Supercritical Active Fluids

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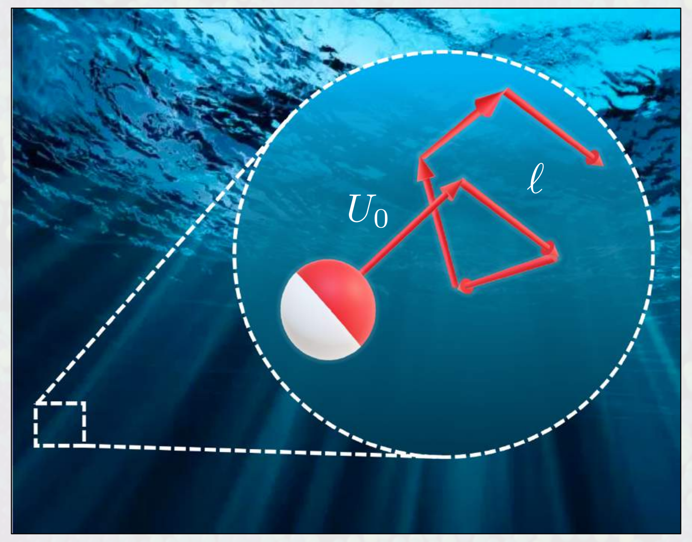
Active Matter

Active matter refers to any material whose constituents can self-propel through the conversion of energy into mechanical motion. These materials are far from equilibrium and exhibit unique collective motion such as flocking, swarming, etc. that makes their dynamics truly unique. Active agents, or "swimmers", swim with a speed U_0, in direction $\mathbf{q}$, and reorient on a timescale τ_R.



Motility Induced Phase Separation

The distance an active particle travels in one reorientation time called the run length $l = U_0\tau_R$. This gives rise to a dimensionless parameter that defines the ratio of the particle radius to the run length $Pe_R = a/l$. If Pe_R is sufficiently large, then particles can phase separate into dense clusters and a dilute gas phase, a phenomena known as motility induced phase separation (MIPS) [1]. MIPS is reminiscent of vapor-liquid coexistence, even though these systems are far from equilibrium and no attractive interactions are present.

Criteria for mechanical instability:

$$\left(\frac{\partial \Pi}{\partial \phi}\right) = 0, \quad \left(\frac{\partial^2 \Pi}{\partial \phi^2}\right) = 0$$

- Phase behavior can be probed using response functions.
- True thermodynamic response functions don't exist outside of equilibrium (e.g. heat capacity)
- Mechanical response functions exist even for nonequilibrium systems.

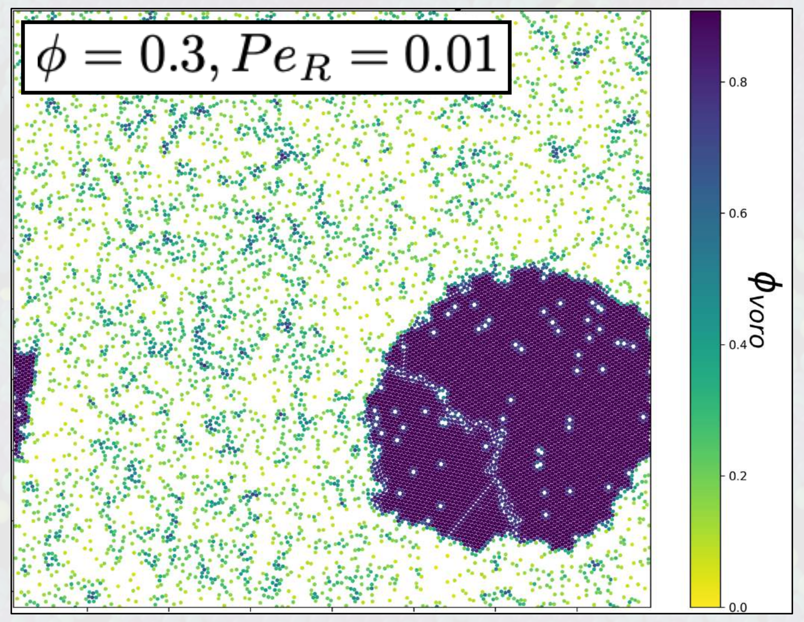


Figure 1: A simulation snapshot of a suspension of athermal active hard disks with volume fraction $\phi = 0.1$ and $Pe_R = 0.01$. Each particle is colored based on their Voronoi volume from dilute (yellow) to dense (purple).

"Thermo"-mechanical Compressibility

- Compressibility can be computed mechanically, through pressure or structurally using the static structure factor.
- Both methods are identical in thermodynamic systems but need not be for systems out of equilibrium.

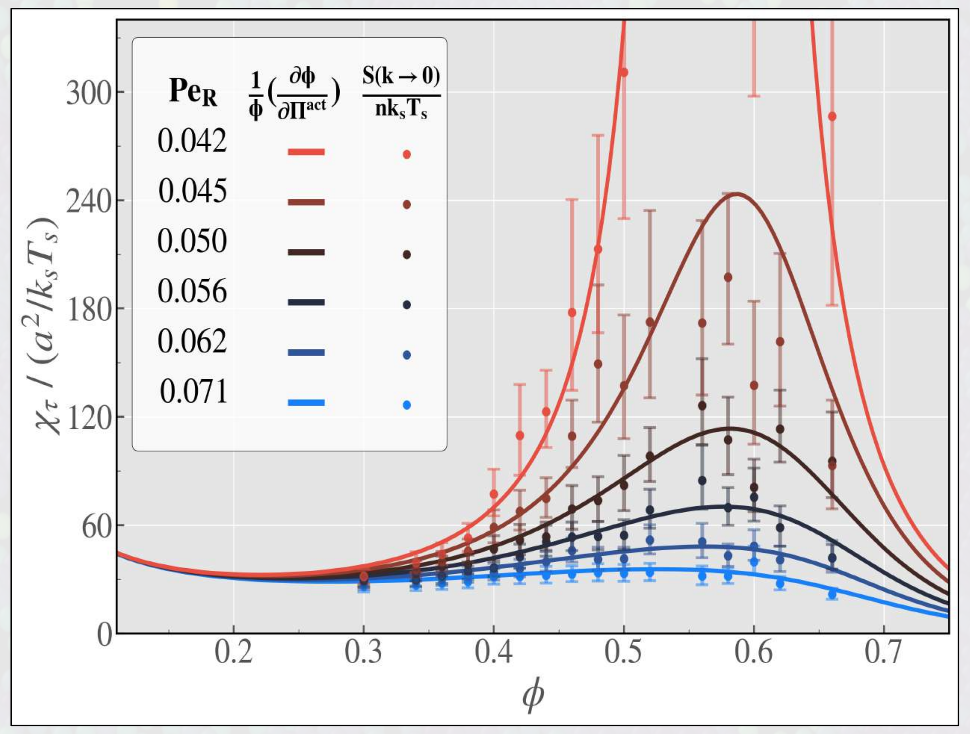


Figure 2: Compressibility computed from active pressure (solid lines) and static structure factor (symbols) [2].

Using an active analogue to the compressibility equation

$$S(\mathbf{k} \to 0) = nk_sT_s\chi_\tau$$

we see that the activity $k_sT_s = U_0^2\tau_R/2$ is the relevant energy scale and the two methods of computing compressibility remain identical, even though the system is far from equilibrium.

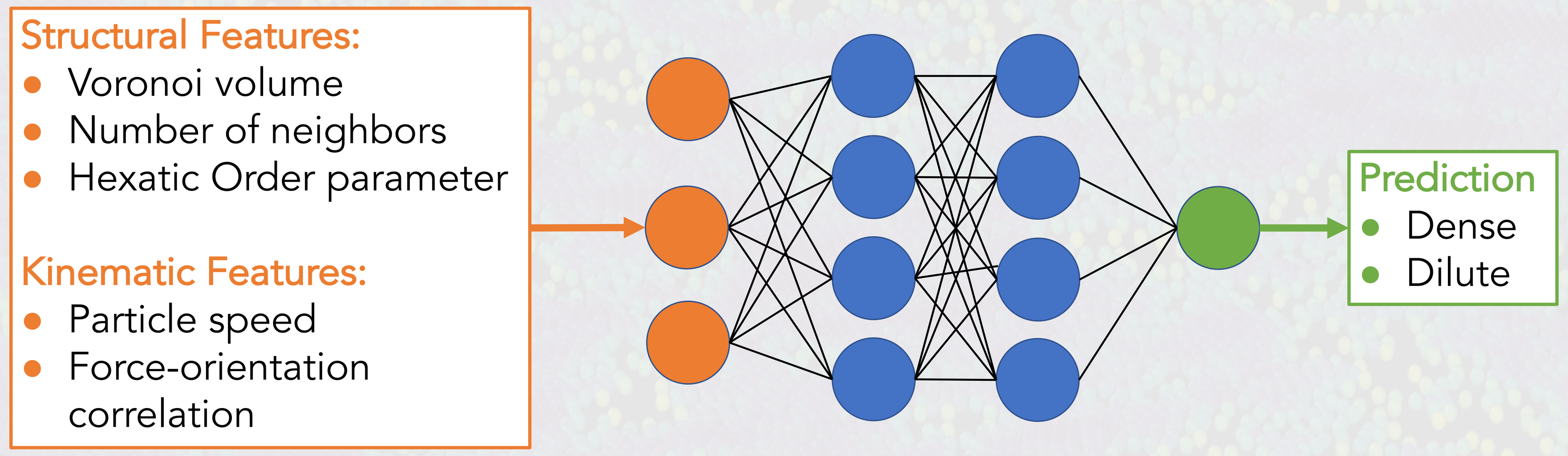
Learning Phase Behavior

Active systems are far from equilibrium, meaning we can't blindly use traditional thermodynamic frameworks. We have used alternative methods to characterizing phase behavior.

Mechanics: Critical points and compressibility can be computed from mechanics alone.

"Thermo"-mechanical relations: Our active compressibility equation gives another measure of the critical point and information on the supercritical region.

Machine Learning: The unique dynamics in active systems are the distinct origin of their phase behavior. Machine learning allows us to lean on those complex, nonlinear correlations to learn some aspect of phase behavior.



Active phase behavior can be predicted at a single particle level using a combination of structural and kinematic features, as shown in Fig. 3!

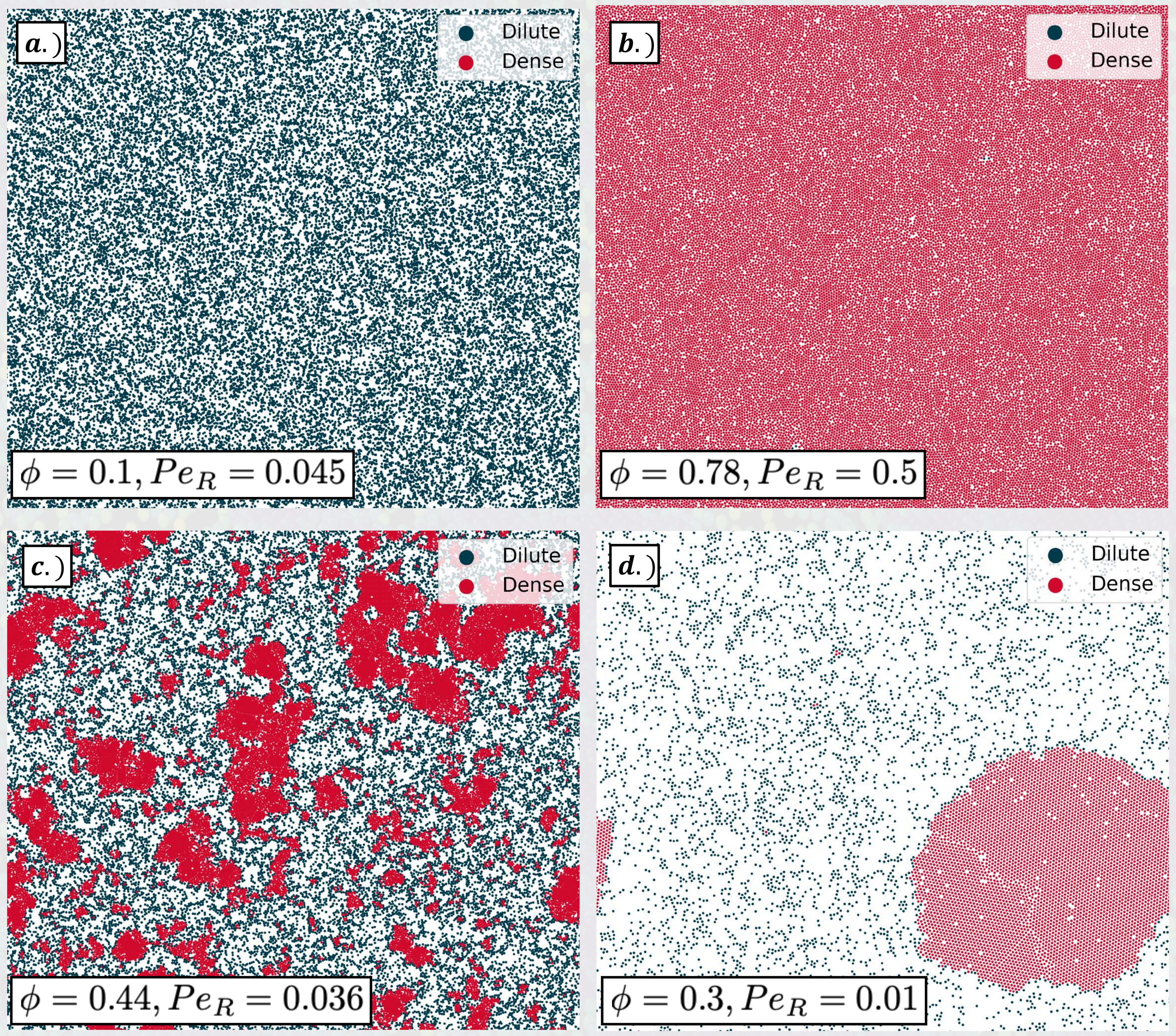


Figure 3: Per particle phase prediction at different points in the phase diagram: ***a.***) dilute single phase $\phi = 0.1, Pe_R = 0.045$, ***b.***) dense single phase $\phi = 0.78, Pe_R = 0.5$, ***c.***) weakly phase separated $\phi = 0.44, Pe_R = 0.036$, ***d.***) strongly phase separated $\phi = 0.3, Pe_R = 0.01$. Dense particles colored in blue and dilute particles are colored in red.

Extending Coexistence

The vapor-liquid coexistence line of molecular fluids can be extended into the supercritical region through the Widom line [3]. The Widom line is comprised of the points where thermodynamic response functions are maximized.

Supercritical fluid properties can smoothly and continuously transition from having more gas-like or liquid-like characteristics. The Widom line marks the points where there is an equal balance of each and is a reference point for tuning these parameters.

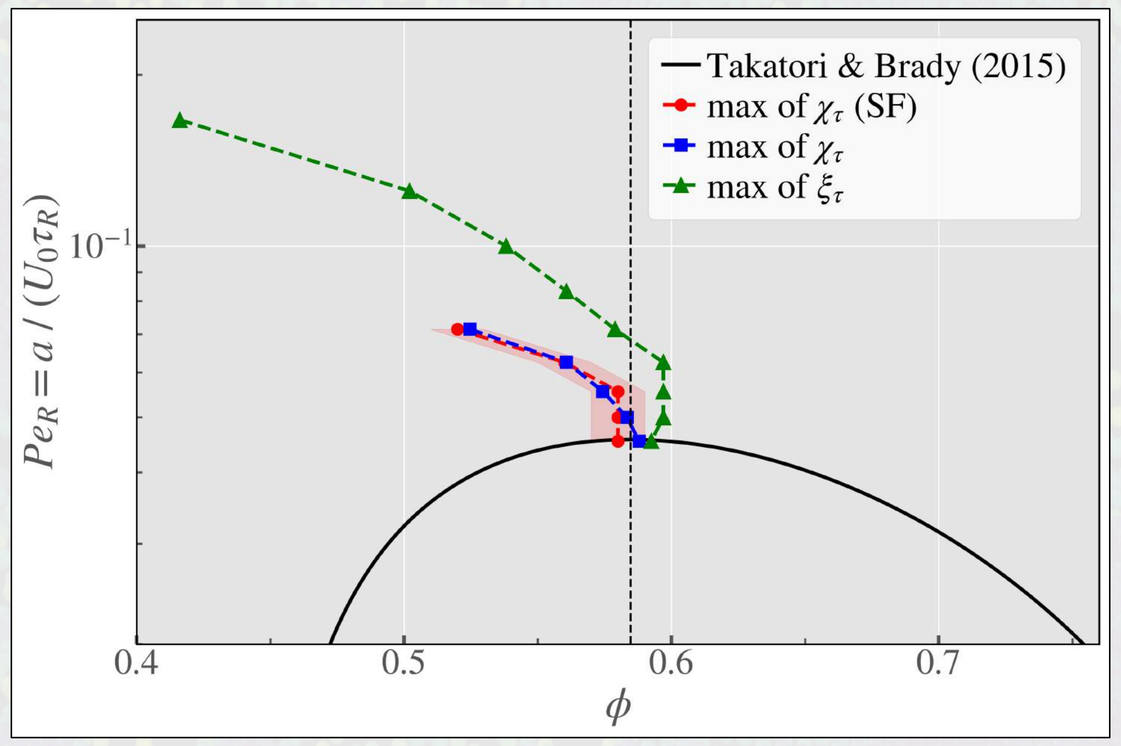


Figure 4: Several Widom lines for an athermal active fluid are presented along with the spinodal computed mechanically from Takatori & Brady [1]. The Widom lines are computed from the maximum density fluctuations (green), maximum mechanical compressibility (blue), and maximum compressibility as computed from the static structure factor (red) [2].

Conclusions

- Active systems exhibit phase behavior similar to vapor-liquid coexistence in the absence of attractive interactions.
- Traditional thermodynamic response functions behave similarly in active systems, as long as the appropriate energy scaling and contributions to pressure are considered.
- Through our ML work we have shown that microscopic detail about the particle dynamics is necessary to determine particle phase.
- Active systems have a supercritical region and the coexistence line can be extended into this region using response functions, just as would be the case for thermodynamic systems.

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[3] M.Y. Ha, *et al. J. Phys. Chem* **9**, 1734 (2018).