Scalar field theories of active systems: Incomplete phase separation

STOCHASTIC THERMODYNAMICS, ACTIVE MATTER AND DRIVEN SYSTEMS

ICTS, 10 August 2017, Bengaluru

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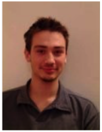

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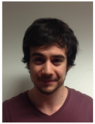

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Cesare Nardini

Introduction

TRS

MIPS

Active Field theories

AMB+

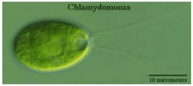
Measuring TRS Breaking

Conclusions

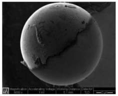
Active Colloids / Micro-Organisms

Self-propulsion via local drive mechanism

- Bacteria, algae



- Autophoretic colloids



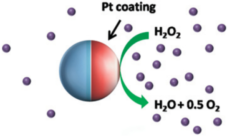
- Pt-coated Janus particles bathed in fuel (H202)

  [JR Howse et al, PRL 99 048102 (2007)]

- Janus particles in binary solvent + laser heating

  [I Buttinoni et al, PRL 110 238301 (2013)]

- ...

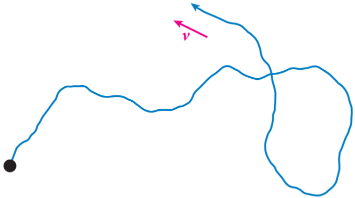


Simplest microscopic model(s)

- No hydrodynamic interactions (albeit, often, they move in a fluid)

- No aligning interactions

persistent Brownian motion speed v, rotational diffusivity D_r



- Decorrelation time-scale $\tau \equiv \frac{1}{(d-1)D_r}$
- Coarse graining $\Longrightarrow$ Brownian motion in d dimensions with diffusivity $D = \frac{v^2\tau}{d}$

Active Matter breaks TSR - I

Measure of broken Time Reversal Symmetry (TRS)

Entropy production $S = \lim_{t\to\infty} \frac{1}{t} \log \left(\mathcal{P}_F / \mathcal{P}_B \right)$

- $\mathcal{P}_F$ probability of forward trajectory $\{\mathbf{x}_i(t)\}$
- $\mathcal{P}_B$ probability of time reversed trajectory $\{\epsilon_i \mathbf{x}_i(-t)\}$
- $\mathbf{x_i}$: degrees of freedom

[Lebowitz, Spohn, J. Stat. Phys., 1999; U. Seifert, Rep. Prog. Phys., 2012]

...active particles transform ‘fuel’ into motion...

This is not the TRS breakdown we will talk about!

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Active Matter breaks TSR - II

Two uncommon active 'particles'

$3km/litre$ $15km/litre$

...two parts of TRS breakdown...

- to transform fuel into motion - dependent on the active particles we consider (Ferrari vs Fiat)
- intrinsic in the fact that particles move persistently in some direction

Active Matter breaks TSR - II

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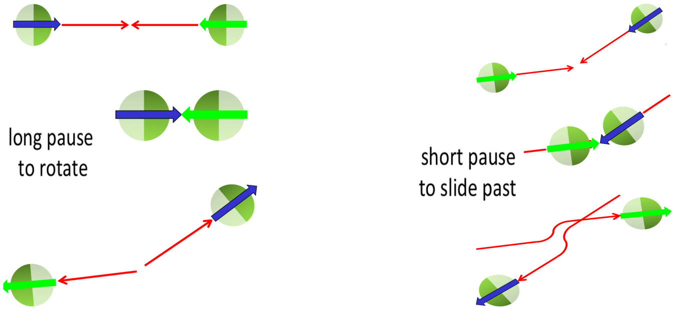
‘intrinsic’ TRS Breaking made manifest by interactions

... with obstacles....

... or among particles...



Part I:
Implications of TRS breakdown
$\Longrightarrow$
Incomplete phase separation

Part II:
How can we quantify TRS breakdown?

Consequence: Motility Induced Phase Separation

Fully established in simulations of minimal models

[Seminal work: Tailleur & Cates, PRL 2008; Ann. Rev. Cond. Mat. 2015]

Particles with purely repulsive interactions (e.g., hard-core)

[Speck et al., PRL 2014, EPL 2013; Fily et al, PRL 2012, Stenhammar et al, PRL 2014]

Video and simulation by J. Stenhammar

MIPS: density dependent speed

Interactions encoded in a density-dependent self-propulsion speed $v(\phi) \downarrow$ with $\phi \uparrow$

- $\phi(\mathbf{r})$: density of particles
- $\langle \xi_i \xi_j \rangle = \frac{2}{\tau} \delta_{ij} \mathbf{1} \, \delta(t-s)$

$$\dot{\mathbf{r}}_i = v(\phi(\mathbf{r}_i))\mathbf{u}_i + \sqrt{2T}\eta_i$$
$$\dot{\mathbf{u}}_i = \mathbf{u}_i \wedge \xi_i$$

- Approximate effect of pairwise interactions
  Backed by kinetic theory of pairwise interacting particles: $v(\phi) = v_0(1 - \phi/\phi^*)$

  [T. Speck et al., PRL, 2014]

- Quorum sensing (QS) particles (due, for ex, to chemical signalling)

[Tailleur & Cates, PRL 2008; Ann. Rev. Cond. Mat. 2015]

MIPS: equilibrium liquid-gas phase separation

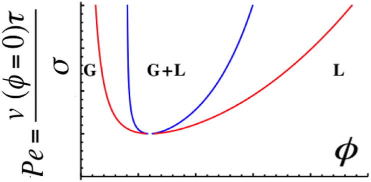
- For $\tau \sim 1/D_r \to 0$, we can eliminate $\mathbf{u}_i$

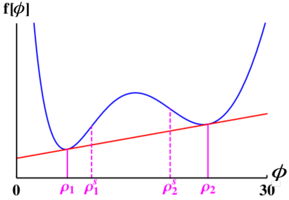
$$\dot{\mathbf{r}}_i \simeq_S v(\phi(\mathbf{r}_i))\xi_i + \sqrt{2T}\eta_i \qquad \simeq_S \ : \text{Stratonovich}$$

- Coarse-graining by standard techniques [Dean, 1995]

Surprise! ... Effective equilibrium with free energy

$$\mathcal{F} = \int d\mathbf{r}\ f(\phi(\mathbf{r})) \qquad f(\phi) = \phi(\log\phi - 1) + \frac{1}{2}\int^{\phi} \log(\tau v^2(y) + T)dy$$





[Tailleur & Cates, PRL 2008; Ann. Rev. Cond. Mat. 2015]

Incomplete phase separation

Experiments: phase separation is often arrested to a cluster phase

Photo-activated colloids

[J. Palacci et al., Science, 2013]

- [Buttinoni et al, PRL 2013]
- [J Schwarz-Linek et al, PNAS 2012]
- [I Theurkauff et al, PRL 2012]
- ...

Janus particles in peroxide, photo-activated catalisys

Incomplete phase separation

- Hydrodynamics:

  [Tiribocchi et al, PRL 2015; F Alarcón et al, Soft Matter, 2017; Matas-Navarro et al, PRE 2014, Zöttl et al, PRL 2014, ...]

- Chemotaxis

  [B Liebchen et al, PRL 2015; ; O Pohl et al, PRL 2014, ...]

- Birth and death

  [Cates et al, PNAS 2010 ...]

Part I

- Natural phenomena from coarse-grained point of view
- Related to bubbly phase separation [J. Stenhammar et al, Soft Matter 2014]

E. Tjhung
(Cambridge)

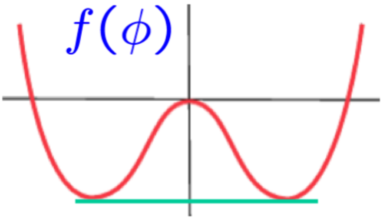
(Equilibrium) Model B

Via gradient expansion (long time and spatial scales)

$$\dot{\phi} = -\nabla \cdot (\mathbf{J} + \eta) \qquad \mathbf{J} = -\nabla \mu$$

$$\mu(\mathbf{r}) = \frac{\delta \mathcal{F}}{\partial \phi(\mathbf{r})} \qquad \mathcal{F} = \int d\mathbf{r} \Big[f(\phi) + k|\nabla \phi|^2 \Big]$$

$$\langle \eta(\mathbf{r}, t)\eta(\mathbf{r}', t')) \rangle = 2D\,\mathbf{1}\,\delta(\mathbf{r} - \mathbf{r}')\delta(t - t')$$



phase equilibria: common tangent construction (equal μ and pressure)

Active field theories

- Minimal modification of Model B allowing breakdown of TRS
- necessary to keep higher orders in a gradient expansion
- Fist possibility: chemical potential does not necessarily derive from a free energy

$$\mu \neq \delta\mathcal{F}/\delta\phi$$

- Second possibility: current is not curl-free

$$\nabla \wedge \mathbf{J} \neq 0$$

- At lowest order in gradients, there are only two such terms

$$\mu \to \mu_B + \lambda|\nabla\phi|^2 \qquad \text{Active Model B: AMB}$$

$$\mathbf{J} \to \mathbf{J}_B - \zeta(\nabla^2\phi)\nabla\phi \qquad \text{Active Model B+: AMB+}$$

AMB

Chemical potential does not derive from Free Energy

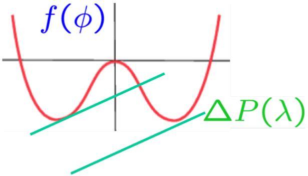
$$\dot{\phi} = -\nabla \cdot (\mathbf{J} + \eta) \qquad \mathbf{J} = -\nabla \mu$$

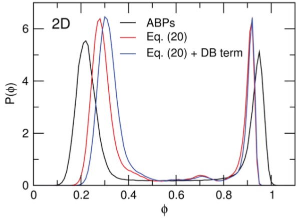
$$\mu(\mathbf{r}) = \frac{\delta \mathcal{F}}{\partial \phi(\mathbf{r})} + \lambda |\nabla \phi|^2 \qquad \mathcal{F} = \int d\mathbf{r} \left[f(\phi) + k|\nabla \phi|^2 \right]$$

$$\langle \eta(\mathbf{r}, t)\eta(\mathbf{r}', t')) \rangle = 2D\,\mathbf{1}\,\delta(\mathbf{r} - \mathbf{r}')\delta(t - t')$$

$$\mu_1 = \mu_2$$

$$\mu_1\phi_1 - f_1 \neq \mu_2\phi_2 - f_2$$





[R. Wittkowski et al., Nat. Comm. 2014; J. Stenhammar et al, Soft Matter 2014]

AMB+

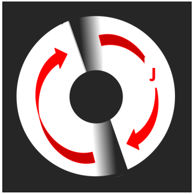
Current is not curl-free

$$\dot{\phi} = -\nabla \cdot (\mathbf{J} + \eta) \qquad \mathbf{J} = -\nabla \mu + \zeta(\nabla^2 \phi)\nabla\phi$$

$$\mu(\mathbf{r}) = \frac{\delta \mathcal{F}}{\partial \phi(\mathbf{r})} \qquad \mathcal{F} = \int d\mathbf{r} \left[f(\phi) + k|\nabla\phi|^2 \right]$$

$$\langle \eta(\mathbf{r},t)\eta(\mathbf{r}',t'))\rangle = 2D\,\mathbf{1}\,\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$$

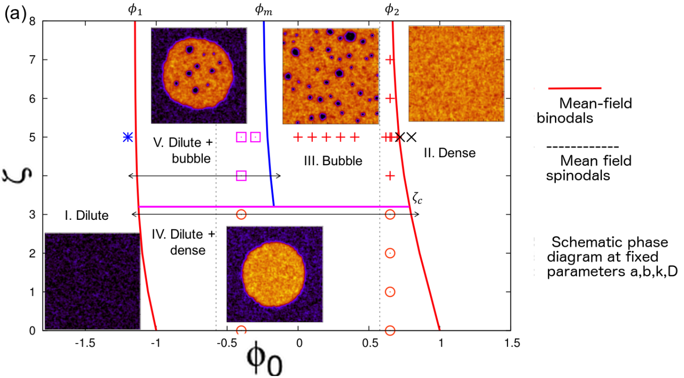
- λ, ζ: same order in a gradient-expansion
- $\nabla \wedge \mathbf{J} \neq 0$



[E. Tjhung, CN, M. Cates, in preparation]

Phase diagram AMB+ $(\zeta > 0, d = 2)$

$$\dot{\phi} = -\nabla \cdot (\mathbf{J} + \eta) \qquad \mathbf{J} = -\nabla\mu + \zeta(\nabla^2\phi)\nabla\phi \qquad \mu = -a\phi + b\phi^3 - k\nabla^2\phi$$



- average density $\phi_0 = \int d\mathbf{r}\phi$
- $\zeta = 0$: Model B
- noise amplitude: $D = 0.1$
- $a = 1, b = 1, k = 1$

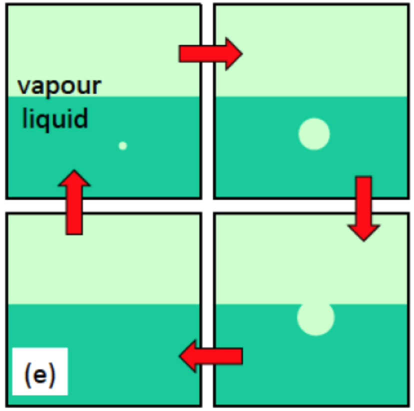
[E. Tjhung, CN, M. Cates, in preparation]

Bubbly phase separation ($\zeta > 0$)

Obvious TRS breakdown in the steady state

- Bubbles are created by nucleation
- They are destroyed by ejection or merging with others

Bubbles violate Time-Reversal-Symmetry: Circulating phase-space current



Incomplete phase separation - Bubbly phase separation

Active Model B+
($\zeta = 5$, low density)

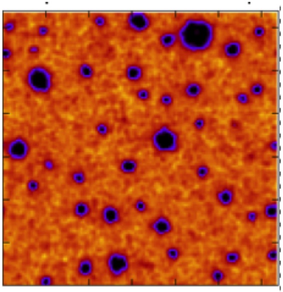
[E. Tjhung, CN, M. Cates, in preparation]

Repulsive particles
(simulations WCA pot)

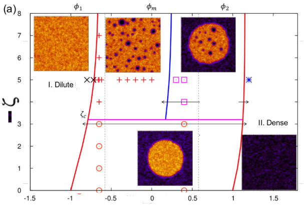
[J. Stenhammar et al, Soft Matter, 2014]

Cluster phase ($\zeta < 0$, low density)

The model is symmetric under $(\zeta, \phi) \to (-\zeta, -\phi)$



$\zeta < 0$:
dense droplets in a dilute environment at low ϕ_0



$D = 0.1$

Incomplete phase separation - Cluster phase

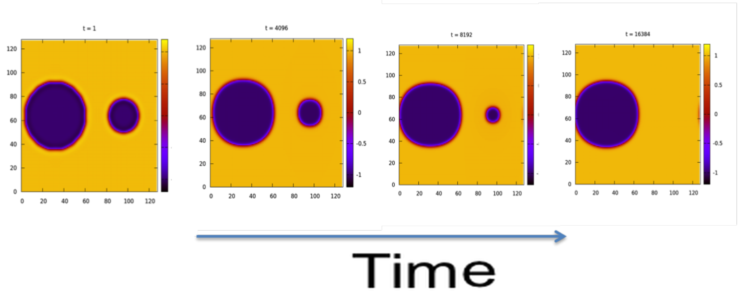
Particles: Attractive U (LJ - cutoff at 5σ)

[Simulations by J. Stenhammar, R. Mari]

Similar simulations result at particle level: [Alarcòn et al., Soft Matter, 2017; Pyramidis et al., Soft Matter, 2015; Mognetti et al., PRL, 2013]

Ostwald Ripening (OR), equilibrium - I

Bubbles/Clusters of different size seem to coexist...



- Very generic (ex. Model A, B, ...), with and without hydrodynamics (Model H)...

OR, equilibrium - II

Mean-field argument (no noise $D = 0$)

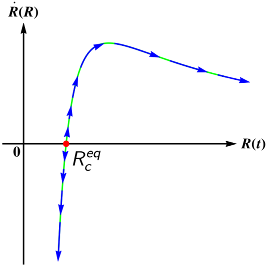
- Quasi-static diffusion of the droplet
- supersaturated environment ($\phi_\infty = \phi_{binodal} - \epsilon$)
- R: droplet radius, $\sigma \equiv \int_{interface} \phi'^2$: surface tension
- Laplace pressure $P \propto \sigma/R$

$$\dot{R} \propto \frac{\sigma\alpha}{R}\left(\frac{1}{R_c^{\zeta=0}} - \frac{1}{R}\right) + \mathcal{O}\left(\frac{1}{R^3}\right)$$

$$\alpha = k/\Delta\phi^2$$

$$\Delta\phi = \text{density difference}$$

$$R_c^{\zeta=0} = \sigma/\epsilon$$



$R \sim t^{1/3}$ at large times $\tau_{coarsening}^{\zeta=0} \sim R(0)^3/\alpha_{\zeta=0}$

Exponentially suppressed OR (AMB+)

- $\lambda \neq 0$ does not alter such a figure [Wittkowski et al., Nat. Comm., 2013]
- $\zeta \neq 0$ causes a strong slow-down of Ostwald Ripening

$$\dot{R} \propto \frac{\sigma \alpha e^{-\zeta \Delta\phi/k}}{R}\left(\frac{1}{R_c} - \frac{1}{R}\right) + \mathcal{O}\left(\frac{1}{R^3}\right)$$

$$R_c = R_c^{\zeta=0} e^{-\zeta\Delta\phi/k} \qquad \sigma = \int_{interface} \phi'^2$$

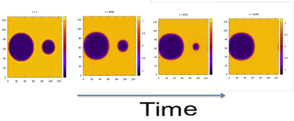
- Still, $R \sim t^{1/3}$ at large times (but exponentially large in ζ/k !)

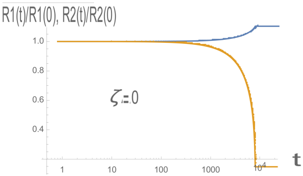
$$t_{coarsening} \sim t_{coarsening}^{\zeta=0} \; e^{\zeta\Delta\phi/k}$$

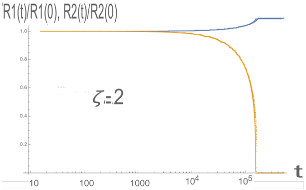
- Small clusters can be nucleated (when $D \neq 0$)

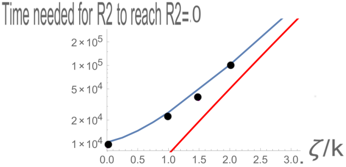
Exponentially suppressed OR: Comparison with simulations

Two droplet configuration:
analytical solution of droplets evolution

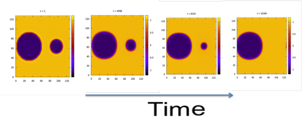








Coexisting densities: mean-field

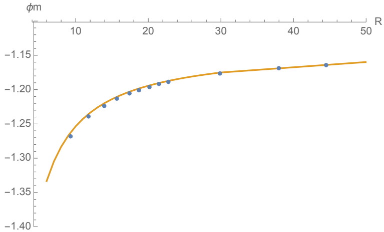


$$\nabla \wedge \mathbf{J} \neq 0 \Longrightarrow \text{Helmoltz decomposition}$$

'Effective μ' coming from ζ is non-local

$$\mu = f'(\phi) - K\phi'' - \frac{(d-1)K}{r}\phi' - \frac{\zeta}{2}\phi'^2 + (d-1)\zeta \int_r^\infty \frac{\phi'^2(y)}{y}\, dy$$

Coexisting densities

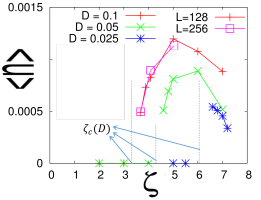


$$\phi_{in}(R) - \phi_{binodal} \sim 1/R$$

$$\phi_{out}(R) - \phi_{binodal} \sim e^{-\zeta/k}/R$$

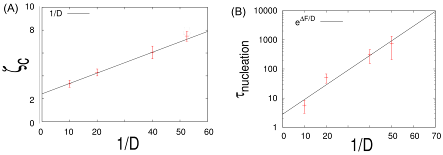
Bubbly/cluster phase: a noise-activated transition

- $\zeta_c = \zeta_c(D) \uparrow$ when $D \downarrow$
- Well defined average density of clusters $\langle n \rangle$



Transition to cluster/bubble phase takes place when

$\tau_{Nucleation} \sim \tau_{coarsening}$



Assuming

$\tau_{Nucleation} \sim e^{-A/D}$

$\implies \zeta_c \sim 1/D$

Part II - Measuring violations of 'intrinsic' TRS

Entropy production

$$S = \lim_{t\to\infty} \frac{1}{t} \log\left(\mathcal{P}_F/\mathcal{P}_B\right)$$

- D. Chaudhuri, T. Speck, U. Seifert, ...

- $\mathcal{P}_F$ probability of forward trajectory $\{\mathbf{x}_i(t)\}$
- $\mathcal{P}_B$ probability of time reversed trajectory $\{\epsilon\mathbf{x}_i(-t)\}$
- ϵ: parity under time-reversal of $\mathbf{x}$
- $S = 0$ if and only if TRS is respected

- S strongly depends on which dof we retain

  [Bo, Celani, J. Stat. Phys, 2014; P Pietzonka, U Seifert, preprint 2017, ...]

- We will instead show some universality

Remark: I will only talk about average EP

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Active Ornstein-Uhlenbeck Particles (AOUPs)

$$\dot{\mathbf{r}}_i = -\sum_j \nabla_i U(\mathbf{r}_i - \mathbf{r}_j) + \mathbf{v}_i$$

$$\langle \mathbf{v}_i(t)\mathbf{v}_j(0)\rangle = \delta_{ij}\mathbf{1}\frac{D}{\tau}e^{-t/\tau}$$

$\mathbf{v}_i$ Gaussian r.v.

E. Fodor (Cambridge)

More details: Etienne's poster

- Stationary measure perturbatively in $\tau \to 0$

$$P_{ss} \propto e^{-\frac{U+p_i^2/2}{D}} \times \left\{1 - \frac{\tau}{2D}\left[(\nabla_i U)^2 + (p_i\cdot\nabla_i)^2 U - 3D\nabla_i^2 U\right] + \tau^{3/2}\left[\frac{1}{6D}(p_i\cdot\nabla_i)^3 U - \frac{1}{2}(p_i\cdot\nabla_i)\nabla_j^2 U\right] + \mathcal{O}(\tau^2)\right\}$$

[E. Fodor, CN, M. Cates, J. Tailleur, P. Visco, F. van Wijland, PRL, 2016; in preparation]

Active Ornstein-Uhlenbeck Particles (AOUPs)

$\mathbf{r}_i$ even under TR $\qquad$ $\mathbf{v}_i$ undefined under TR $\qquad$ $\mathbf{p}_i = \dot{\mathbf{r}}_i$ odd under TR

Standard field-theoretical techniques

$$S = \frac{\sqrt{\tau}}{2D} \sum_{ij} \left\langle (\mathbf{p}_i - \mathbf{p}_j)^3 : \nabla^3 U(\mathbf{r}_i - \mathbf{r}_j) \right\rangle$$

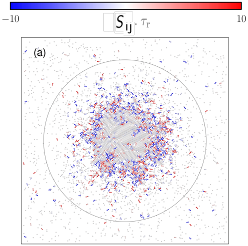
- S is a global measure: little information for extended systems

w short-ranged $\Longrightarrow$ coarse graining of S well defined

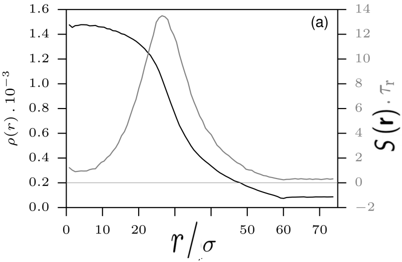
Local EP in AOUPs

$$U(\mathbf{r}) = w_0 \exp\left(-\frac{1}{(\sigma/r)^2 - 1}\right) \qquad S \to \int d\mathbf{r} S(\mathbf{r})$$

$S(\mathbf{r})$: entropy produced in a $l \times l$ box centered in $\mathbf{r}$ ($\sigma \ll l \ll L$) measured in units of $\tau_r^{-1} = \sigma^2/w_0$



$D = 1$, $\tau = 10$, $N \sim 10^4$, $\sigma = 1$, $w_0 = 10$



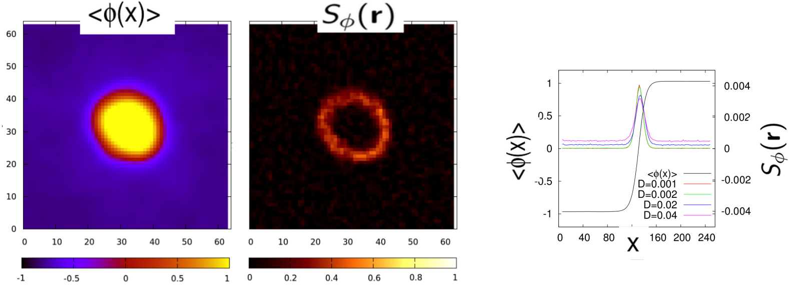
[E. Fodor, CN, M. Cates, J. Tailleur, P. Visco, F. van Wijland, PRL, 2016; in preparation]

AMB: Local EP

$$\dot{\phi} = -\nabla \cdot (\mathbf{J} + \eta) \qquad \mathbf{J} = -\nabla \mu \qquad \mu(\mathbf{r}) = \frac{\delta \mathcal{F}}{\partial \phi(\mathbf{r})} + \lambda |\nabla \phi|^2$$

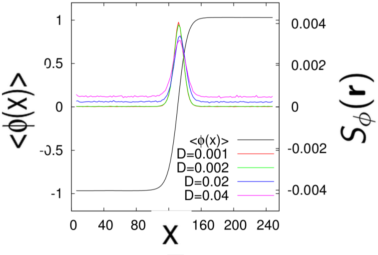
$\mathcal{P}_F, \mathcal{P}_B$: probabilities of a trajectory of the density $\{\phi(\mathbf{r}, t)\}_{0<t<\infty}$

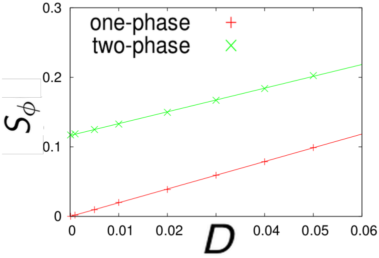
$$S = \int_{Volume} S_\phi(\mathbf{r})\, d\mathbf{r} \qquad S_\phi(\mathbf{r}) = \langle \dot{\phi} \mu_{NE} \rangle \qquad \mu_{NE} = \lambda |\nabla \phi|^2$$



[CN, E. Fodor, E. Tjhung, F. van Wijland, J. Tailleur, M. Cates, PRX, 2017]

Active Model B: EP in the bulk





- $S_\phi \sim \mathcal{O}(D)$ in the bulk for D small
- $S_\phi \sim \mathcal{O}(1)$ at the interfaces

EP in the bulk: Harada-Sasa relation

- In the bulk we need more refined methods to measure EP
- Generalisation of Harada-Sasa relation [Harada & Sasa, PRL, 2005]

$$S_\phi = \int_{\mathbf{k},\omega} S_\phi(\mathbf{k},\omega)$$

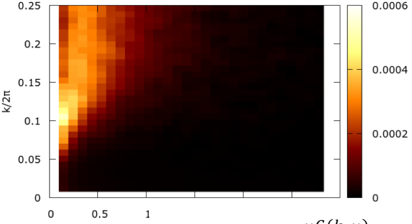
$$S_\phi(\mathbf{k},\omega) = \frac{\omega}{Dk^2}\left[\omega C(\mathbf{k},\omega) - 2DR(\mathbf{k},\omega)\right]$$

- $\tilde{C}(\mathbf{r}_1 - \mathbf{r}_2, t - s) = \langle \phi(\mathbf{r}_1, t)\phi(\mathbf{r}_2, s)\rangle$
- R: Response to perturbing $\mu \to \mu - h$

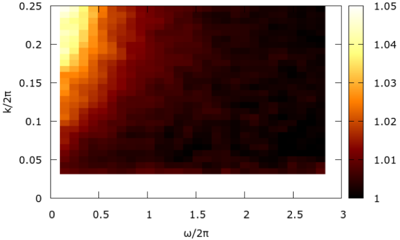
Quantitative link between EP and violation of FDT

EP in the bulk: Harada-Sasa relation vs effective T

$$\omega C(k,\omega) - 2D\tilde{R}(k,\omega) = \frac{k^2}{\omega}\sigma(k,\omega)$$



$$\frac{\omega C(k,\omega)}{2D\tilde{R}(k,\omega)} = T_{eff}$$



Confirmation that effective temperature is not a quantitative measure of breakdown of TRS

Conclusions and outlook

Incomplete phase separation

- Bubbly PS or cluster phases often observed in simulations/experiments
- Two faces of the same phenomena
- Analogous phenomenology found in Ginzburg-Landau + minimal violation of detailed balance (gradient expansion)

Measuring breakdown of TRS

- Notion of local EP
- Harada-Sasa: quantitative link between EP and violation of FDT

Thank you!

Incomplete phase separation

E. Tjhung, CN, M. Cates, in preparation

F. Caballero, CN, M. Cates, in preparation

Quantifying TRS breakdown

E. Fodor, CN, M. Cates, J. Tailleur, P. Visco, F. van Wijland, PRL, 2016

CN, E. Fodor, E. Tjhung, F. van Wijland, J. Tailleur, M. Cates, PRX, 2017

E. Fodor, CN, M. Cates, J. Tailleur, P. Visco, F. van Wijland, in preparation