

TD5 : Nonequilibrium phase separation

Statistical Mechanics – iCFP M2

Particles driven out of equilibrium can display rather counter-intuitive behaviors. Here we study one such example, where particles cluster (phase separate) despite having purely repulsive interactions. This phenomenon was first observed in two-dimensional numerical simulations of self-propelled hard spheres [1], then observed experimentally in colloidal swimmers with a light-activated self-propulsion [2] (Fig. 1).

Here we study a simpler, analytically tractable model of two populations of particles subjected to two different temperatures (you may think of the self-propelled particles as the “hot” ones while the solvent is represented by the “cold” ones) [3]. We consider the evolution of a collection of particle positions $\{x_i\}_{i=1..N}$ governed by the Langevin equation:

$$\partial_t x_i = -\mu_i \partial_i U + (2\mu_i T_i)^{1/2} \xi_i(t), \quad (1)$$

where μ_i and T_i are the mobility and temperature of particle i , ∂_i is the derivative with respect to coordinate x_i , $U = \sum_{i<j} u(|x_j - x_i|)$ is a repulsive pair interaction energy and $\xi_i(t)$ is a Gaussian noise with $\langle \xi_i(t) \rangle = 0$ and $\langle \xi_i(t) \xi_j(t') \rangle = \delta_{ij} \delta(t' - t)$.

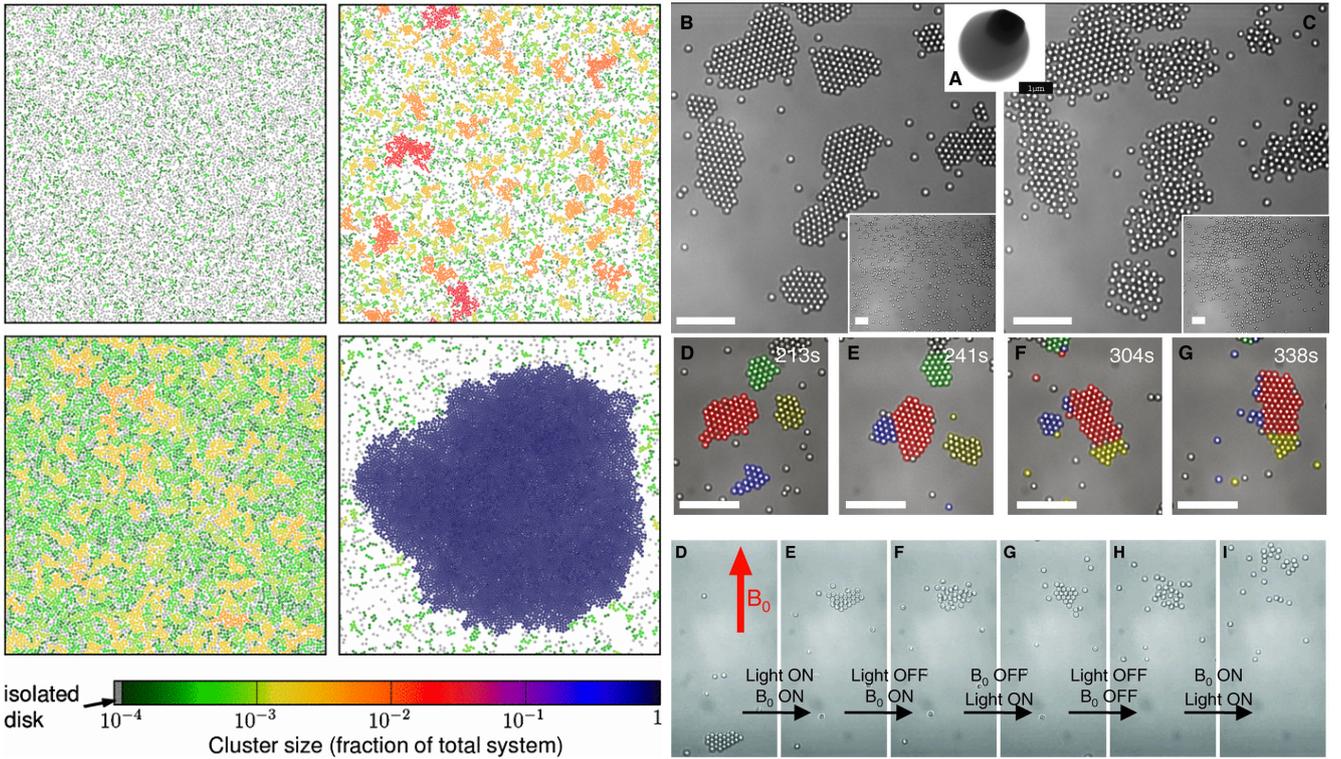


Figure 1: Examples of active (nonequilibrium) phase separation in collections of self-propelled particles [1, 2]. (left) Clustering of numerically simulated swimmers with equations of motion $\partial_t \mathbf{r} = v_0 \hat{v}_i + \mu \sum_{j \neq i} \mathbf{F}_{ij} + \xi_i^{\text{transl}}(t)$; $\partial_t \theta_i = \xi_i^{\text{rot}}(t)$, where \mathbf{r}_i is the position of the particle, \hat{v}_i is a unitary vector making an angle θ_i with the x -axis, \mathbf{F}_{ij} is a repulsive force between particles i and j and the ξ s are usual Gaussian white noises. (top right) Experimental realization in a collection of self-propelled colloidal swimmers moving on a surface (picture of an individual colloid in panel A). (bottom right) The aggregates quickly dissolve when the light-activated self-propulsion is turned off (which sets $v_0 = 0$). When turned on, the magnetic field B_0 dictates the direction of particle swimming (*i.e.*, the angle θ_i).

1 Interactions between two particles

The interaction between $N = 2$ particles subjected to two different temperatures already display surprising behaviors.

- 1.1 Following the discussion of Einstein's equation given in the main lecture, show that an equilibrium state (*i.e.*, a state without probability current) can only exist if $T_1 = T_2$.
- 1.2 Now considering $T_1 \neq T_2$, write an effective Langevin equation for the relative position $r = x_2 - x_1$. What is the associated effective mobility? Compute the variance of the noise acting on r and show that it corresponds to an effective temperature $T_{12} = (\mu_1 T_1 + \mu_2 T_2)/(\mu_1 + \mu_2)$.
- 1.3 Write the corresponding Fokker-Planck equation for r , and show that at steady-state r is distributed according to the pseudo-Boltzmann distribution

$$P(r) = e^{-u(r)/T_{12}}/z, \quad (2)$$

with z a normalization factor.

- 1.4 Going back to the position variables (x_1, x_2) , write the Fokker-Planck equation associated to the joint probability distribution $P(x_1, x_2; t)$ as

$$\partial_t P(x_1, x_2; t) = - \sum_{i=1}^2 \partial_i J_i, \quad (3)$$

what are the expressions of the J_i s? How do you interpret them physically? Use Eq. (2) to prove that J_1 and J_2 do not vanish at steady state.

- 1.5 What does that mean for the particles in concrete terms? Qualitatively trace the flow lines for the probability current in the (x_1, x_2) plane. Discuss how work can be extracted out this system, implying that it is definitely not at equilibrium (unless you believe in perpetual motion engines).
- 1.6 As the particles move, energy is transferred everywhere from the hot heat bath to the cold heat bath. Assuming $T_1 > T_2$, the power transferred is given by the work performed by 1 onto 2, namely $w = \langle -v_2 \partial_2 u \rangle$, where the velocity of particle 2 is given by $v_2 = J_2/P(r)$. Show that

$$w = \frac{\mu_1 \mu_2 (T_1 - T_2)}{\mu_1 T_1 + \mu_2 T_2} \int [\partial_r u(r)]^2 z^{-1} e^{-u(r)/T_{12}} dr. \quad (4)$$

2 Nonequilibrium evolution equations for a many-particle system

While we cannot solve the Fokker-Planck equation for an arbitrarily large number of particles, here we derive an approximate equation for the one-particle probability density (*i.e.*, the local concentration of particles) valid in the low density limit.

We consider a collection of N_A particles of type A (with mobility μ_A , temperature T_A) and N_B particles of type B . All particle pairs still interact through the pair potential $u(r)$. As in the previous section we perform our derivations in one spatial dimension to simplify our notation; nevertheless you can easily check that all our steps as well as our final results are also valid in higher dimension.

- 2.1 Following the model of Eq. (3), write the Fokker-Planck equation for the probability density of all particles $P(\mathbf{x}; t) = P(x_1^A, x_2^A, \dots, x_{N_A}^A; x_1^B, x_2^B, \dots, x_{N_B}^B; t)$.

- 2.2 Defining the one-particle and two-particle marginal distributions by

$$p_1^A(x; t) = \int \delta(x_i^A - x) P(\mathbf{x}; t) d\mathbf{x} \quad (5a)$$

$$p_2^{AA}(x, x'; t) = \int \delta(x_i^A - x) \delta(x_j^A - x') P(\mathbf{x}; t) d\mathbf{x} \quad (5b)$$

and using similar definitions for $p_1^B(x; t)$, $p_2^{AB}(x, x'; t)$ and $p_2^{BB}(x, x'; t)$, multiply the Fokker-Planck equation by, *e.g.*, $\delta(x_1^A - x)$ and integrate over all coordinates to find

$$\begin{aligned} \partial_t p_1^A(x; t) = & \mu_A(N_A - 1) \partial_x \left[\int \partial_x u(x - x') p_2^{AA}(x, x'; t) dx' \right] \\ & + \mu_A N_B \partial_x \left[\int \partial_x u(x - x') p_2^{AB}(x, x'; t) dx' \right] + \mu_A T_A \partial_x^2 p_1^A(x; t). \end{aligned} \quad (6)$$

A similar equation obviously holds for $p_1^B(x; t)$.

2.3 Equation (6) expresses p_1^A as a function of p_2^{AX} . It is similarly possible to derive an equation giving p_2^{AX} as a function $p_3^{AXX'}$, *etc.*. Such hierarchies of equations are very common in statistical mechanics¹, and solving them exactly is clearly as difficult as solving for the whole probability distribution $P(\mathbf{x}; t)$. This is not however the standard approach to these problems; instead, one typically looks for an approximation scheme which allows to *truncate* the hierarchy. This is indeed the way to go here, and writing the equations for $p_2^{XX'}$ reveals that the $p_3^{XX'X''}$ terms can be neglected at low particle densities. This results in a closed set of equations for $p_2^{XX'}$, which can be used to show

$$p_2^{XX'}(x, x'; t) = p_1^X(x, t) p_1^{X'}(x', t) \exp[-u(x - x')/T_{XX'}]. \quad (7)$$

Give a simple interpretation of this equation.

2.4 Inserting Eq. (7) into Eq. (6), show that in the thermodynamic limit the particle concentrations $c^A(x; t) = N_A p_1^A(x; t)$ satisfy a closed system of equations

$$\partial_t c^A(x; t) = \mu_A \partial_x (c^A \partial_x \zeta_A), \quad (8)$$

where the nonequilibrium analog ζ_A of the chemical potential for species A is given by

$$\zeta_A = T_A \ln c^A + T_A \int \left\{ \left[1 - e^{-u(x-x')/T_A} \right] c^A(x') \right\} dx' + T_{AB} \int \left\{ \left[1 - e^{-u(x-x')/T_{AB}} \right] c^B(x') \right\} dx'. \quad (9)$$

Similar equations hold for particles of type B .

3 Virial expansion, phase transition and phase coexistence

3.1 For short-range interactions acting on smooth enough concentration fields, we assume that u varies on much shorter length scales than c^A . Show that in that case

$$\zeta_A = T_A \ln c^A + T_A B_{AA} c^A + T_{AB} B_{AB} c^B \quad (10)$$

and that a similar expression holds for ζ_B . Give the expression of the virial coefficients $B_{XX'}$ and compare your results with the equilibrium virial coefficients encountered in the appendix of our earlier exercise on nematic liquid crystals (don't worry about the numerical prefactor).

3.2 How are the chemical potentials of two species with concentration c^A and c^B related to the free energy density f in an equilibrium system? Show that a miracle happens in this specific model in that you can find a nonequilibrium f from which your ζ s *both* derive. Ponder the fact that there was no *a priori* reason for this to happen.

3.3 Spinodal decomposition in our system can be assessed by considering a homogeneous state $c^A(x) = c_0^A$, $c^B(x) = c_0^B$ and introducing small perturbations $c^A(x; t) = c_0^A + \delta c^A(x; t)$, $c^B(x; t) = c_0^B + \delta c^B(x; t)$. Expand Eq. (8) and its B -counterpart to linear order in δ , then translate them into coupled evolution equations for the spatial Fourier modes $\delta \tilde{c}^A(q; t)$, $\delta \tilde{c}^B(q; t)$ of the perturbations. The system is linearly stable when any initial perturbation decays to zero for long times. Show that this is equivalent to

$$\frac{\phi_A}{1 + \phi_A} \frac{\phi_B}{1 + \phi_B} < \frac{T_A T_B}{T_{AB}^2} \frac{B_{AA} B_{BB}}{B_{AB}^2}, \quad (11)$$

where $\phi_A = B_{AA} c_0^A$ and similarly for ϕ_B .

¹For those interested in researching the subject further, the best known of these is the so-called BBGKY hierarchy.

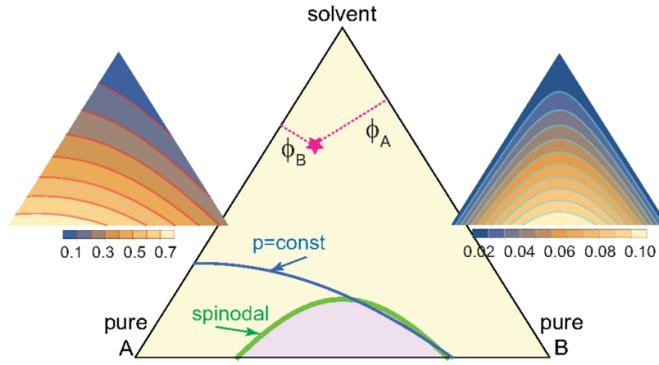


Figure 2: Triangular phase diagram, for a three-component system of $A + B + \text{solvent}$ (from Ref. [3]. See original paper from specific parameter values). For every point in the triangle (exemplified by a star), the volume fractions of A and B particles are given by the distances to the triangle sides, while the volume fraction of the solvent $1 - \phi_A - \phi_B$ is the distance to the bottom of the triangle. The symmetric line is the spinodal Eq. (11). Below this line, the uniformly mixed state is unstable. The asymmetric curve represents a line of constant osmotic pressure p . This line crosses the instability region thus indicating the possibility of two coexisting phases. *Left inset*: Lines of constant pressure. *Right inset*: Level lines of the left-hand side of formula Eq. (11).

- 3.4 An unstable system phase separates in a way similar to that observed in the equilibrium systems encountered earlier in this course. In characterizing phase equilibrium in a binary system (*i.e.*, with two independent volume fractions ϕ_A and ϕ_B), list the unknowns to be solved for as well as the equations to be solved. You may assume that the two phases equilibrate their pressures $p = c^A \zeta_A + c^B \zeta_B - f$, which can be shown to act as a mechanical pressure on a wall.
- 3.5 Can you generalize the bitangent construction to this three-component (A , B and solvent) system? An example of the resulting phase diagram is shown in Fig. 2.
- 3.6 The expression of the dissipation Eq. (4) generalizes to a dissipation per unit volume

$$w = c^A c^B \frac{\mu_A \mu_B (T_A - T_B)}{\mu_A T_A + \mu_B T_B} \int [\partial_r u(r)]^2 z^{-1} e^{-u(r)/T_{12}} dr. \quad (12)$$

Where does the dissipation happen in a strongly phase separated system?

References

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