Large Deviations of Active Matter Fields

- Active phase separation
- Classical nucleation theory in equilibrium
- Classical nucleation theory without detailed balance[1]
- Phase separation with birth and death of particles
- Population dynamics for global density
- Effect of phase separation on density dynamics
  - Limit cycles[2]
  - Extinction rates[3]
- Conclusions

1. C Nardini + MEC arXiv:2210.05263
2. T Grafke et al PRL 119 188003 (2017)
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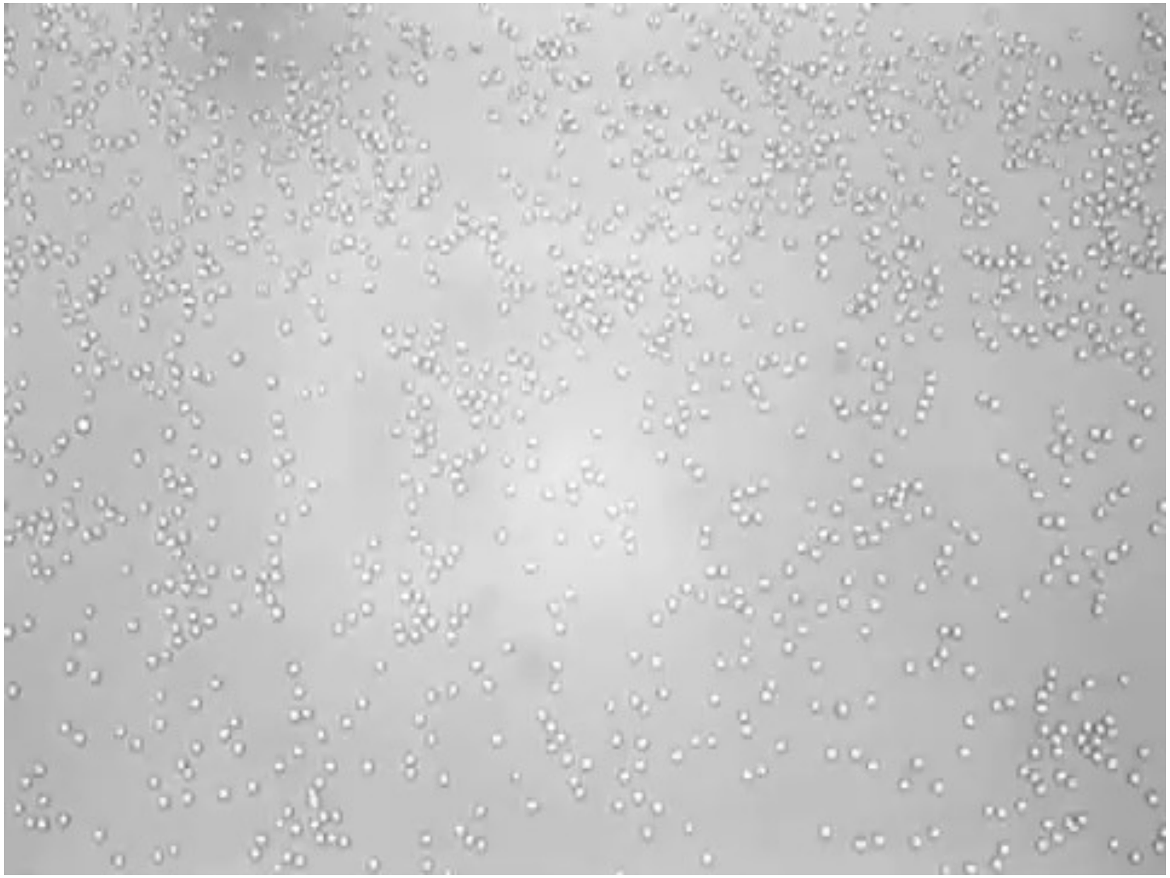
Active Phase Separation of Self-Propelled Colloids

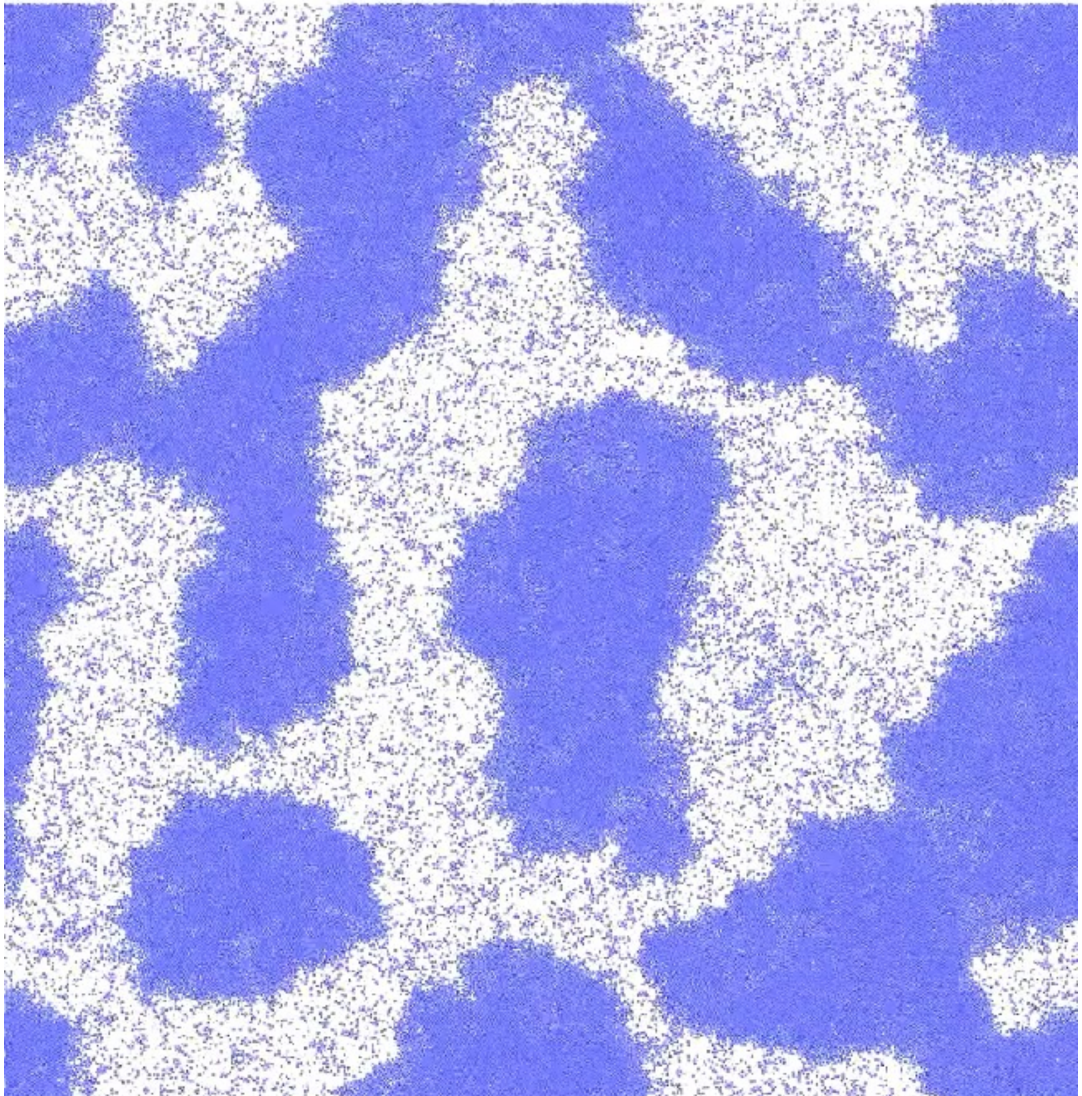


Motility-Induced
Phase Separation
(MIPS)

Janus particles in peroxide, light activated catalysis

J Palacci et al, Science 2013

Motility-Induced Phase Separation (MIPS)



coexisting densities

$\rho = \rho_c \pm \phi_b$

purely repulsive active Brownian particles (ABPs)

MEC + J Tailleur, Ann Rev CMP 2015

movie: J Stenhammar

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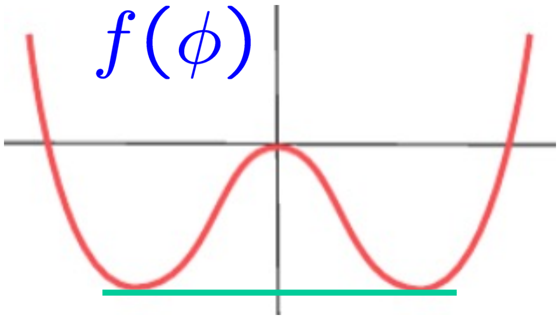
Field Theory of Phase Separation

$$\dot{\phi} = -\nabla.\mathbf{J}$$
$$\mathbf{J} = -\nabla\mu + \sqrt{2D}\boldsymbol{\Lambda}$$
$$\mu = a\phi + b\phi^3 - \kappa\nabla^2\phi$$

Λ = unit white noise
$D = k_B T M$
M = 1 mobility

MODEL B

$$\mu = \delta\mathcal{F}/\delta\phi$$
$$\mathcal{F} = \int dV[f(\phi) + \tfrac{\kappa}{2}(\nabla\phi)^2]$$
$$f(\phi) = \tfrac{a}{2}\phi^2 + \tfrac{b}{4}\phi^4$$



phase equilibria:
common tangent

$$\mu_1 = \mu_2$$
$$P_1 = P_2 \qquad \text{where } P = \mu\phi - f$$

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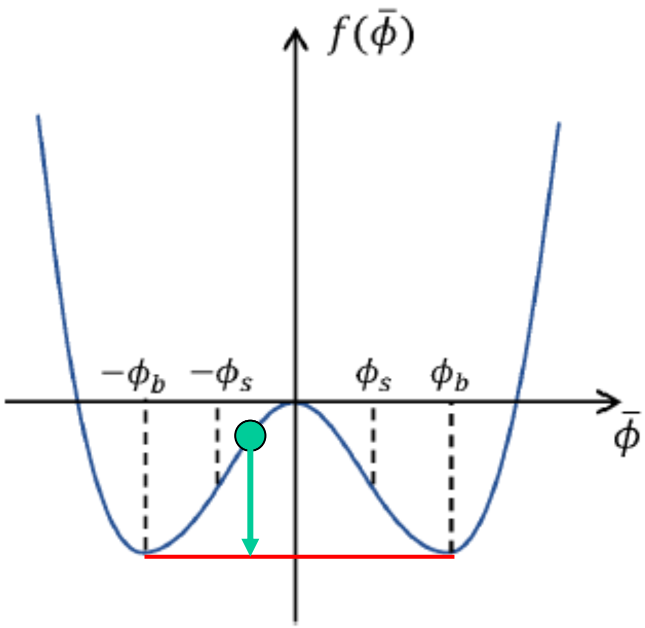
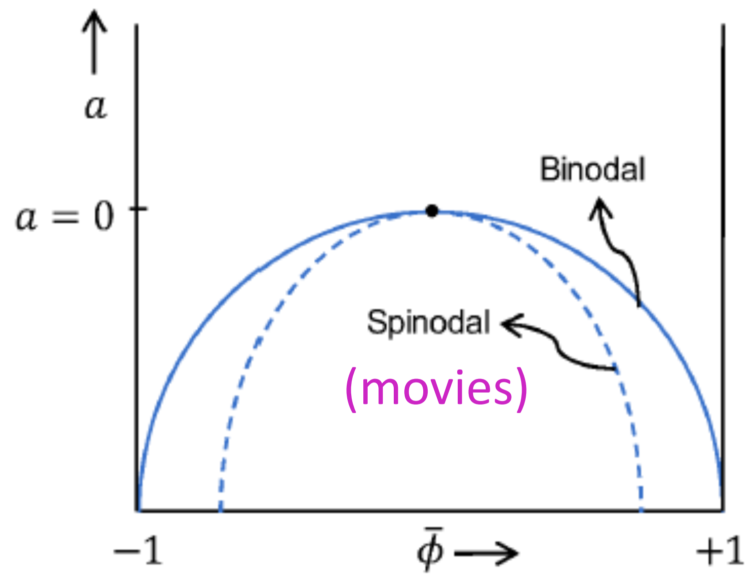
$D = k_B T M$
$M = 1$ mobility

MODEL B

Model B has Time Reversal Symmetry:
Forward and backward dynamics statistically identical
once steady state is achieved

Thermodynamics of the Density Field





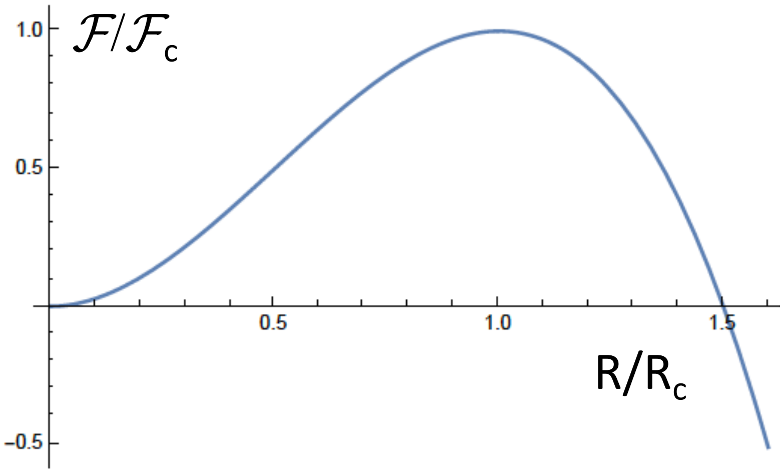
For global density $\bar{\phi}$ obeying $-\phi_b < \bar{\phi} < +\phi_b$:

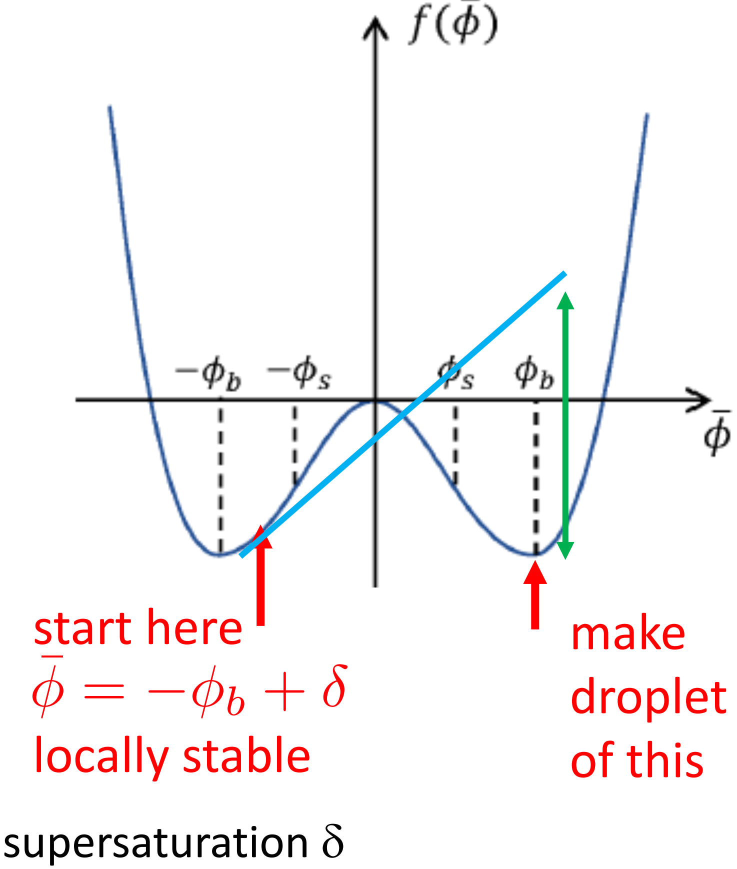
- phase separation reduces overall free energy $\mathcal{F}$
- resulting $\mathcal{F}/V$ lies on convex hull of $f(\phi)$ = common tangent
- **Locally stable between binodal and spinodal: instanton required**

Classical Nucleation Theory

Nucleation and growth (3 dimensions)

$\mathcal{F} = \gamma\, 4\pi R^2 - (2\, \phi_b\, \delta\, f''(\phi_b))\, 4\pi R^3/3$





γ (a,b,κ) = interfacial tension

competes with bulk free energy gain

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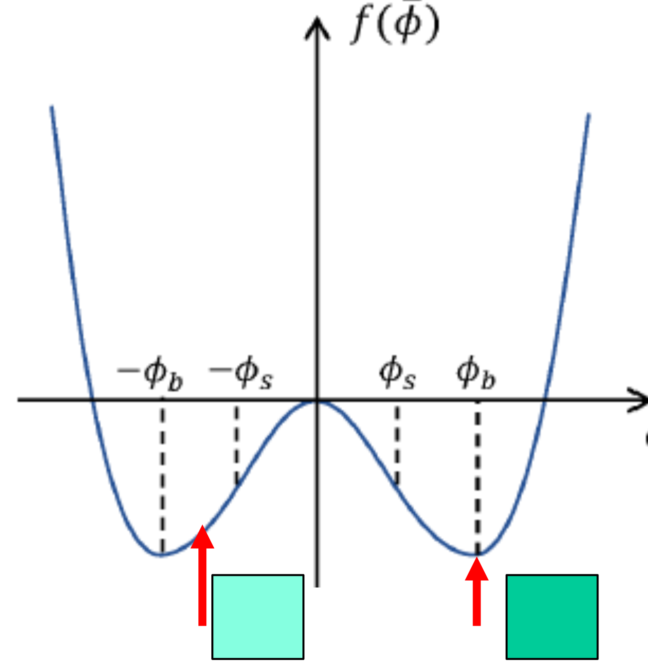
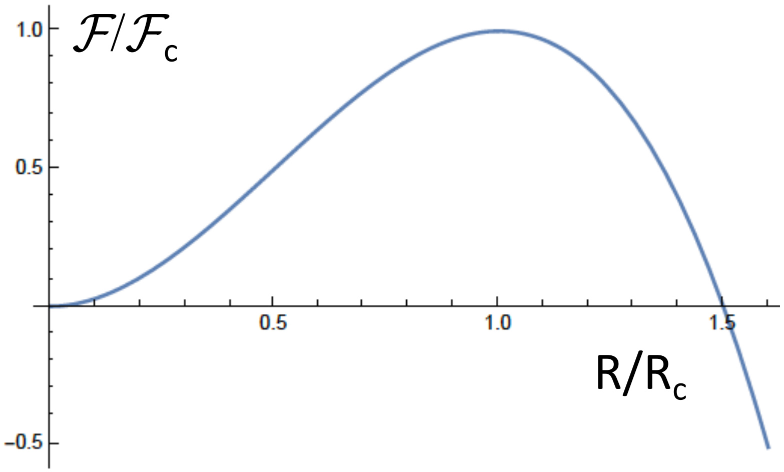
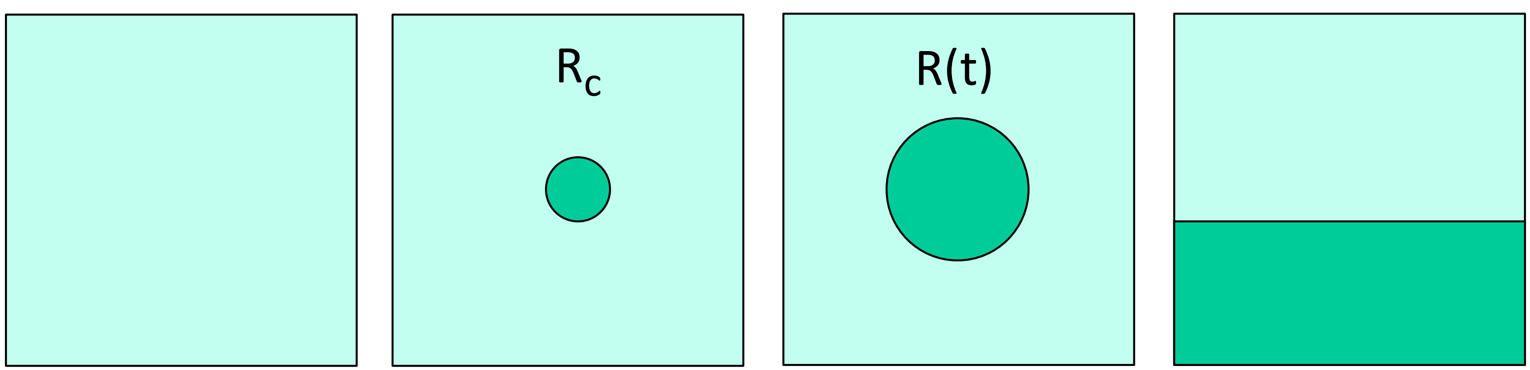




noise driven rare event (instanton)

nucleation rate $\propto \exp[-\mathcal{F}_c/D]$



Classical Nucleation Theory from Kinetics

$$\dot{\phi} = -\nabla.\mathbf{J}$$

$$\mathbf{J} = -\nabla\mu + \sqrt{2D}\mathbf{\Lambda}$$

$$\mu = a\phi + b\phi^3 - \kappa\nabla^2\phi$$

quasi stationary solution for radially symmetric interfacial profile

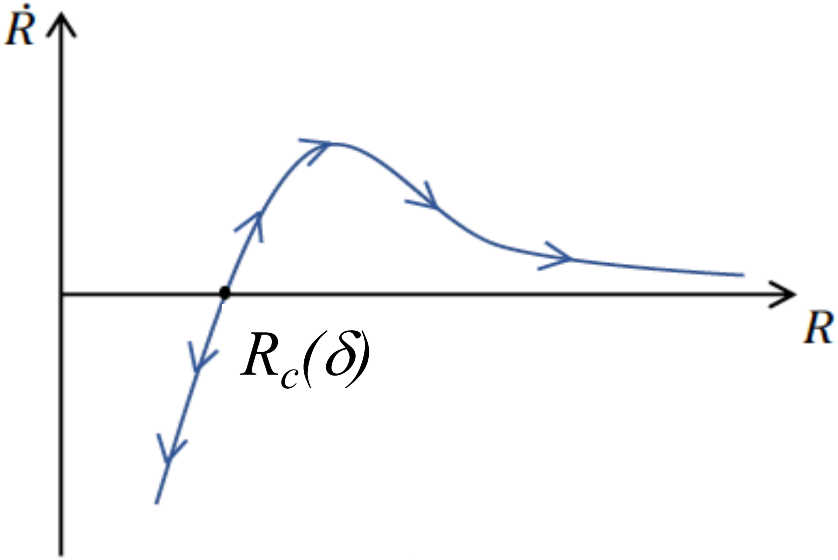
$\phi(r) = \tilde{\phi}(r/R)$, expand in powers of 1/R

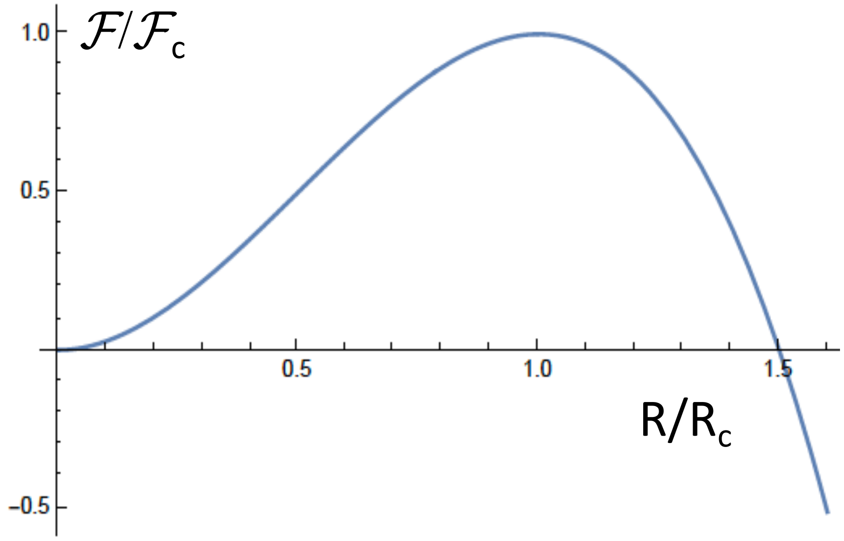
resulting $J(R^+)$ gives $\dot{R}(R)$ as:

$$\dot{R} = \frac{1}{2\phi_b}\left(\frac{f''(\phi_b)}{R}\left(\delta - \frac{\gamma}{f''(\phi_b)\phi_b R}\right)\right) + (8\pi D\phi_b^2 R^3)^{-1/2}\Lambda + \ldots$$

unit white

Classical Nucleation Theory from Kinetics





$$\dot{R} = \frac{1}{2\phi_b}\left(\frac{f''(\phi_b)}{R}\left(\delta - \frac{\gamma}{f''(\phi_b)\phi_b R}\right)\right) + (8\pi D\phi_b^2 R^3)^{-1/2}\Lambda + \ldots$$

equivalently: $\dot{R} = -\mathcal{M}(R)\frac{d\mathcal{F}}{dR} + \sqrt{2\mathcal{M}(R)D}\,\Lambda + \mathcal{O}(R^{-3})$

$\mathcal{M}(R) = 1/(16\pi\phi_b^2 R^3)$ = mobility of reaction coordinate R

Classical Nucleation Theory from Kinetics

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With only one coordinate, read off from $\dot{R}(R)$:

- Mobility $\mathcal{M}$ (via noise)
- Hence effective force d$\mathcal{F}$/dR
- Integrate to give barrier $\mathcal{F}_c$ and nucleation rate $\propto$ exp[- $\mathcal{F}_c$ /D]
- Noise term: sum random currents over surface of sphere

Kinetic approach via $\dot{R}(R)$ does not require $\mathcal{F}$ = a free energy...

... but with one degree of freedom, it discovers one

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$$f(\phi) = \frac{a}{2}\phi^2 + \frac{b}{4}\phi^4$$

Active Field Theory of Phase Separation

$$\dot{\phi} = -\nabla.\mathbf{J}$$

$$\mathbf{J} = -\nabla\hat{\mu} + \sqrt{2D}\boldsymbol{\Lambda} \quad +\zeta(\nabla^2\phi)\nabla\phi$$

$$\hat{\mu} = a\phi + b\phi^3 - \kappa\nabla^2\phi \;\; +\lambda(\nabla\phi)^2$$

ACTIVE MODEL B

$\lambda(\nabla\phi)^2 \neq \delta\mathcal{F}/\delta\phi$ for any $\mathcal{F}$

= **minimal** violation of TRS

ACTIVE MODEL B+

Expansion of active currents to order ∇^3, ϕ^2

ζ term: strong effects at curved interfaces; elsewhere $\lambda \to \lambda'$

R Wittkowski et al, Nat Comms 2014

C Nardini et al, PRX 2017; E Tjhung et al, PRX 2018

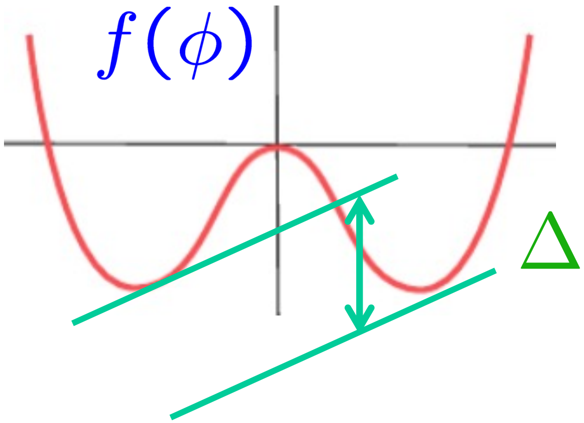
Active Field Theory of Phase Separation

Uncommon tangent construction

(not convex hull)

offset $\Delta = \Delta(\lambda - \zeta/2)$

Calculation Method:



(a) quasi-1D flat interface between phases

(b) seek J = 0 solutions with $\partial_x \phi = 0$ at $x = \pm\infty$

- Binodals are shifted
- Spinodals are not
- Between these lies an active nucleation regime

R Wittkowski et al, Nat Comms 2014

A Solon et al, PRE 2018

Classical Nucleation Theory from Kinetics

$$\dot{\phi} = -\nabla.\mathbf{J}$$
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Passive
Model B+

quasi stationary solution for radially symmetric interfacial profile

$\phi(r) = \tilde{\phi}(r/R)$ + noise, expand in powers of 1/R

resulting $J(R^+)$ gives $\dot{R}(R)$ as:

$$\dot{R} = \frac{1}{2\phi_b}\left(\frac{f''(\phi_b)}{R}\left(\delta - \frac{\gamma}{f''(\phi_b)\phi_b R}\right)\right) + (8\pi D\phi_b^2 R^3)^{-1/2}\Lambda + \ldots$$

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Active Model B+

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resulting $J(R^+)$ gives $\dot{R}(R)$ as:

$$\dot{R} = -\frac{\mathcal{A}(a,b,\kappa,\lambda,\zeta)}{R^2} + \frac{\mathcal{B}(a,b,\kappa,\lambda,\zeta)}{R} + (8\pi D\phi_b^2 R^3)^{-1/2}\Lambda + \dots$$

noise term unchanged

equivalently: $\dot{R} = -\mathcal{M}(R)\frac{d\mathcal{F}}{dR} + \sqrt{2\mathcal{M}(R)D}\,\Lambda + \mathcal{O}(R^{-3})$

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- Hence effective force $d\mathcal{F}/dR = 16\,\pi^2\,\phi_b^2\,(\mathcal{A}\,R - \mathcal{B}\,R^2)$
- Integrate to give barrier $\mathcal{F}_c$ and nucleation rate $\propto \exp[-\mathcal{F}_c/D]$

Effective barrier height $\mathcal{F}_c(a, b, \kappa, \lambda, \zeta) = 16\pi^2\phi_b^2\,\mathcal{A}^3/3\mathcal{B}^2$

Everything calculable for large $R_c \leftrightarrow$ modest supersaturation

C Nardini + MEC arXiv:2210.05263

Classical Nucleation Theory from Kinetics

Comments:

Noise terms and hence mobility $\mathcal{M}$(R) unaffected by κ,ζ

$\mathcal{A}$(a,b,κ,λ,ζ) $\propto$ pseudo-interfacial tension strongly affected

$\mathcal{B}$(a,b,κ,λ,ζ) $\propto$ pseudo-chemical-potential-difference likewise

Resulting $\mathcal{F}_c$ can be larger or smaller than the passive model

Complete large deviation theory *à la* CNT whenever $\mathcal{F}_c$ large

$\mathcal{F}$(R) = quasipotential governing instanton + rates

C Nardini + MEC arXiv:2210.05263

Interfacial Tension in Active Systems

In thermodynamic equilibrium

γ_F [mechanical energy]

γ_L [Laplace pressure at curved interface]

γ_C [capillary waves]

γ_S [integral of deviatoric stress]

all the same

In active systems, these all differ (even in sign)

$\mathcal{F}(R)$ via $1/R$ expansion solely involves γ_L

large ζ activity: $\gamma_L < 0$, expansion fails.... micro-nuclei?

larger ζ activity: $\gamma_{L,C} < 0$ instanton pathway totally unclear

G Fausti et al PRL 127 068001 (2021)

C Nardini + MEC arXiv:2210.05263

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Phase Separation with Birth and Death

Motivation: Bacterial colonies

- population dynamics: growth at low density, decline at high
- quorum sensing: seek strength in numbers to attack or defend

E.g.: planktonic – colonial life cycle

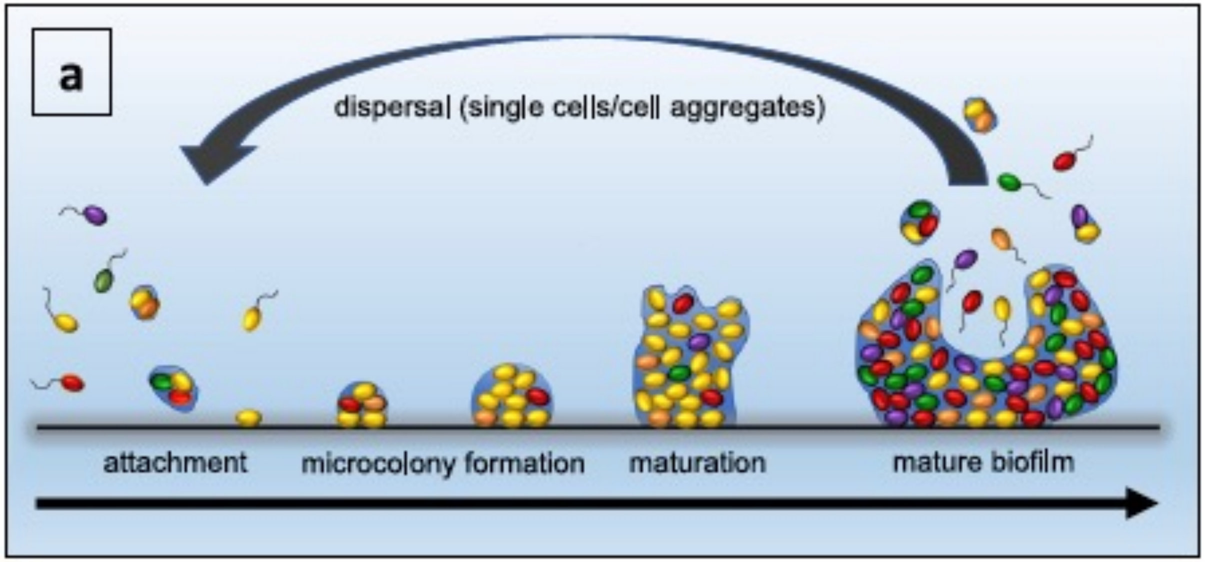


image: A Penesyan et al NPJ Biofilms and Microbiomes (2021)

Population Dynamics in Uniform State

global density $\rho(t)$ not conserved

$$\dot{\rho} = -\mathcal{M}(\rho) f'(\rho) + \sqrt{2D\mathcal{M}(\rho)}\ \Lambda$$

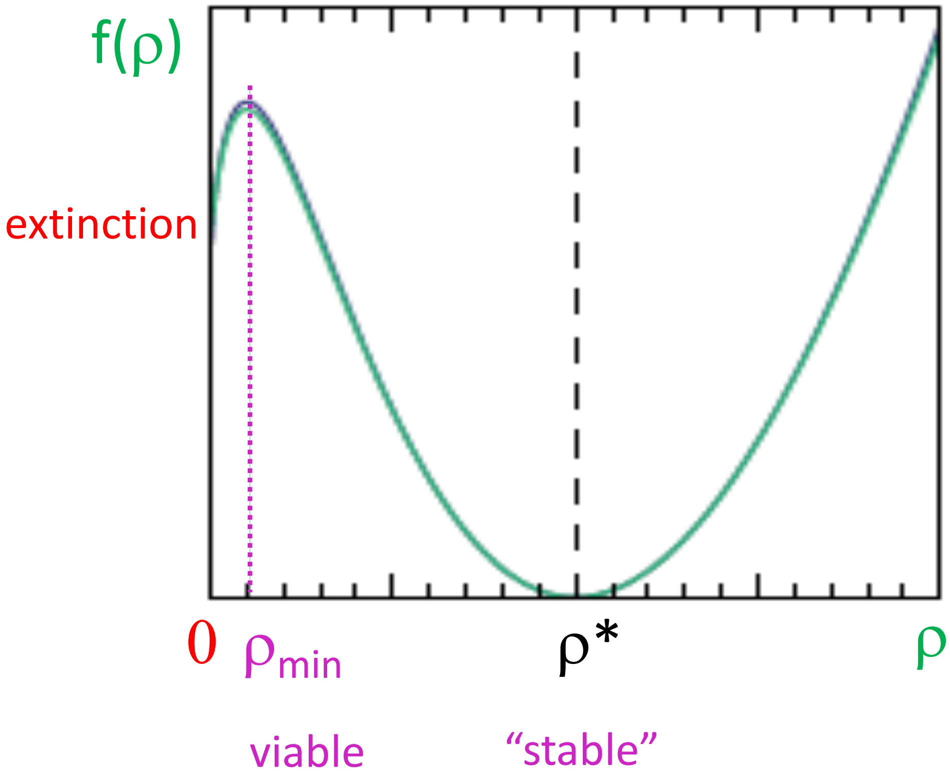
$f(\rho)$ = effective free energy

$D \propto 1/V$

Λ = unit white noise

$\mathcal{M}$ = mobility along ρ axis

extinction: $\mathcal{M}(0) = 0$



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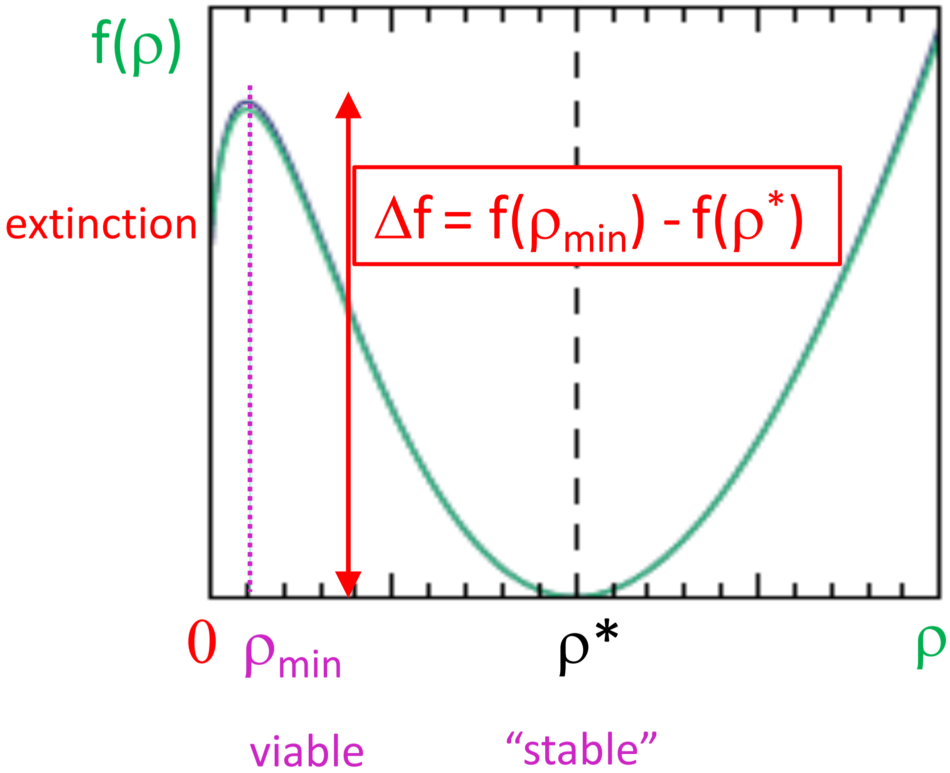

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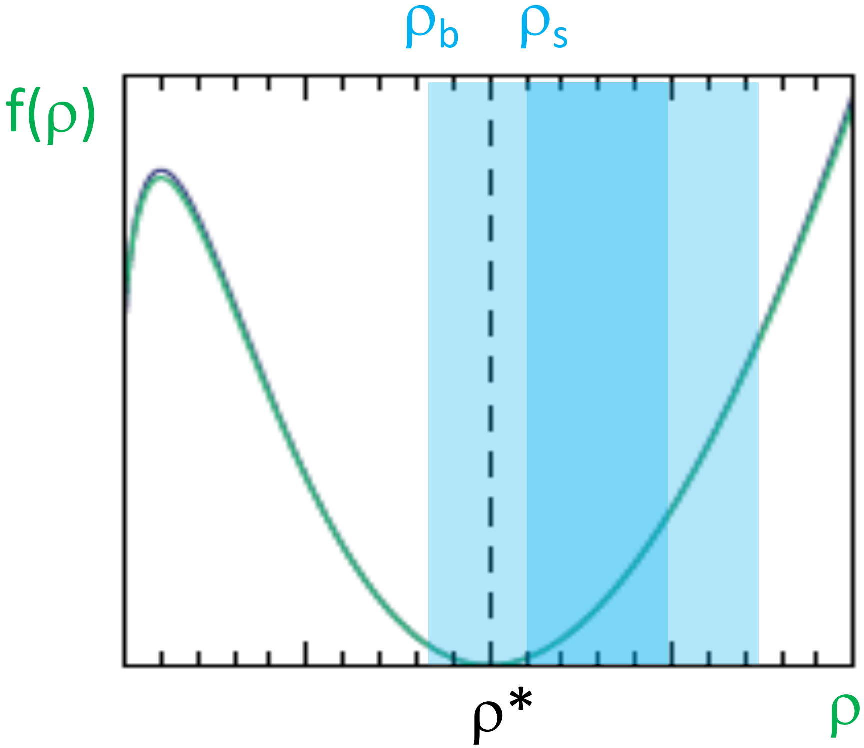
Effects of Phase Separation: Limit Cycles

suppose $\rho*$ lies within nucleation regime for Model B dynamics

except for nucleation: PS fast compared to Birth/Death



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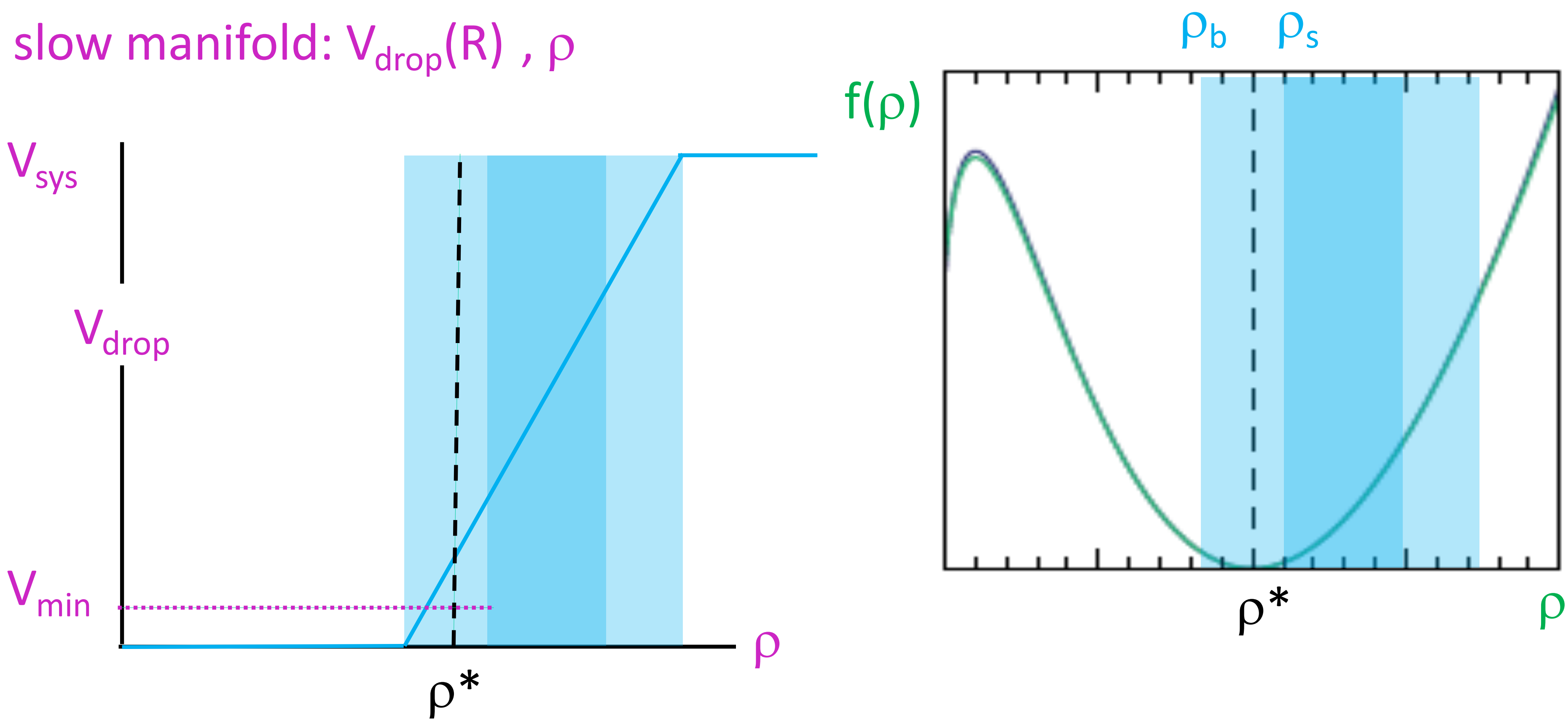
slow manifold: $V_{drop}(R)$, ρ



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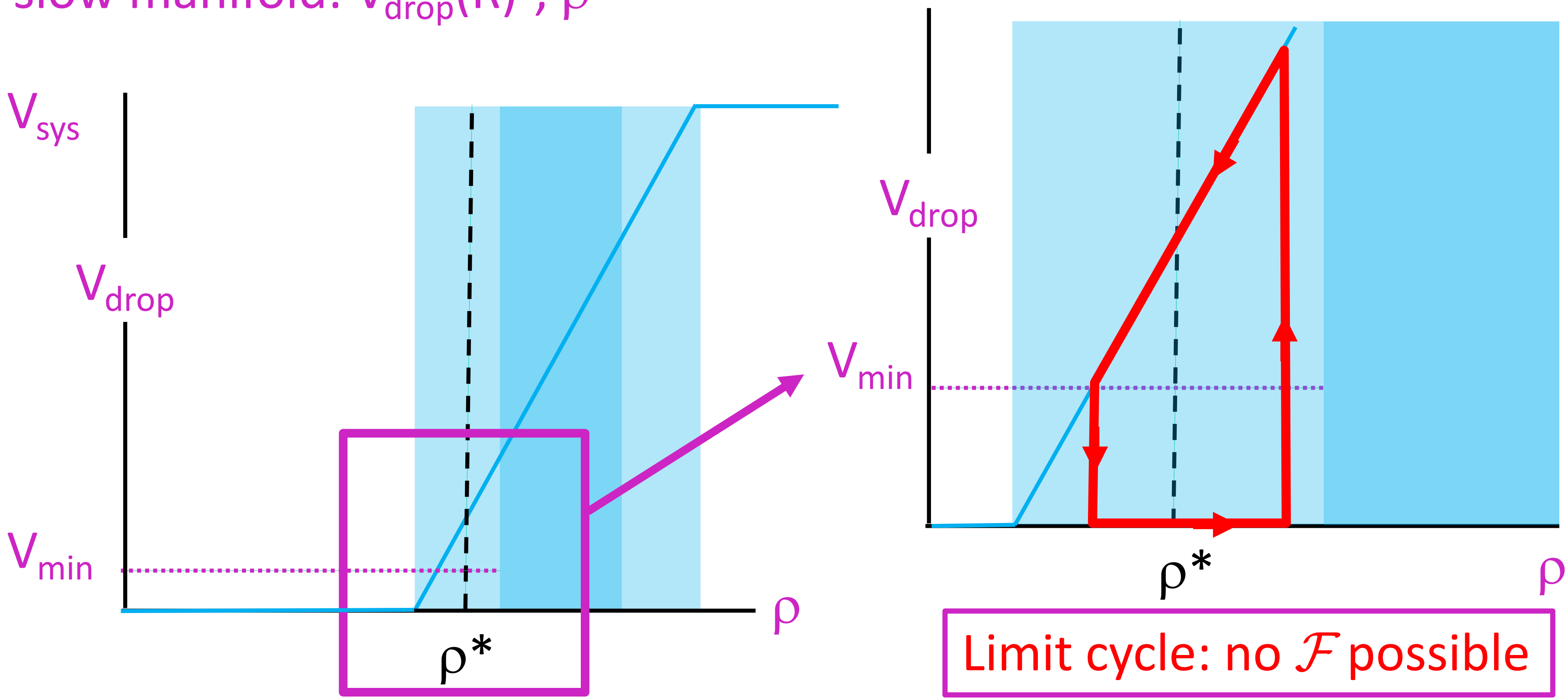

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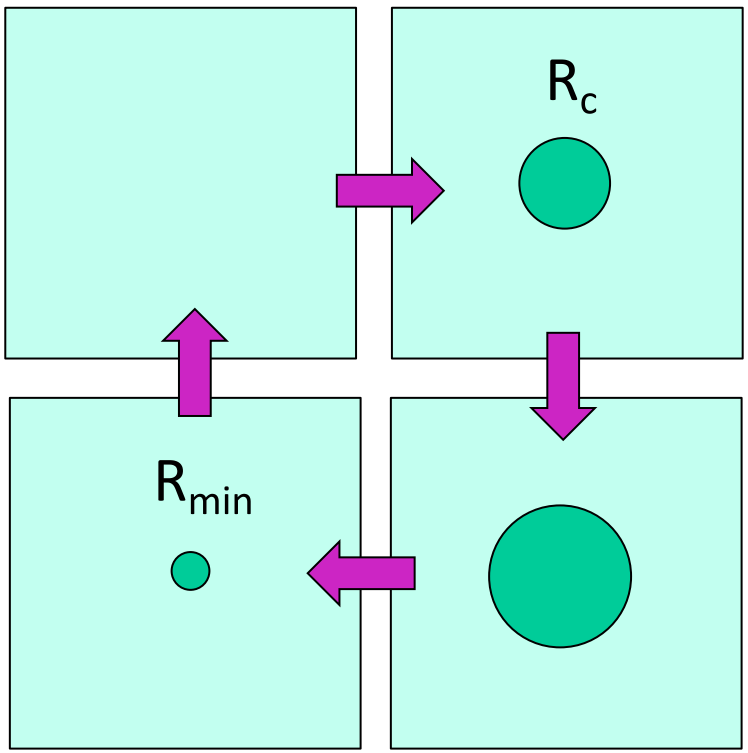
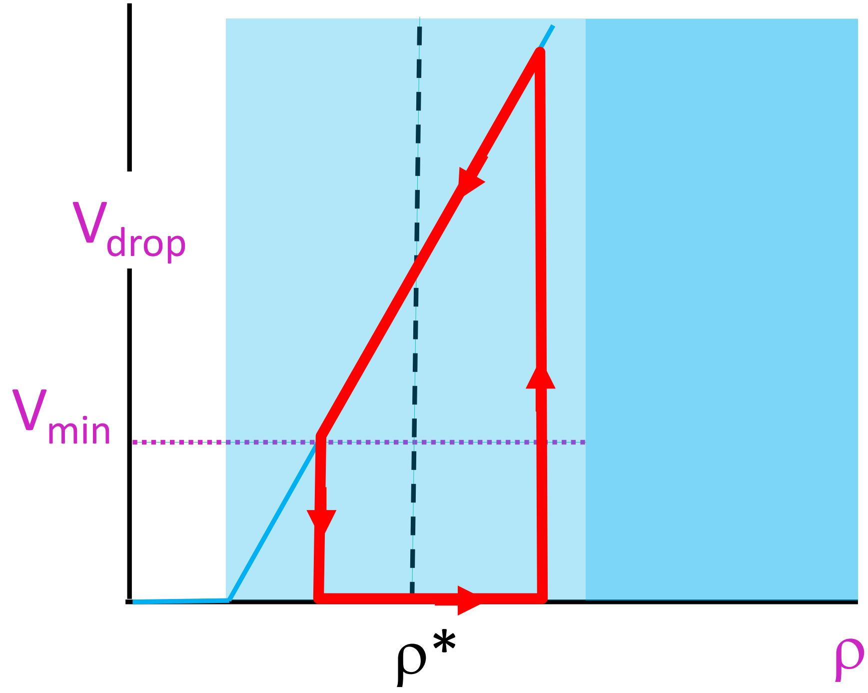




Limit cycle: no $\mathcal{F}$ possible

T Grafke et al PRL 119 188003 (2017), Y I Li + MEC JSTAT 053206 (2020)

Effects of Phase Separation: Extinction

suppose PS region lies in $(0, \rho^*)$ **and even nucleation is fast**

$$\dot{\rho}(\rho, V) = -\mathcal{M}(\rho) f'(\rho) + \sqrt{2D\mathcal{M}(\rho)}\ \Lambda$$

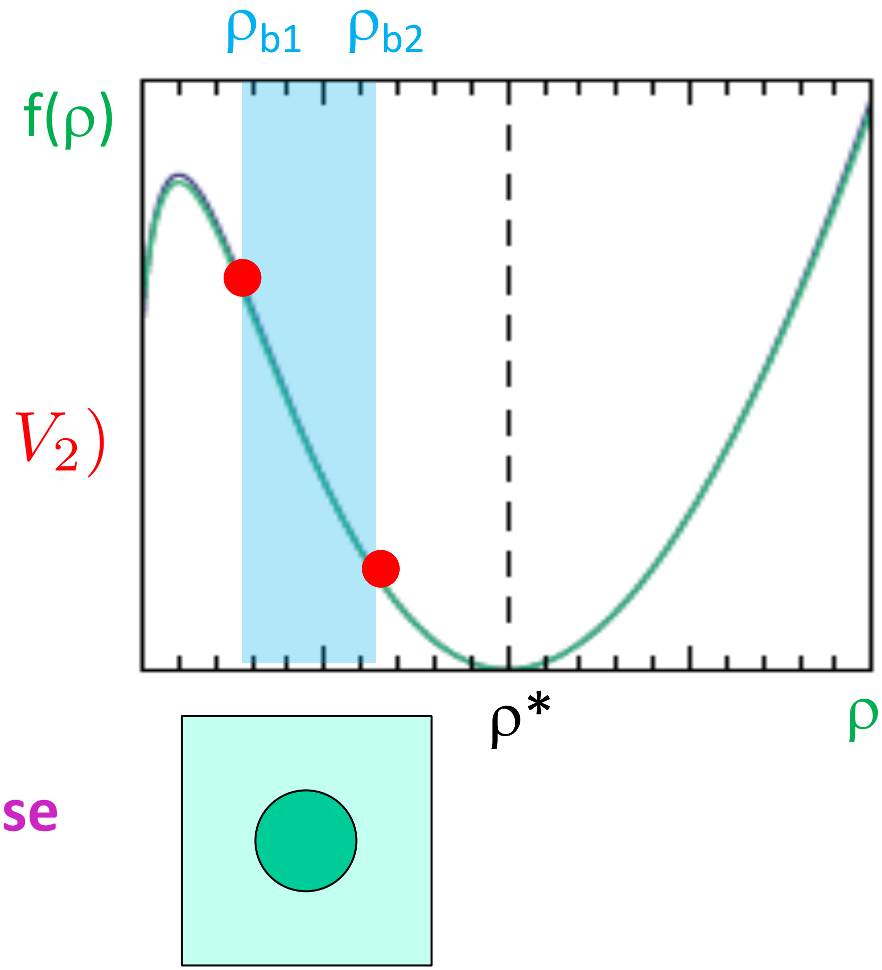
still holds outside PS region

$D \propto 1/V$, V = system volume

within PS region:

$$V\dot{\rho}(\rho) = V_1\dot{\rho}(\rho_{b1}, V_1) + V_2\dot{\rho}(\rho_{b2}, V_2)$$

where $V_1\rho_{b1} + V_2\rho_{b2} = V\rho$



domains contribute independently
to population dynamics **including noise**

J Schuettler, R Jack + MEC in progress

Effects of Phase Separation: Extinction

suppose PS region lies in (0, ρ^*) **and even nucleation is fast**

slow manifold now fully one-dimensional: $\rho(t)$

global equation of motion becomes

$$\dot{\rho}(\rho, V) = -\mathcal{M}_C(\rho)\mathcal{F}'(\rho) + \sqrt{2D\mathcal{M}_C(\rho)}\ \Lambda$$

$\mathcal{F}(\rho)$ knows about $f(\rho)$, $\mathcal{M}(\rho)$ at and outside binodals only

$\mathcal{F}(\rho)$ = exact quasipotential

$\mathcal{M}_C(\rho)$ = composite mobility across PS region

$\mathcal{F}(\rho) \neq$ state function

Extinction rate $\propto$ exp[-[Max($\mathcal{F}$)-$\mathcal{F}(\rho^*)$]/D]

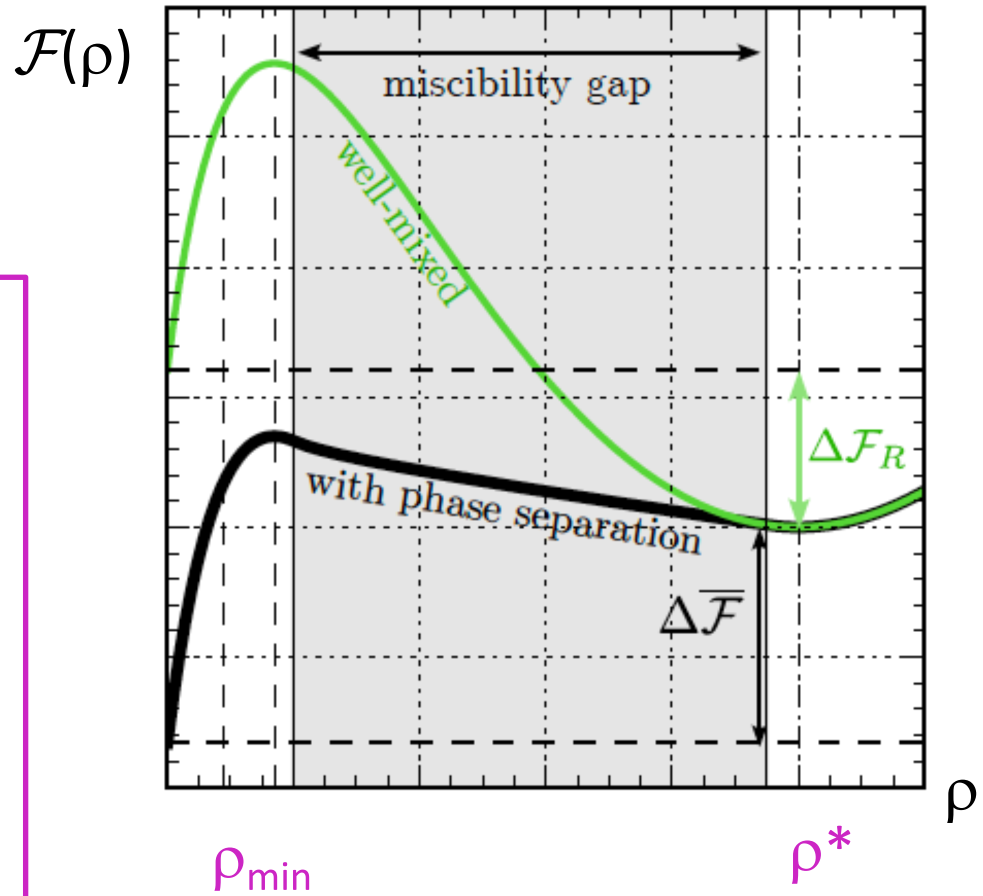
J Schuettler, R Jack + MEC in progress

Effects of Phase Separation: Extinction

Example: $A \to 0; 2A \leftrightarrow 3A$

with Model B phase separation

- Phase separation can help **or** hinder extinction
- Strong effects even when **neither** starting state **nor** near-extinct states show PS
- can alter 'Allee class'
  Meerson+ Sasorov, PRE (2011)



Extinction rate $\propto \exp[-[\mathrm{Max}(\mathcal{F})-\mathcal{F}(\rho^*)]/D]$

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Large Deviations of Active Matter Fields

Instantons: temporally isolated rare events at low noise

Passive fields: CNT for phase separation: free energy $\mathcal{F}(R)$

Active fields: Kinetic CNT still applicable $\Rightarrow$ quasipotential $\mathcal{F}(R)$

Add birth and death:

Limit cycles: slow manifold (R,ρ) $\Rightarrow$ difficult (2D)

Extinction with very fast PS: $R = R(\rho)$ $\Rightarrow$ again simple (1D)

C Nardini + MEC arXiv:2210.05263

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