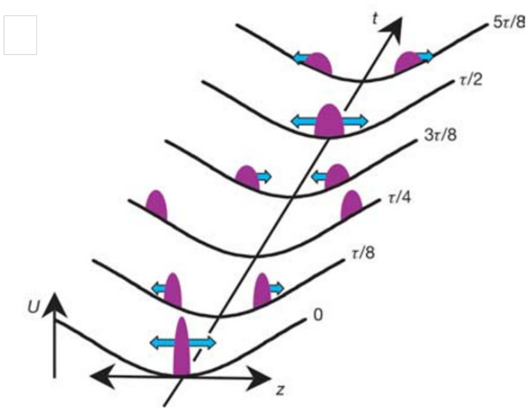
Too many constants of motion inhibit equilibration to the Gibbs ensembles

e.g., **$1d$ bosonic gases**

Motivation

Isolated quantum systems: experiments and theory $\sim$ 15y ago





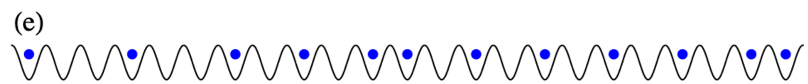
A quantum Newton's cradle
cold atoms in isolation

Kinoshita, Wenger & Weiss 06

Quantum quenches & Conformal field theory

Calabrese & Cardy 06

Numerics of lattice hard core bosons



Rigol, Dunjko, Yurovsky & Olshanii 07

and many others

$1d$ lattice models & 1+1 field theories

Bernard, Calabrese, Caux, Doyon, Essler, Gambassi, Konik, Mussardo, Polkovnikov, Prosen, Silva, Santoro, Spohn...

Impressive SISSA School

Alba, Bastianello, Bertini, Chiocchetta, Collura, De Luca, De Nardis, Fagotti, Foini, Kormos, Marcuzzi, Marino, Pappalardi, Piroli, Ros, Ruggiero, Sotiriadis, ...

Quantum quenches

Definition & questions

- Take an isolated quantum system with Hamiltonian $\hat{H}_0$
- Initialize it in, say, $|\psi_0\rangle$ the ground-state of $\hat{H}_0$ (or any $\hat{\rho}(t_0)$)
- Unitary time-evolution $\hat{U} = e^{-\frac{i}{\hbar}\hat{H}t}$ with a Hamiltonian $\hat{H} \neq \hat{H}_0$.

Does the system reach (locally) a steady state?

Are the expected values of local observables determined by $e^{-\beta\hat{H}}$?

Does the evolution occur as in equilibrium ?

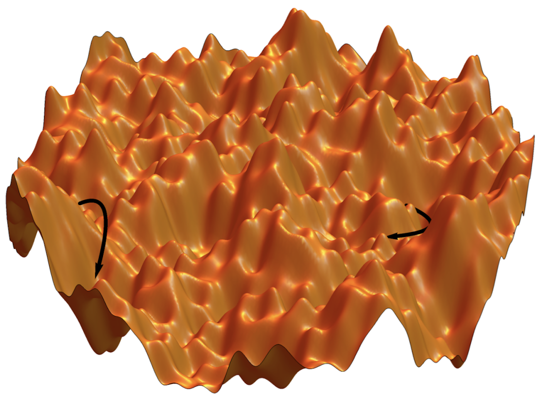
Not for integrable models. Alternative, the **Generalized Gibbs Ensemble**

.

$$\hat{\rho}_{\mathrm{GGE}} = \mathcal{Z}^{-1}(\{\gamma_\mu\})\, e^{-\sum_{\mu=1}^{N}\gamma_\mu \hat{I}_\mu} \quad \& \quad \langle\psi_0|\hat{I}_\mu|\psi_0\rangle = \langle\hat{I}_\mu\rangle_{\mathrm{GGE}} \text{ *fix* } \{\gamma_\mu\}$$

Out of equilibrium

Something in common ?



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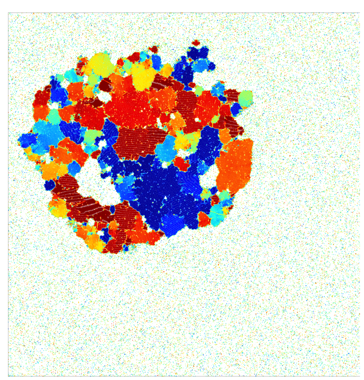

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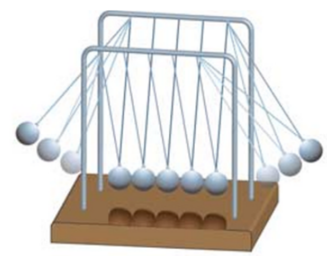
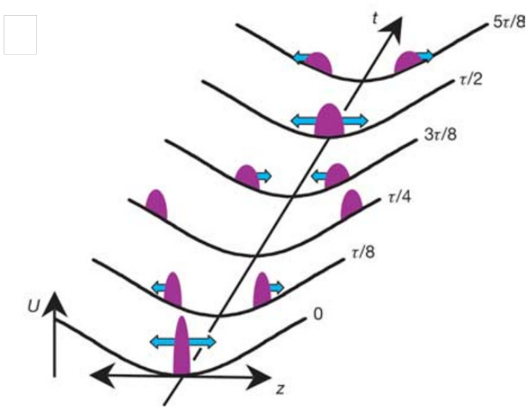
$$I_\mu = \text{ct} \qquad \mu = 1, \dots, N$$





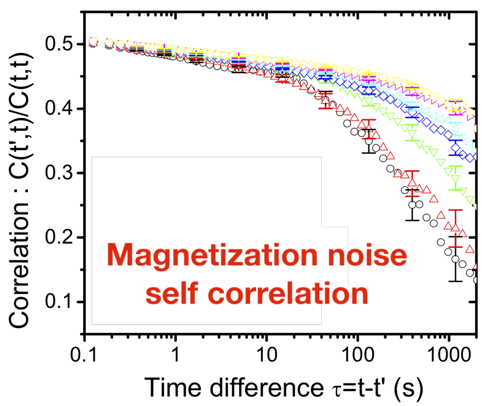
Spin glasses

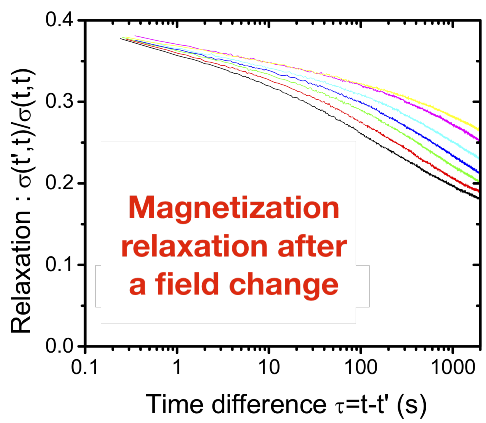
Aging, weak memory and fluctuation dissipation relations

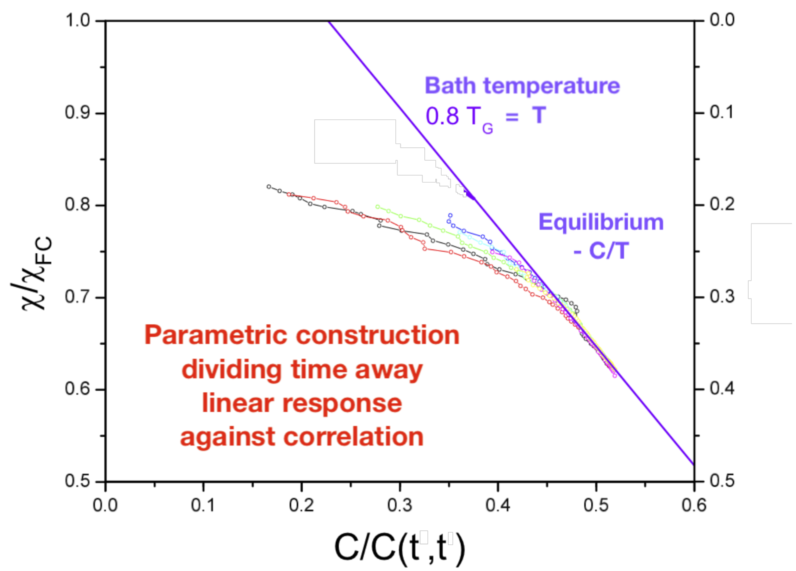
$$\chi(t,t') = \int_{t'}^{t} dt'' \, \frac{1}{T_{\rm eff}(t,t'')} \, \frac{\partial C(t,t'')}{\partial t''} \qquad \text{General}$$

$$= \int_{t'}^{t} dt'' \, \frac{1}{\boldsymbol{T_{\rm eff}(C(t,t''))}} \, \frac{\partial C(t,t'')}{\partial t''} \qquad \text{Hypothesis}$$

$$= \int_{C(t,t')}^{C(t,t)} dC'' \, \frac{1}{T_{\rm eff}(C'')} = \chi(C)$$





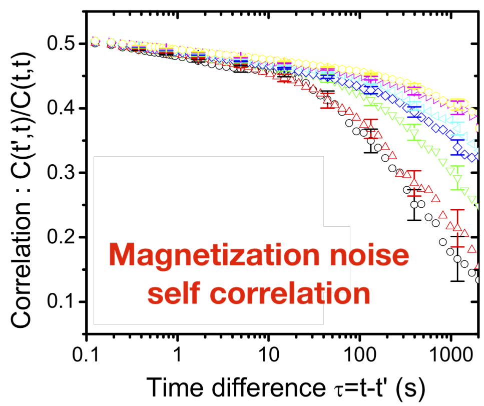


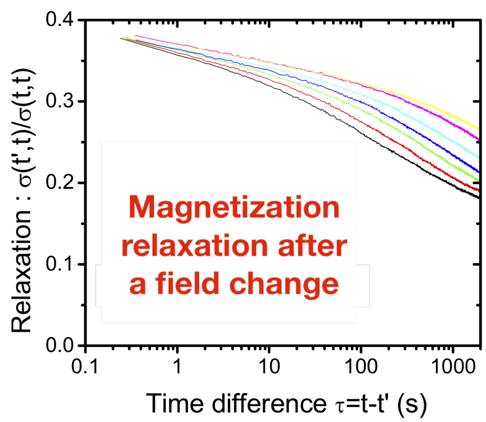
Analytic results on mean-field models **LFC & Kurchan 93-94**

Experiments **Hérisson & Ocio 02-04**

Spin glasses

Putting two-time scales in evidence



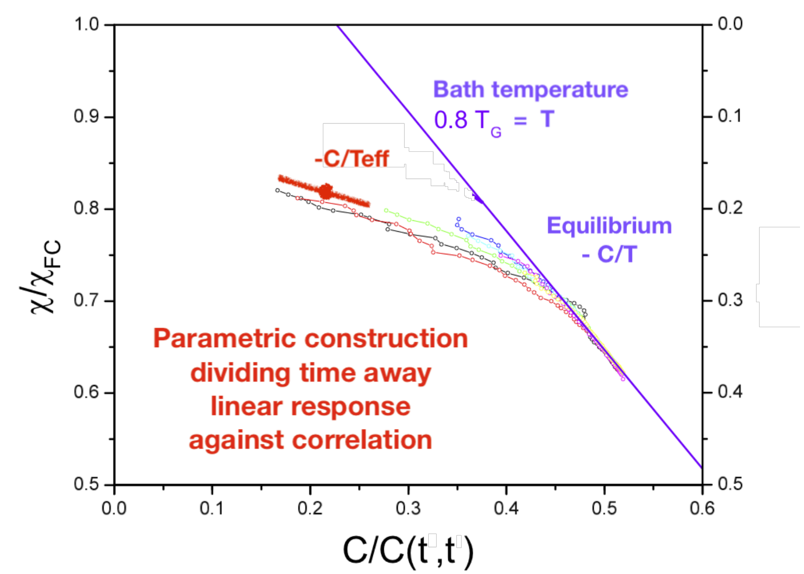


Global observables, χ and C

Separation of two-time scales

one with bath temperature T

the rest with $T_{\rm eff}(C)$



FDR & Effective temperatures LFC, Kurchan & Peliti 97 **Experiments** Hérisson & Ocio 02-04 **Relation to replica symmetry breaking** Franz *et al* 98, Kurchan 20

Curved $\chi(C)$?

Glassy models

Aging, weak memory and fluctuation dissipation relations

One can interpret the mismatch between the linear response and correlation function as evidence for an **effective temperature** whi-chdepends on the time-scale at which we look at the relaxation

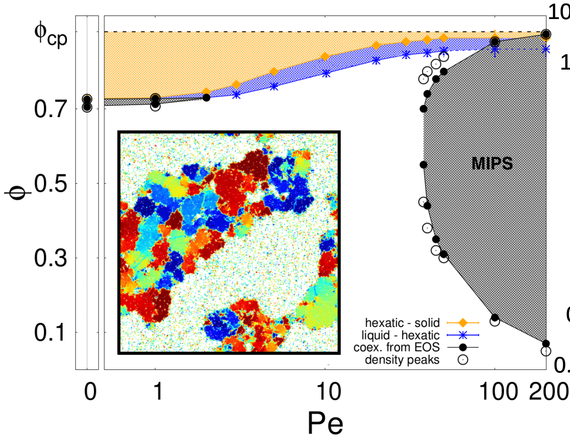
$$\frac{1}{T_{\text{eff}}(C)} = -\frac{d\chi(C)}{dC}$$

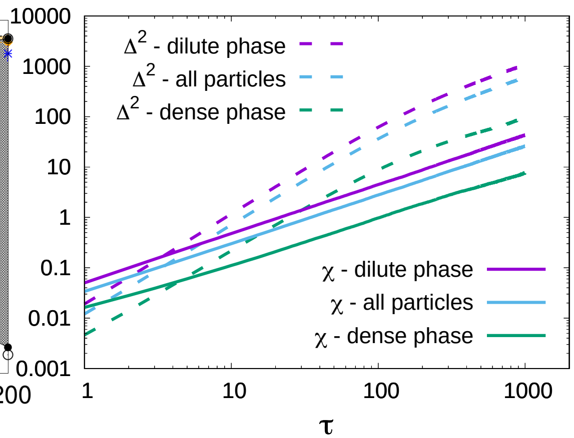
Active Brownian Particles

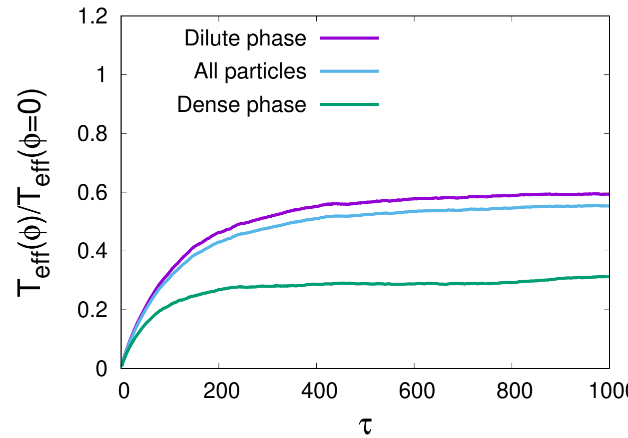
Co-existence in stationary MIPS: dense & dilute

Pe = 50 $\phi = 0.5$

Integrated linear response & mean-square displacement: their ratio (FDR) $\tau = t - t'$







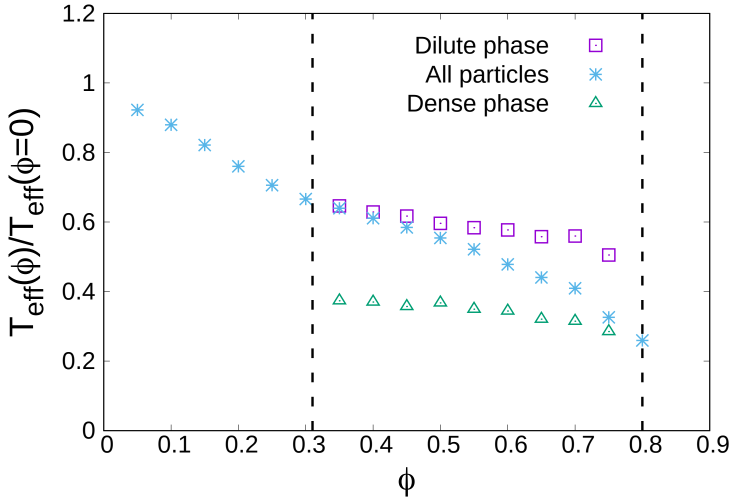
In a driven heterogeneous system

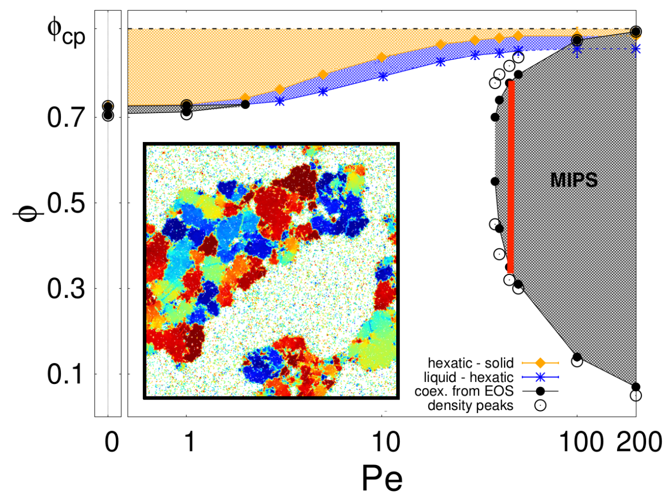
Linear response computed with Malliavin weights (no perturbation applied) as proposed by **Warren & Allen 12**, and **Szamel 17** for active matter systems.

Active Brownian Particles

Dependence on the global packing fraction in MIPS

Pe = 50 ϕ dependence





Vertical dashed lines are at the boundaries of MIPS $\phi_<$ and $\phi_>$ at this Pe

$T_{\rm eff}(\phi) \approx T_{\rm eff}^{\rm dil}(\phi_<) n_{\rm dil}(\phi) + T_{\rm eff}^{\rm dense}(\phi_>) n_{\rm dense}(\phi)$ with $n_{\rm dil} = N_{\rm dil}/N$, *etc.*

and for the dilute component the pressure is $P = \rho_{\rm dil} k_B T_{\rm eff}^{\rm dil}$ like in a gas

Petrelli, LFC, Gonnella & Suma 20

Active Brownian Particles

Co-existence in stationary MIPS

Co-existence of

– fast and hot particles in the dilute phase with $T_{\rm eff}^{\rm dil}$

– slow and cold particles in the dense phase with $T_{\rm eff}^{\rm dil}$

Quantum Ising chain

Integrable system $\equiv$ free fermions in $1d$

The initial Hamiltonian

$$\hat{H}_{\Gamma_0} = -\sum_i \hat{\sigma}_i^x \hat{\sigma}_{i+1}^x + \Gamma_0 \sum_i \hat{\sigma}_i^z$$

The initial state $|\psi_0\rangle$ is the ground state of $\hat{H}_{\Gamma_0}$

Instantaneous quench in the **transverse field** $\Gamma_0 \to \Gamma$

Evolution with $\hat{H}_\Gamma$ **Iglói & Rieger 00**

Equivalent to $\hat{H}_\Gamma = \sum_k \epsilon_k(\Gamma)\, \hat{\eta}_k^\dagger \hat{\eta}_k$ with $[\hat{H}_\Gamma, \hat{I}_k] = 0$ and $\hat{I}_k = \hat{\eta}_k^\dagger \hat{\eta}_k$

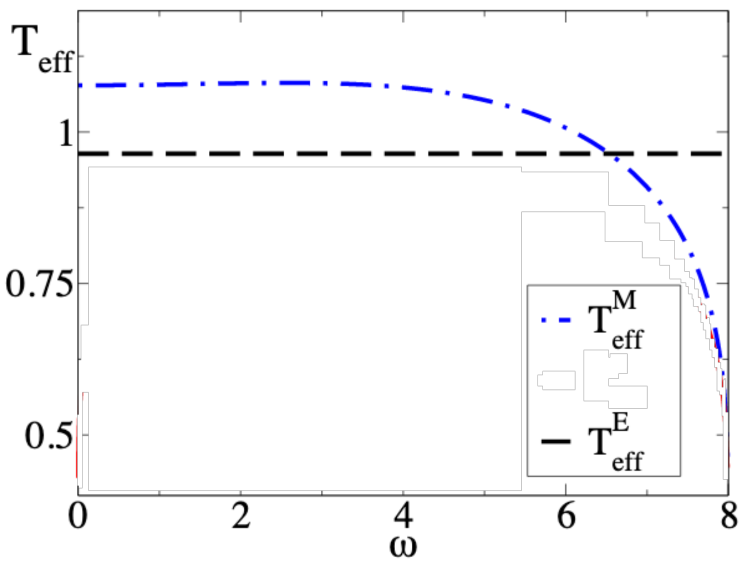
Reviews: **Karevski 06, Polkovnikov** *et al* **10, Dziarmaga 10**

Specially interesting case $\Gamma_c = 1$ the critical point **Rossini** *et al* **09**

Quantum Ising chain

Transverse magnetization quantum fluctuation-dissipation relation

$$\hbar \, \text{Im} R^M(\omega) = \tanh\left(\frac{\beta^M_{\text{eff}}(\omega)\omega\hbar}{2}\right) C^M_+(\omega)$$



$$\text{Tr}\, \hat{H}_\Gamma \, \frac{e^{-\beta^E_{\text{eff}} \hat{H}_\Gamma}}{\mathcal{Z}(\beta^E_{\text{eff}})} = \langle \psi_0 | \hat{H}_\Gamma | \psi_0 \rangle$$

$$T^M_{\text{eff}}(\omega) \neq \text{ct} \implies$$

Out of equilibrium

de Nardis, Foini, Panfil, LFC, Gambassi & Konik 11-12, 17-19

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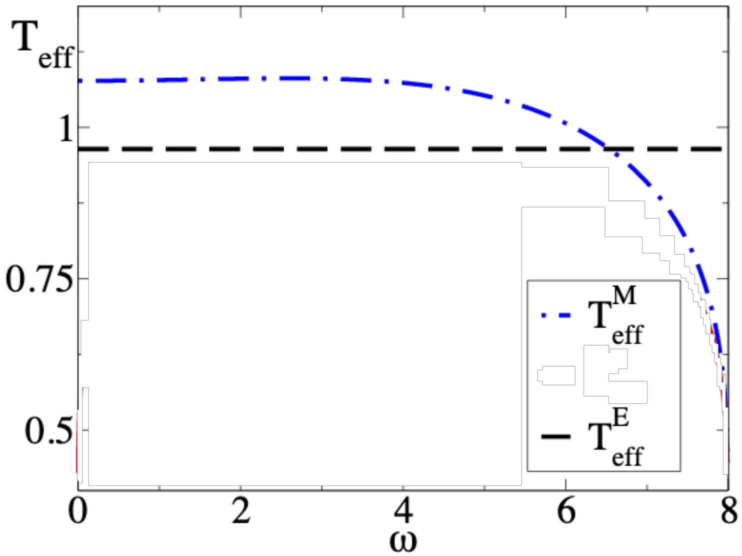

$$\hat H_\Gamma = \sum_k \epsilon_k(\Gamma)\, \hat\eta^\dagger_k \hat\eta_k$$

At $\omega = \epsilon_k(\Gamma)$ $\boxed{\beta^M_{\rm eff}(\epsilon_k) = \gamma_k}$

the Lagrange multipliers in the GGE

$\hat\rho_{\rm GGE} \propto e^{-\sum_k \gamma_k \hat I_k}$

with $\hat I_k = \hat\eta^\dagger_k \hat\eta_k$

de Nardis, Foini, Panfil, LFC, Gambassi & Konik 11-12, 17-19

Quantum quenches

Integrable models

With judiciously chosen operators, the frequency dependent effective temperature of the quantum fluctuation dissipation relation gives us access to the Lagrange multipliers of the Generalized Gibbs Ensemble

$$\beta_{\rm eff}(\omega) \Leftrightarrow \gamma_\mu$$

Conclusions

The talk exhibited three out of equilibrium macroscopic situations:

slow relaxation of open complex systems, driven interacting systems with energy injection from the surroundings, quenches in closed quantum - also classical - systems.

Some basic statistical physics questions were discussed and concerned

phase diagrams, universality, role of topological defects, ...

Thermodynamic concepts out of equilibrium?

Effective temperatures (heat flows, entropy production, partial equilibrations, fluctuations,...) importance of time-scales & observables. Also stochastic thermodynamics, fluctuation theorems, *etc.*

There is much more to be done and understood

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There is much more to be done and understood **Thanks!**

Beyond

Econophysics

Social physics

Ecology

Biophysics

Computer science

X-physics

Fluctuation-dissipation relations

Any evolution

Just measure

$$\text{Im}\,\tilde{R}^{AB}(\omega) \qquad \text{and} \qquad \tilde{C}_{\pm}^{AB}(\omega)$$

take the ratio and extract $\tanh(\beta_{\text{eff}}^{AB}(\omega)\hbar\omega/2)$

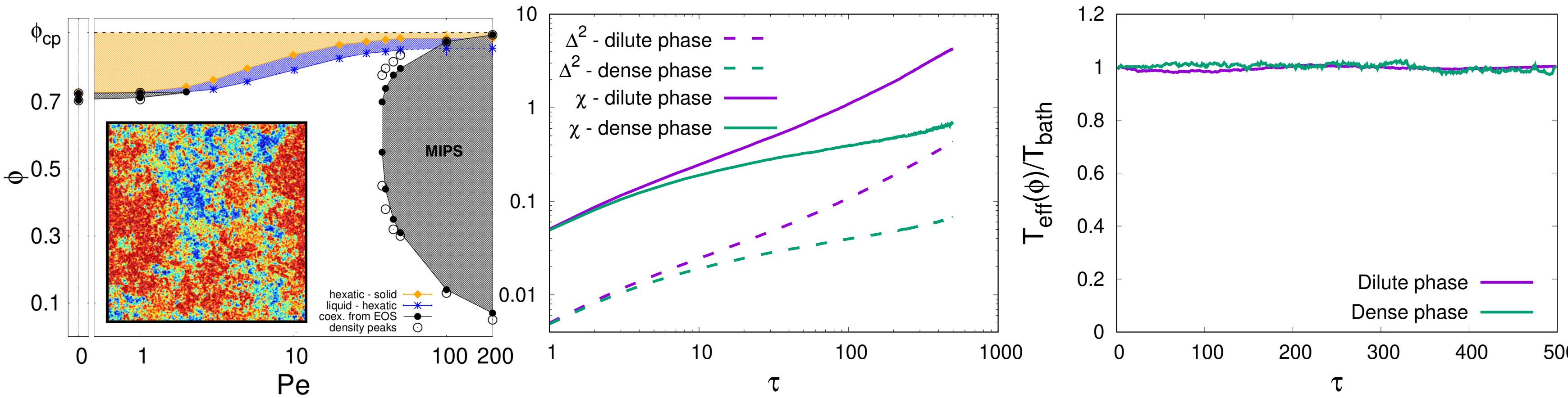
In equilibrium all $\beta_{\text{eff}}^{AB}(\omega)$ should be equal to the same constant

Active Brownian Particles

Co-existence in equilibrium $T_{\rm eff} = T$

Pe = 0 $\phi = 0.710$

Integrated linear response & mean-square displacement: their ratio (FDR) $\tau = t - t_w$



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$C_+^z(t) = \langle \psi_0 | [\hat{s}_i^z(t+t_0), \hat{s}_i^z(t_0)]_+ | \psi_0 \rangle$ $\quad R(t) = \langle \psi_0 | [\hat{s}_i^z(t+t_0), \hat{s}_i^z(t_0)]_- | \psi_0 \rangle$