Soft Matter

PAPER

View Article Online
View Journal | View Issue

Cite this: *Soft Matter*, 2015, **11**, 7920

A theory for the phase behavior of mixtures of active particles†

Sho C. Takatori and John F. Brady*

Received 21st July 2015,
Accepted 21st August 2015

DOI: 10.1039/c5sm01792k

www.rsc.org/softmatter

Systems at equilibrium like molecular or colloidal suspensions have a well-defined thermal energy k_BT that quantifies the particles' kinetic energy and gauges how "hot" or "cold" the system is. For systems far from equilibrium, such as active matter, it is unclear whether the concept of a "temperature" exists and whether self-propelled entities are capable of thermally equilibrating like passive Brownian suspensions. Here we develop a simple mechanical theory to study the phase behavior and "temperature" of a mixture of self-propelled particles. A mixture of active swimmers and passive Brownian particles is an ideal system for discovery of the temperature of active matter and the quantities that get shared upon particle collisions. We derive an explicit equation of state for the active/passive mixture to compute a phase diagram and to generalize thermodynamic concepts like the chemical potential and free energy for a mixture of nonequilibrium species. We find that different stability criteria predict in general different phase boundaries, facilitating considerations in simulations and experiments about which ensemble of variables are held fixed and varied.

1 Introduction

Active matter systems like colonies of bacteria and self-propelled synthetic microswimmers are a rich area of study for soft matter. The fundamental and seemingly elementary ability of self-propulsion allows active systems to free themselves from classical thermodynamic constraints and to control their own motion and the surrounding environment. Their inherently nonequilibrium properties engender intriguing behavior such as spontaneous self-assembly and pattern formation,[1,2] making active matter a fascinating but challenging system to study.

Recently a new "swim pressure" concept was introduced—namely, all active entities exert a unique mechanical pressure owing to their self-motion.[3,4] This perspective was applied[5] to predict the self-assembly of a suspension of active particles into regions of dense and dilute phases observed in both experiments and simulations.[6–10] The usefulness of the mechanical pressure to illuminate active matter's physical principles begs the question: what is the temperature of active matter? Do active swimmers "thermally equilibrate" with their surroundings? Although it is clear that the mechanical pressure can be quantified and is valid out of equilibrium, it is uncertain whether the notion of a temperature exists and can be explained in basic physical quantities.

To understand the temperature of active matter, we shall first discuss a simple experiment involving passive Brownian suspensions (*i.e.*, no self-propulsion) which can be rigorously related to conventional thermodynamic quantities like the temperature and free energy. Suppose we have a purely Brownian suspension with thermal energy $(k_BT)_H$ that is separated by a thermally-insulated partition from another Brownian system with a different temperature $(k_BT)_C$, as shown in Fig. 1. The partition is suddenly removed and the particles at different temperatures are allowed to mix. The "hot" and "cold" particles undergo many collisions, share their kinetic energy with

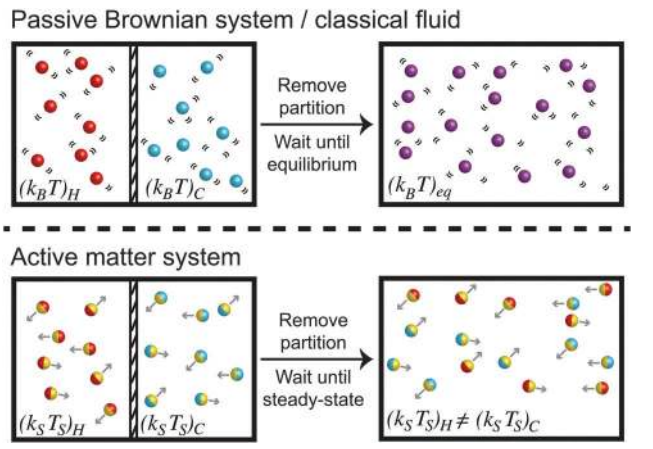

Fig. 1 Schematic of the mixing process of purely Brownian suspensions (top) and active systems (bottom) that are initially at two different "temperatures." The Brownian particles thermally equilibrate their thermal energy k_BT whereas the active swimmers do not share their characteristic "energy scale" $k_sT_s \equiv \zeta U_0^2\tau_R/2$.

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125 USA. E-mail: Takatori@caltech.edu

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5sm01792k

each other, and eventually equilibrate to a common temperature $(k_BT)_{eq}$.

Now suppose we do the same mixing experiment with self-propelled swimmers at two different activity levels. For simplicity we consider self-propelled spheres of radii a that translate with an intrinsic swim speed U_0, reorient with a reorientation time τ_R, and experience a hydrodynamic drag factor ζ from the surrounding continuous Newtonian fluid. Their motion can be described as a random-walk process for times $t > \tau_R$ with a diffusivity $D^{swim} = U_0^2\tau_R/2$ in two dimensions (2D). Their characteristic "energy scale" is not the thermal energy $k_BT = \zeta D_0$ where D_0 is the Stokes–Einstein–Sutherland translational diffusivity, but comes from their self-propulsive activity, defined as $k_sT_s \equiv \zeta D^{swim} = \zeta U_0^2\tau_R/2$ (see later section for a more detailed treatment).

A system of "hot" active swimmers with $(k_sT_s)_H$ is initially separated from "cold" swimmers with $(k_sT_s)_C$ as shown in Fig. 1. When the partition is removed, the swimmers with different activity levels spontaneously mix and undergo collisions with each other. When a swimmer collides into another swimmer, it displaces the body by its size a until they move completely clear of each others' trajectories. After the collision, each swimmer then continues its motion with the same activity it had initially—there is no sharing of kinetic activity (k_sT_s) upon collisions. This implies that the swimmers' activity scale $k_sT_s \equiv \zeta U_0^2\tau_R/2$ does not get shared *via* collisions and thus does not "equilibrate" like the temperature of a classical fluid k_BT. This simple experiment already reveals the richness and challenge to understand the "temperature" of nonequilibrium active systems.

A simple multicomponent mixture of self-propelled particles with two different activities is an ideal system to discover and study this problem in greater detail. Previous studies have provided various interpretations of the temperature in a non-equilibrium active matter system.[11–13] We discuss a new perspective by developing a mechanical pressure theory for predicting the phase behavior of a mixture of active swimmers over the entire phase space of the system. Our theory applies in general to a multicomponent suspension with swimmers of different activities, but perhaps the most straightforward mixture is that of active self-propelled particles and passive Brownian particles in a single solvent. In this mixture we must treat active swimmers and passive particles as independent species, because their compositions vary in space due to the phase-separating behavior of active suspensions. This is true in general for multicomponent systems—in a simple polymeric solution of polyethylene in benzene, the polyethylene molecules do not all have the same number of segments or molecular weight, and thus generally need to be treated as different components. Experiments also often use mixed solvents in which the solvent composition inside a polymer coil (or gel) is in general different from the outer regions, as certain solvent species preferentially remain inside (or outside) the polymer coil.[14]

We consider a simple mixture of spherical active and passive Brownian particles with equal size a; the passive particles translate by Brownian motion but are otherwise inactive (see Appendix A for the equations of motion). We do not include the effects of hydrodynamic interactions, and there is no polar order of the swimmers or any large-scale collective motion (*e.g.*, bioconvection). We find that many new insights about the temperature of active matter can be obtained from this simple system.

In the next section we further extend the mixing example discussed above (Fig. 1) by analyzing the effects of adding a small concentration of passive Brownian particles into an active system. We analyze the quantities that "equilibrate" in an active system by studying the collisions between a swimmer and a passive particle. In Section 3 we develop a simple mechanical theory by identifying the different contributions that make up the total active pressure of the mixture. Since active matter is an inherently nonequilibrium system, we do not rely upon the thermodynamic free energy or chemical potential to predict the phase behavior of the system. Unlike these thermodynamic quantities, the mechanical stress (or pressure) is defined out of equilibrium and can be used to analyze mechanical instability of active matter. We then take our equation of state to compute what would be the nonequilibrium analogs of the free energy and chemical potential. Lastly, we analyze different stability criteria, facilitating discussion about the variables that may be held fixed and varied in experiments and computer simulations.

2 Do active particles "thermally" equilibrate?

From the mixing process in Fig. 1 we learned that the characteristic activity scale of the swimmers do not equilibrate (*i.e.*, $(k_sT_s)_H \neq (k_sT_s)_C$) unlike the thermal energy k_BT of passive Brownian particles. To gain further insight into the quantities that get shared in an active system, suppose now that we have a dilute concentration of passive bath particles in a sea of active swimmers. The motion and behavior of passive bath particles are influenced markedly by the swimmers' reorientation Péclet number $Pe_R \equiv a/(U_0\tau_R)$, a ratio of the swimmer size a to its run length $U_0\tau_R$.

Swimmers with run lengths small compared to their size ($Pe_R \gg 1$) reorient rapidly and take small swim steps behaving as Brownian walkers. When a swimmer takes a step and collides into a bath particle, the passive particle gets a displacement of order the swimmer's step size $\sim \mathcal{O}(U_0\tau_R)$. After many such collisions, the change in the translational diffusivity of the passive bath particle is $(D^{bath} - D_0) \sim U_0(U_0\tau_R)\phi_a$, where $D_0 = k_BT/\zeta$ is the Stokes–Einstein–Sutherland diffusivity of an isolated bath particle and ϕ_a is the area (or volume in 3D) fraction of the swimmers. In this limit active swimmers repeatedly displace the bath particle by their run length $U_0\tau_R$, which allows the bath particle to sense the activity or 'temperature' of the swimmers *via* collisions. In other words, the bath particle behaves as a 'thermometer' of the active suspension,[12] where the collisional displacements it receives from the swimmer can be used to infer the swimmers' characteristic 'energy scale' $k_sT_s = \zeta U_0^2\tau_R/2$. This activity scale is analogous to the thermal energy k_BT, the kinetic activity of passive Brownian particles, which can also be probed by analyzing the collisions between

two passive particles. In this sense a suspension of swimmers with small run lengths $U_0\tau_R < a$ behaves similarly to a purely Brownian suspension with an effective 'temperature' k_sT_s. For active Brownian particles, this contribution is in addition to the thermal k_BT that gets shared as usual as a result of translational Brownian motion. However, one would not be able to distinguish between the two contributions because the dynamics of swimmers with $Pe_R \gg 1$ is equivalent to that of passive Brownian particles. If we placed active swimmers that behave identically to passive Brownian particles behind an osmotic barrier, we would not be able to distinguish one from the other. In this sense a Brownian particle can be interpreted as a "swimmer" having an extreme value of the reorientation Péclet number $Pe_R^B \to \infty$.

The swim activity k_sT_s can also be understood by comparing the statistical correlation of the self-propulsive swim force, $\boldsymbol{F}^{swim} \equiv \zeta U_0 = \zeta U_0 \boldsymbol{q}$ where $\boldsymbol{q}$ is the unit orientation vector specifying the swimmer's direction of self-propulsion, to that of the Brownian force, $\boldsymbol{F}^B$. The swim force correlation $\langle \boldsymbol{F}^{swim}(t)\boldsymbol{F}^{swim}(t')\rangle = (\zeta U_0)^2\langle \boldsymbol{q}(t)\boldsymbol{q}(t')\rangle = (\zeta U_0)^2 \exp(-(t-t')/\tau_R)$ turns into a delta-function correlation $\langle \boldsymbol{F}^{swim}(t)\boldsymbol{F}^{swim}(t')\rangle \sim (\zeta U_0)^2\tau_R\delta(t-t')$ as $\tau_R \to 0$.[15] Recall that as $\tau_R \to 0$ the active swimmers behave as random Brownian walkers, which have the white noise statistics $\overline{\boldsymbol{F}^B(t)\boldsymbol{F}^B(t')} = 2k_BT\zeta\delta(t-t')$ where the overline indicates an average over the solvent fluctuations. A comparison of these two correlations again suggests that the swimmers' kinetic activity can be interpreted by $k_sT_s \equiv \zeta {U_0}^2\tau_R/2$.

For swimmers with run lengths large compared to their size, ($Pe_R \ll 1$), we observe a different behavior. Colliding into a bath particle, the swimmer continues to push the bath particle until it moves completely clear of the swimmer's trajectory. The bath particles receive a displacement of $\sim \mathcal{O}(a)$ upon colliding with a swimmer, not the run length $U_0\tau_R$. Therefore the length scale associated with collisions is the swimmer size a, and the change in the long-time diffusivity of the bath particles $(D^{bath} - D_0) \sim U_0 a\phi_a$. Unlike the limit of $Pe_R \gg 1$ discussed above, here the bath particles cannot probe the activity or 'temperature' of the swimmers because it only receives a displacement of its size a, even though the swimmers actually diffuse with their swim diffusivity $D^{swim} \sim {U_0}^2\tau_R$. The ratio of the two diffusivities $(D^{bath} - D_0)/D^{swim} \sim U_0 a\phi_a/({U_0}^2\tau_R) = \phi_a Pe_R$, suggesting that the reorientation Péclet number $Pe_R \equiv a/(U_0\tau_R)$ is the quantity that gets shared between the swimmers *via* collisions for small Pe_R.[5] This implies that the swimmers' energy scale $k_sT_s = \zeta {U_0}^2\tau_R/2$ does not get shared in the collisions and thus does not represent the 'temperature' in the classical sense.

The bath particles' entirely different behavior for large and small Pe_R reveals the richness and challenge to understanding the 'temperature' of nonequilibrium active systems. This marked change in the quantity that gets shared in active systems is due to the capability of swimmers to have run lengths $U_0\tau_R$ that can be small or large compared to their size a. This is a key fundamental difference between the swimmers' activity k_sT_s and the thermal energy k_BT. In a classical molecular fluid, k_BT is always the quantity that equilibrates because the displacements of a passive Brownian particle are small compared to its size a (or any other length scale), *i.e.* $Pe_R^B \equiv a/(U_B\tau_B) \to \infty$ where $U_B = D_0/a$ is the characteristic speed of a Brownian step and τ_B is its momentum relaxation timescale.

Moreover, the swimmers must continuously collide with the passive particle to impart information about their kinetic activity, k_sT_s—even after many collisions, the passive particle only possesses k_BT units of thermal energy once all collisions stop. This is in stark contrast with a molecular or kinetic fluid particle that is able to completely transmit its kinetic activity to another particle upon collisions. If a molecular fluid particle with initially zero activity is placed inside a container full of fluid particles with energy k_BT, the inactive particle would collide repeatedly and eventually attain the thermal energy k_BT. Furthermore, it will keep its k_BT activity even when the other particles are removed. In contrast, a passive particle would cease to move (aside from its translational Brownian motion) if active swimmers are removed because of the damping due to the solvent. In this sense the temperature of an active nonequilibrium fluid is not well defined, as each swimmer has its own unique intrinsic kinetic activity that does not get shared and equilibrated.[5]

In pursuant of the discussion above we conducted Brownian dynamics (BD) simulations (see Appendix) and computed the long-time self diffusivity $D^{bath} = (1/2)\lim_{t\to\infty} d\langle x_d x_d\rangle/dt$, where x_d is the position of the passive bath particles. As shown in Fig. 2, for small Pe_R we indeed find that $D^{bath} = D_0 + U_0 a\phi_a/2$ fits the data for all $\phi \lesssim 0.4$. At higher ϕ the passive particles are trapped into clusters by the swimmers and D^{bath} decays to 0. Fig. 2 suggests that the parameter Pe_R gets shared upon swimmer collisions and not the scale k_sT_s.

Finally, an important concept here is that the departure induced by a swimmer is the same whether it collides into a

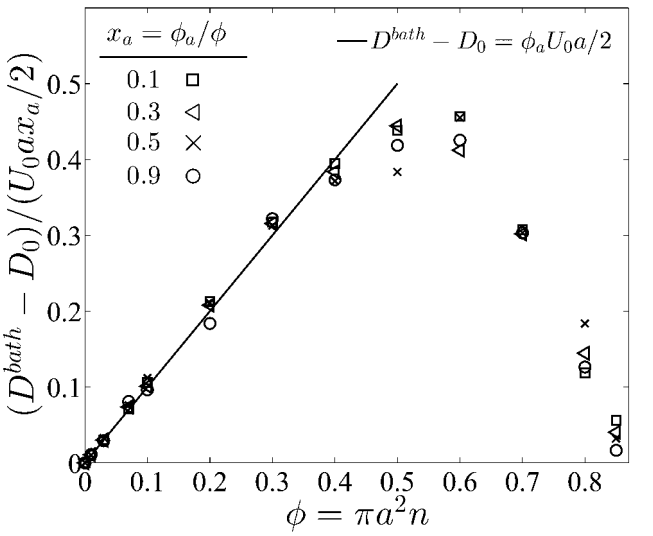

Fig. 2 Long-time self diffusivity of a passive particle as a function of the total area fraction for different values of the active swimmer fraction x_a. The known Brownian diffusivity D_0 was subtracted from the results. The solid line is the analytical theory and symbols are Brownian dynamics (BD) simulations. All data collapse onto a single curve when the diffusivity is scaled with $U_0 a x_a/2$.

passive particle or into another active swimmer. In both cases the displacement due to the collision is the swimmer size a (for small $\mathrm{Pe_R}$), and this is the key idea underlying the mechanical theory which we explain below.

3 Mechanical theory

Our theory applies in general to a mixture of active swimmers with different activity levels, but here we focus on a mixture of active swimmers and passive particles. Since a passive particle behaves equivalently to an ''active'' particle with a very small reorientation time and step size, this system corresponds to the limiting case of a mixture of one group of swimmers with a finite, nonzero $\mathrm{Pe_R}$ and another group of ''swimmers'' with $\mathrm{Pe_R} \to \infty$. The general case is a mixture of active swimmers with two different, finite $\mathrm{Pe_R^a}$ and $\mathrm{Pe_R^d}$. However, the active and passive limit is interesting from an experimental perspective because a mixture of passive and active particles is easy to make. Mixtures of swimmers with different, finite $\mathrm{Pe_R}$ are difficult to analyze because of the inherent variations in activity in living organisms and in synthetic self-propelled particles due to fabrication defects.

We are now in a position to derive a simple mechanical pressure theory to predict the phase behavior of a mixture of active and passive particles. The total active pressure of the mixture is given by

$$\Pi^{\mathrm{act}} = \Pi^{\mathrm{swim}} + \Pi_{\mathrm{a}}^{\mathrm{P}} + \Pi_{\mathrm{d}}^{\mathrm{P}} + nk_{\mathrm{B}}T, \qquad (1)$$

where Π^{swim} is the 'swim pressure', $\Pi_{\mathrm{a}}^{\mathrm{P}}$ and $\Pi_{\mathrm{d}}^{\mathrm{P}}$ are the inter-particle pressure contributions of the active swimmer and passive particle, respectively, and $nk_{\mathrm{B}}T$ is the Brownian osmotic pressure. It is permissible to add the separate contributions of the pressure in what appears to be a superposition; this is true in general for molecular, Brownian and active systems. Eqn (1) is the additional pressure contribution due to the particles (both active and passive); the solvent pressure p_{f} is arbitrary and constant in our analyses.

In general Π^{act} is a function of (ϕ, x_{a}, $\mathrm{Pe_R}$, $k_{\mathrm{s}}T_{\mathrm{s}}$, $k_{\mathrm{B}}T$), where ϕ is the total area fraction ($\phi = \phi_{\mathrm{a}} + \phi_{\mathrm{d}}$), ϕ_{a} and ϕ_{d} are the area fractions of the active and passive particles, respectively, $x_{\mathrm{a}} = \phi_{\mathrm{a}}/\phi$ is the active swimmer composition, the reorientation Péclet number $\mathrm{Pe_R} \equiv a/(U_0\tau_{\mathrm{R}})$ is the ratio of swimmer size a to its run length $U_0\tau_{\mathrm{R}}$, $k_{\mathrm{s}}T_{\mathrm{s}} \equiv \zeta U_0{}^2\tau_{\mathrm{R}}/2$ is the swimmers' characteristic 'energy scale' as discussed earlier, and $k_{\mathrm{B}}T$ is the thermal energy. We can also express the active pressure using the area fractions of the active and passive particles, $\Pi^{\mathrm{act}}(\phi_{\mathrm{a}}, \phi_{\mathrm{d}}, \mathrm{Pe_R}, k_{\mathrm{s}}T_{\mathrm{s}}, k_{\mathrm{B}}T)$. To reduce the number of parameters, we take equal size active and passive particles $a_{\mathrm{a}} = a_{\mathrm{d}} = a$ and assume that swimmer reorientation is thermally induced so that the translational and reorientational diffusivities are related *via* the Stokes–Einstein–Sutherland expressions: $(D_0/a^2)/\tau_{\mathrm{R}} = 4/3$. Thus the ratio of the thermal energy to the swim activity is $k_{\mathrm{B}}T/(k_{\mathrm{s}}T_{\mathrm{s}}) = 8\mathrm{Pe_R}{}^2/3$. This is not a requirement; one can also vary a swim Péclet number, $\mathrm{Pe_s} \equiv U_0a/D_0$ in addition to the reorientation Péclet number $\mathrm{Pe_R} \equiv a/(U_0\tau_{\mathrm{R}})$.

We now explain the independent pressure contributions in detail below. The theory is presented for 2D, but it is straightforward to generalize to 3D.

3.1 Swim pressure of active swimmers, Π^{swim}

The swim pressure is defined as the first moment of the swim force $\Pi^{\mathrm{swim}} = -n_{\mathrm{a}}\langle \boldsymbol{x}\cdot\boldsymbol{F}^{\mathrm{swim}}\rangle/2$ (in 2D), where n_{a} is the number density of swimmers and the angle brackets denote an average.[3] It is permissible for computing the stress to interpret the self-propulsion of an active swimmer as arising from a swim force, $\boldsymbol{F}^{\mathrm{swim}} \equiv \zeta\boldsymbol{U}_0$,‡ where $\boldsymbol{U}_0 = U_0\boldsymbol{q}$; U_0 is the swimming speed and $\boldsymbol{q}$ is the unit orientation vector defining the swimmer's direction of self-propulsion. Physically, $\boldsymbol{F}^{\mathrm{swim}}$ represents the force required to prevent an active swimmer from moving, for example by optical tweezers. The origin of the swim pressure stems from the notion that confined self-propelled bodies exert a pressure on the container boundaries as they collide into the surrounding walls. The same notion applies to molecular gases that collide into the container walls to exert a pressure or to colloidal solutes that collide into a semipermeable membrane to exert an osmotic pressure. The swim pressure is the ''osmotic'' pressure of active particles.

A dilute system of purely active swimmers exerts an 'ideal-gas' swim pressure given by $\Pi^{\mathrm{swim}} = n_{\mathrm{a}}\zeta U_0{}^2\tau_{\mathrm{R}}/2 = n_{\mathrm{a}}k_{\mathrm{s}}T_{\mathrm{s}}$ in 2D.[3] The swim pressure is a single-particle self contribution in which the relevant length scale (*i.e.* moment arm) is the swimmers' run length $U_0\tau_{\mathrm{R}}$. As discussed earlier the ratio of the swimmer size a to the run length $U_0\tau_{\mathrm{R}}$ is the reorientation Péclet number $\mathrm{Pe_R} \equiv a/(U_0\tau_{\mathrm{R}})$, and this parameter impacts the phase behavior of active systems.[5] For large $\mathrm{Pe_R}$ the swimmers take small swim steps and behave as Brownian walkers, exerting the swim pressure $\Pi^{\mathrm{swim}} = n_{\mathrm{a}}\zeta U_0{}^2\tau_{\mathrm{R}}/2 = n_{\mathrm{a}}k_{\mathrm{s}}T_{\mathrm{s}}$ for all concentrations.

For small $\mathrm{Pe_R}$ the swimmers have large run lengths and undergo many collisions with passive particles and other swimmers in a time τ_{R}. The average distance traveled by a swimmer between reorientation events is reduced and the same is true for the swim pressure. Extending the results for a purely active system,[5] we take (for small $\mathrm{Pe_R}$)

$$\Pi^{\mathrm{swim}} = n_{\mathrm{a}}k_{\mathrm{s}}T_{\mathrm{s}}(1 - \phi - 0.2\phi^2), \qquad (2)$$

where n_{a} is the number density of active swimmers, $k_{\mathrm{s}}T_{\mathrm{s}} \equiv \zeta U_0{}^2\tau_{\mathrm{R}}/2$ is the characteristic 'energy scale' of a swimmer. Inside the parenthesis of eqn (2) is the total area fraction because both active and passive particles hinder the run length of an active swimmer. Recall our discussion from Section 2 that the displacement induced by a swimmer is the same whether it collides into another swimmer or a passive particle. For a dilute system $\phi \to 0$ we recover the 'ideal-gas' swim pressure $\Pi^{\mathrm{swim}} = n_{\mathrm{a}}k_{\mathrm{s}}T_{\mathrm{s}}$. As the area fraction increases, both passive and active particles collide and obstruct the motion of swimmers, decreasing the run length and therefore the swim pressure. The decrease in Π^{swim} is the principle destabilizing term that facilitates a phase transition in active systems. This is fundamentally different than a

‡ This however does not imply that the intrinsic swimming mechanism generates a long-range ($1/r$) Stokes velocity field as does an external force.[16,17]

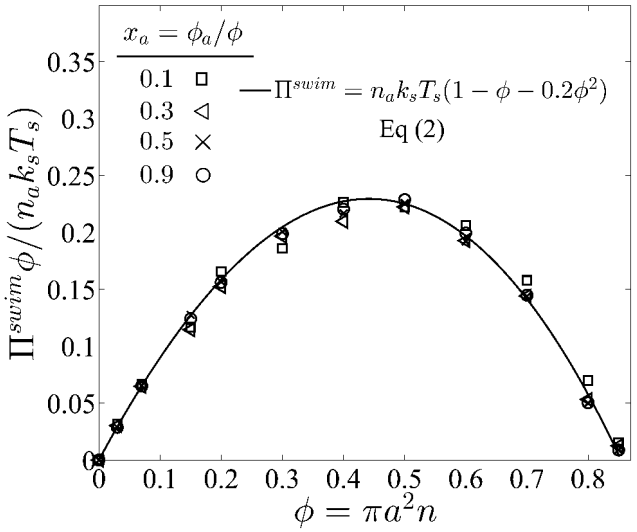

Fig. 3 Swim pressure exerted by active swimmers in a mixture as a function of the total area fraction $\phi = \phi_a + \phi_d$ for different values of active composition $x_a = \phi_a/\phi$ and fixed $Pe_R \equiv a/(U_0\tau_R) = 0.1$. Subscripts "a" and "d" refer to active and passive particles, respectively. The solid curve is the mechanical theory eqn (2) and the symbols are BD simulations. The swimmer activity $k_sT_s \equiv \zeta U_0{}^2\tau_R/2$.

purely Brownian system where repulsive interactions (*e.g.*, excluded volume) necessarily increase the pressure and have a stabilizing effect. Recall the concept that a passive Brownian particle with the thermal energy k_BT is equivalent to a "swimmer" with $Pe_R^B \to \infty$. In this work we focus on small Pe_R since this is the limit that engenders interesting phase behavior in active matter.

Fig. 3 confirms that all data from BD simulations collapse onto eqn (2). To better understand eqn (2), we can analyze the limits for large and small concentrations of active swimmers relative to passive particles. Expanding the swim pressure for small $\phi_d/\phi_a = (1 - x_a)/x_a$, we find

$$\Pi^{swim} = n_a k_s T_s\left(1 - \phi_a - 0.2{\phi_a}^2\right) - n_a k_s T_s(1 + 0.4\phi_a)\phi_d + \mathcal{O}\left(\frac{\phi_d}{\phi_a}\right)^2. \quad (3)$$

The first term on the right is the swim pressure for a purely active system, and the second term is the leading-order correction of the hindrance provided by passive particles. As expected, it is a 2-body correction of an active swimmer colliding into a passive particle, $\sim n_a\phi_d$.

In the other limit of small concentration of active swimmers relative to passive particles (*i.e.*, small $\phi_a/\phi_d = x_a/(1 - x_a)$), we find

$$\Pi^{swim} = n_a k_s T_s\left(1 - \phi_d - 0.2{\phi_d}^2\right) + \mathcal{O}\left(\frac{\phi_a}{\phi_d}\right)^2. \quad (4)$$

Unlike the large active concentration limit, the reduction in the swim pressure is caused entirely by the sea of passive particles. Due to the small concentration of swimmers, a swimmer exerts the self-term 'ideal-gas' swim pressure $n_a k_s T_s$ but does not hinder the motion of other active swimmers.

3.2 Interparticle (collisional) pressure

In addition to the swim pressure, which is a single-particle contribution to the mechanical pressure, there is also an interparticle (or collisional) pressure arising from interactions between the particles. Since two bodies are required for an interaction (or collision for a hard-sphere potential) and the relevant length scale is the particle size a, the interparticle pressure scales as $\Pi^P \sim n^2\zeta U_0 a^3 \sim nk_sT_sPe_R\phi$, fundamentally different from the swim pressure. Furthermore, the interparticle pressure monotonically increases with concentration for a repulsive potential and helps stabilize a system. The competition between the destabilizing effect of the swim pressure and the stabilizing effect of the interparticle (or collisional) pressure controls the phase behavior of active systems. For clarity we split the interparticle pressure into two contributions—collisions induced by active swimmers and passive particles separately.

3.2.1 Active swimmer, Π_a^P. Extending the nonlinear microrheology analysis,[3] the collisional pressure contribution for active swimmers (for small Pe_R) is

$$\Pi_a^P = n_a\left[\frac{4}{\pi}k_sT_sPe_R + 2k_BT\right]\phi g(\phi), \quad (5)$$

where k_BT is the thermal energy and $g(\phi)$ is the pair-distribution function at contact. The first and second terms in the bracket are the collisional pressures due to self-propulsion and Brownian fluctuation, respectively. The former scales as $\sim n_a n\zeta U_0 a^3$ whereas the latter scales as $\sim n_a n\zeta(D_0/a)a^3$; the characteristic Brownian speed D_0/a replaces the swim speed U_0 in the collisional pressure arising from thermal noise. We again use the total area fraction in eqn (5) since the active swimmers impart the same departure whether they collide with a passive or an active particle. Rigorously, the pair-distribution function is different for each pair, *i.e.*, $g_{aa}(\phi)$, $g_{ad}(\phi)$, *etc.*, but we assume that they are all the same and equal to $g(\phi)$ since we have taken $a_a = a_d$. We adopt $g(\phi) = (1 - \phi/\phi_0)^{-1}$ where ϕ_0 is the area fraction at close packing ($\phi_0 = 0.9$ in this study).[5,18]

3.2.2 Passive particle, Π_d^P. The collisional pressure contribution of a passive particle is given by

$$\Pi_d^P = n_d\left[\frac{4}{\pi}k_sT_sPe_Rx_a + 2k_BT\right]\phi g(\phi). \quad (6)$$

The first term in the brackets is the interparticle pressure due to collisions with active swimmers, which scale as $n_d n_a\zeta U_0 a^3$ because these collisions are induced only by the active swimmers. The second term is the usual Brownian collisional pressure. Unlike eqn (5) we see that the collisional pressure of passive particles has an additional dependence on the active-swimmer fraction x_a. If there are no active swimmers (*i.e.*, $x_a = 0$) then eqn (6) reduces to the usual collisional pressure of Brownian hard-spheres.[19]

Fig. 4 graphs the sum of the collisional pressures of the contributions from both active and passive particles as a function of the total area fraction. We see a dependence on the composition of active swimmers x_a especially at high area coverage. We assume that swimmer reorientation is thermally induced so that the translational and reorientational

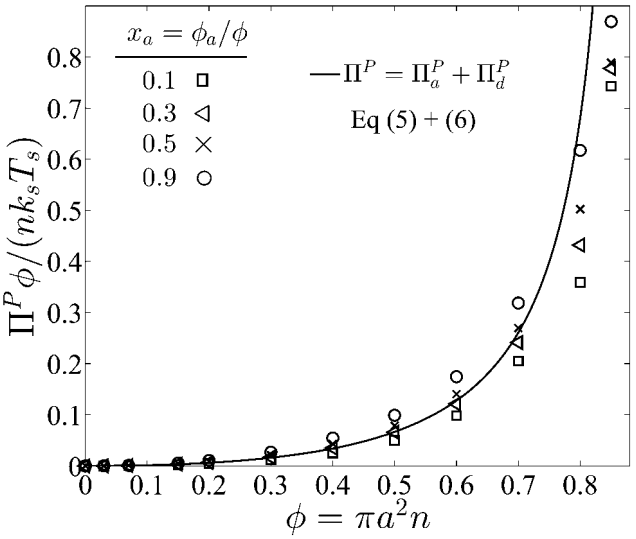

Fig. 4 Collisional pressure exerted by active and passive particles $\Pi^P = \Pi_a^P + \Pi_d^P$ for fixed $Pe_R \equiv a/(U_0\tau_R) = 0.1$ as a function of the total area fraction $\phi = \phi_a + \phi_d$ and different values of active composition $x_a = \phi_a/\phi$. The solid curve is the mechanical theory eqn (5) and (6) for $x_a = 0.3$, and the symbols are BD simulations. We take the swimmer reorientation to be thermally induced so that $k_BT/(k_sT_s) = 8Pe_R^2/3$.

diffusivities are related *via* the Stokes–Einstein–Sutherland expressions, $(D_0/a^2)/\tau_R = 4/3$, and the ratio of the thermal energy to the swim activity is $k_BT/(k_sT_s) = 8Pe_R^2/3$.

4 Phase behavior

Experiments and computer simulations have shown that a suspension of purely active particles may self-assemble into regions of dense and dilute phases, resembling an equilibrium liquid–gas coexistence.[6–10] The source of this phase separation is that swimmers collide and obstruct each others' movement, causing large clusters to form at sufficiently high concentrations.[13] Now, if this active system also contained passive Brownian particles, recent computer simulations[20] and experiments[21] have shown that the composition of passive particles inside the dense cluster phase is generally larger than that in the dilute phase, as they tend to stay inside the cluster once they are pushed into one by an active swimmer. In contrast, the active swimmers prefer to swim freely in the dilute phase because their activity allows them to escape the dense clusters.

Theory and simulations have produced phase diagrams for a suspension of purely active swimmers,[5,8,15,22–24] but a mixture of active and passive particles is yet to be thoroughly analyzed. Recently Stenhammar *et al.*[20] conducted Brownian dynamics simulations of a mixture of active and passive Brownian particles and used a kinetic model to locate the phase boundaries. The kinetic model based upon Redner *et al.*[8] accurately predicts many regions of phase space, but due to the theory's inherent assumptions the lower spinodal boundary is not well characterized.

Our theory is based upon the new 'swim pressure' perspective which accurately predicts the phase behavior of a system of active swimmers.[3–5] Others have subsequently used the swim pressure to study phase-separating active systems.[25,26] We now have eqn (1), an equation of state that allows us to predict the phase behavior of the active/passive mixture.

Interpreting the total density derivative of the active pressure as a global mechanical instability, $(\partial\Pi^{act}/\partial\phi)_{x_a,T_s,Pe_R} = 0$, we can identify the regions of stability in the phase diagram. This is a purely mechanical definition of the spinodal and does not rely upon thermodynamic arguments. As shown by the red curve in Fig. 5, our prediction agrees well with Stenhammar *et al.*'s[20] simulation data. Here the spinodal and the simulation data correspond to a global dense/dilute-phase separation based upon fluctuations in the total particle—active plus passive—density. This is different from the phase separation that may occur locally within each phase, as commonly seen in immiscible polymer mixtures. There are no adjustable parameters in the comparison.

Compared to a purely active swimmer system, onset of phase transition occurs at lower Pe_R when passive particles are present. For $x_a = \phi_a/\phi = 0.5$ shown in Fig. 5, phase transition is possible for $Pe_R \lesssim 0.025$, compared to $Pe_R \lesssim 0.04$ for a purely active system $x_a = 1$. Therefore, given a fixed total area fraction the presence of passive particles makes it more difficult for phase separation to occur, which may be an important consideration in the design of experiments of active systems.

In Section 2 we discussed that the reorientation Péclet number Pe_R is the quantity that gets shared upon collisions between swimmers for $Pe_R \ll 1$. Using the swimmer activity $k_sT_s \equiv \zeta U_0^2\tau_R/2$, we can rewrite $Pe_R \equiv a/(U_0\tau_R) = \zeta U_0 a/(2k_sT_s)$, which is interpreted as the interactive energy of the swimmer $(\zeta U_0)a$ to its swim activity scale k_sT_s. In Fig. 5 phase separation becomes possible for small Pe_R, or large k_sT_s. In contrast, phase transition in a classical thermodynamic system is usually driven by attractive enthalpic interactions and becomes possible for

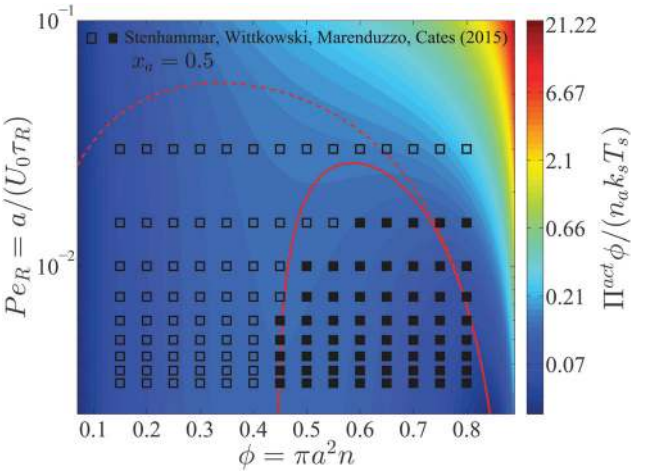

Fig. 5 Phase diagram in the $Pe_R - \phi$ plane in 2D for a fixed active swimmer composition $x_a = 0.5$. The colorbar shows the active pressure scaled with the swim activity $k_sT_s = \zeta U_0^2\tau_R/2$. The open and filled symbols are simulation data of Stenhammar *et al.*[20] with a homogeneous and phased-separated state, respectively. The solid and dashed red curves are the spinodals delineating the regions of stability based upon fluctuations in the total particle density and the thermodynamic definition, respectively.

small k_BT (low temperatures). If k_sT_s is interpreted as the "temperature" of active matter, Fig. 5 suggests that mixtures of active and passive particles may exhibit a lower critical solution temperature (LCST) transition,[27] commonly seen in thermosensitive polymer systems.[28] The LCST phase transition is dominated by entropy—as Pe_R decreases (k_sT_s increases), the run length of the swimmer increases, and the particle becomes effectively larger in size and has less space available for entropic mixing.[5] However, because Pe_R is the quantity that gets shared upon collisions for $Pe_R \ll 1$ (and not the activity k_sT_s), the activity k_sT_s does not play the same role as the thermal energy scale k_BT in LCST phase transitions of polymer mixtures. This further verifies that the "temperature" of active matter is an elusive quantity that does not have a direct mapping to the temperature of an equilibrium system.

5 Limits of active pressure

Recent experiments by Kümmel *et al.*[21] analyzed the phase behavior of a mixture of passive particles with a small concentration of active swimmers ($\phi_a \approx 0.01$). They observed swimmers gathering and compressing the passive particles into clusters. By varying the concentration of passive particles, they observed a phase separation of the mixture even at very small active swimmer concentrations.

Our BD simulations agree qualitatively with the experiments.[21] The active swimmers create tunnels in the sea of passive particles, which open a path for other trailing swimmers to move through. This leads to the formation of large clusters composed of purely passive particles and individual swimmers moving in the dilute phase, as shown in simulation images in Fig. 6. Based upon our mechanical theory, there is an equality between the Brownian collisional pressure of the dense passive clusters and the swim pressure of the dilute active swimmers compressing the crystals. A video of the BD simulation is available in the ESI.†

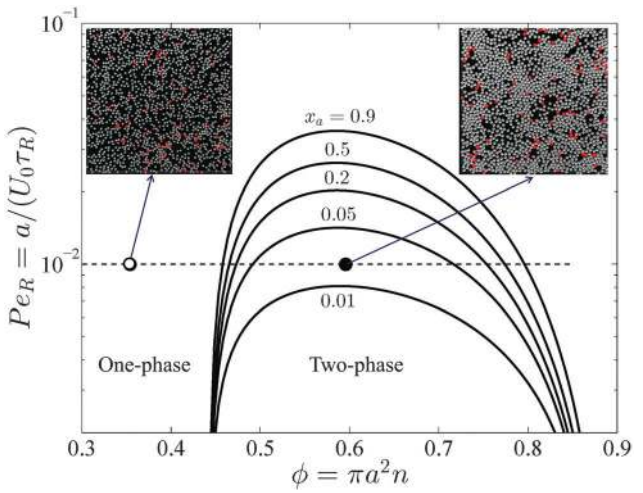

Fig. 6 Phase diagram in the $Pe_R - \phi$ plane in 2D for different active swimmer compositions $x_a = \phi_a/\phi$. The solid curves are the spinodals delineating the regions of stability based upon fluctuations in the total particle density. The two-phase region diminishes as x_a decreases. Steady-state images from BD simulations are shown for $Pe_R = 0.01$, $x_a = 0.05$ at $\phi = 0.35$ (left) and $\phi = 0.6$ (right), corresponding to a homogeneous and phased-separated state, respectively. The red and white circles are the active and passive particles, respectively.

To model these observations, it is instructive to analyze the limits of the active pressure for large and small concentrations of active swimmers relative to passive particles. Since the mechanical pressure exerted by a system of purely active swimmers and purely Brownian particles are known, we can interrogate the effect of adding a small amount of passive or active particles into the suspension. This may be particularly useful for further experimental pursuits of active/passive mixtures.

In the limit of small active swimmer concentration relative to passive particles, the active pressure is

$$\Pi^{act} = \Pi^{osm} + \Pi''(\phi_d, T_s, Pe_R)\phi_a + \mathcal{O}\left(\frac{\phi_a}{\phi_d}\right)^2, \qquad (7)$$

where the first term on the right is the osmotic pressure of a purely Brownian suspension:

$$\Pi^{osm} = n_d k_B T(1 + 2\phi_d g(\phi_d)), \qquad (8)$$

and the second term in eqn (7) is

$$\begin{aligned}\Pi''(\phi_d, T_s, Pe_R) &= n_a k_s T_s\left(1 - \phi_d - 0.2\phi_d^2\right)/\phi_a \\ &+ 2n_d\left[\frac{4}{\pi}k_s T_s Pe_R + 2k_B T\left(2 + \frac{\phi_d}{2\phi_0}g(\phi_d)\right)\right]g(\phi_d) \\ &+ n_d k_B T/\phi_d.\end{aligned} \qquad (9)$$

In this limit, the swim pressure and swimmers' interparticle collisions appear in the leading-order correction. Taking the global density fluctuation $\partial\Pi^{act}/\partial\phi = 0$, we find that the spinodal qualitatively agrees with the experiments of Kümmel *et al.*[21]—a lower spinodal boundary of $\phi \sim 0.45$ and the divergence of the interparticle pressure near close packing. A phase diagram in the $Pe_R - \phi$ plane for different active swimmer compositions is shown in Fig. 6. As x_a decreases the spinodal curve lowers to smaller Pe_R because phase separation becomes more difficult to observe with a smaller fraction of swimmers. For smaller x_a, the Brownian crystals have more time to melt and dissolve into a homogeneous system, and hence the swimmer must have a small Pe_R that is in commensurate with the small x_a. Kümmel *et al.*[21] report phase separation in swimmers with $Pe_R \approx 0.04$, but our theory suggests that Pe_R must be smaller ($Pe_R \lesssim 0.01$) for phase separation to be possible at the small concentration of active swimmers used in their study.

In the other limit of large active swimmer concentration relative to passive particles, we expect phase behavior similar to those observed in purely active suspensions.[5] The passive particles can act as nucleation sites for cluster formation, which may spark an earlier onset of phase separation. The active pressure has the form

$$\Pi^{act} = \Pi^{act}(\phi_a, \phi_d = 0, T_s, Pe_R) + \Pi'(\phi_a, T_s, Pe_R)\phi_d + \mathcal{O}\left(\frac{\phi_d}{\phi_a}\right)^2, \qquad (10)$$

where the first term on the right is the active pressure for a purely active swimmer suspension[5] (*i.e.*, eqn (1) with $\phi_d = 0$):

$$\begin{aligned}\Pi^{act}(\phi_a, \phi_d = 0, T_s, Pe_R) &= n_a k_s T_s(1 - \phi_a - 0.2{\phi_a}^2) \\ &+ n_a\left(\frac{4}{\pi}k_s T_s Pe_R + 2k_B T\right)\phi_a g(\phi_a) \\ &+ n_a k_B T,\end{aligned} \tag{11}$$

and the second term in eqn (10) is

$$\begin{aligned}\Pi'(\phi_a, T_s, Pe_R) &= -n_a k_s T_s(1 + 0.4\phi_a) \\ &+ n_a\left(\frac{4}{\pi}k_s T_s Pe_R + 2k_B T\right)\left(2 + \frac{\phi_a}{\phi_0}g(\phi_a)\right)g(\phi_a) \\ &+ n_a k_B T/\phi_a.\end{aligned} \tag{12}$$

As expected the leading-order correction to the swim and interparticle pressures scales as $\sim n_a\phi_d$. As shown in Fig. 6, the spinodal curve for $x_a \approx 1$ remains high because phase separation is dominated by the hindered motion of the active swimmers.

6 'Thermodynamic' quantities

Thermodynamic quantities like the chemical potential and free energy are defined only for equilibrium systems. However, standard macroscopic mechanical balances can be applied to define quantities that are nonequilibrium analogs for active systems.[3,5] Here we extend the derivation of the nonequilibrium free energy and chemical potential to mixtures of active and passive particles, and interpret these quantities as a natural extension for nonequilibrium systems.

The virtual work done by an external mechanical force (*i.e.*, stress) due to an infinitesimal change in the system volume δV is given by $\delta W = -\Pi\delta V$ where Π is the applied mechanical pressure. One can interpret this virtual work as the change in Helmholtz free energy of the system due to an applied mechanical stress, as is commonly done in elasticity theory.[29] Upon carefully imposing incompressibility of the solvent, one can relate the nonequilibrium free energy to the mechanical pressure of a multicomponent mixture as[14]

$$\Pi = -f + \sum_{i=1}^{N_c}\phi_i\frac{\partial f}{\partial\phi_i} + f(0), \tag{13}$$

where N_c is the number of species in the mixture and $f(0)$ is the free energy density of the pure solvent (which is arbitrary and constant in our analysis). We interpret eqn (13) as the definition of the free energy for nonequilibrium active systems with Π^{act} in place of Π. For our two-component (plus the solvent) system, we have $N_c = 2$ and the nonequilibrium free energy $f^{act}(\phi_a, \phi_d, T_s, Pe_R)$ can be defined as

$$\Pi^{act} + f^{act} = \phi_a\frac{\partial f^{act}}{\partial\phi_a} + \phi_d\frac{\partial f^{act}}{\partial\phi_d}. \tag{14}$$

The general solution is

$$\begin{aligned}&f^{act}(\phi_a, \phi_d, T_s, Pe_R) \\ &= \frac{k_s T_s}{\nu}\left[\phi_a\log\phi_a - \phi_a\phi\left(\frac{\phi}{10} + 1\right)\right. \\ &\quad \left. - 4Pe_R\phi_0\phi_a\log(\phi_0 - \phi)\left(\frac{1}{\pi}\left(1 + \frac{\phi_d}{\phi}\right) + \frac{4\phi}{3\phi_a}Pe_R\right)\right] \\ &\quad + \frac{k_B T}{\nu}(\phi_a\log\phi_a + \phi_d\log\phi_d),\end{aligned} \tag{15}$$

where $\nu \equiv \pi a^2$ is the projected area of a particle. This definition for the nonequilibrium free energy agrees with the true thermodynamic free energy for molecular or colloidal solutes in solution (*i.e.*, $f^{act}(\phi_a = 0, \phi_d, T_s, Pe_R) = f^{osm}$).[14] To gain further insight into the free energy, in the Appendix we analyze the limits of f^{act} for our mixture for large and small concentrations of active swimmers relative to passive particles.

As done previously for a purely active system,[3] we can derive the nonequilibrium chemical potential for multicomponent mixtures using purely mechanical arguments (see Appendix C). For a mixture of active and passive particles, it is given by

$$n_a\frac{\partial\mu_a^{act}}{\partial\phi} + n_d\frac{\partial\mu_d^{act}}{\partial\phi} = (1 - \phi_a - \phi_d)\frac{\partial\Pi^{act}}{\partial\phi}. \tag{16}$$

Again this expression agrees with the rigorous thermodynamic definition of the chemical potential for mixtures of molecular solutes in solution.[14] The chemical potential for each species i in a multicomponent system can thus be obtained from

$$\mu_i^{act} = \nu_i\left[\frac{\partial f^{act}}{\partial\phi_i} - \Pi^{act}\right], \tag{17}$$

where the reference states were absorbed into the free energy. We can invoke eqn (15) and (1) to obtain the chemical potential for the active (μ_a^{act}) and passive (μ_d^{act}) species.

From the thermodynamics of mixtures, the stability criterion using the free energy is given by $\det(\partial^2 f/\partial\phi_i\partial\phi_j) = 0$.[14] For our system this reduces to

$$\left(\frac{\partial^2 f^{act}}{\partial{\phi_a}^2}\right)\left(\frac{\partial^2 f^{act}}{\partial{\phi_d}^2}\right) - \left(\frac{\partial^2 f^{act}}{\partial\phi_a\partial\phi_d}\right)^2 = 0. \tag{18}$$

This gives us the reorientation Péclet number as a function of the active and passive concentrations, $Pe_R = Pe_R(\phi_a, \phi_d)$.

The dashed curve in Fig. 5 is the spinodal curve using eqn (18) for a fixed active swimmer fraction $x_a = 0.5$. This spinodal boundary does not agree with the simulation data of Stenhammar *et al.*,[20] as eqn (18) predicts a different phase boundary than those observed in a simulation. The simulations reflect a global dilute/dense phase separation based upon fluctuations in the total particle (both active and passive) density. In contrast, eqn (18) interrogates the stability of the free energy due to fluctuations in the active particle concentration while keeping the passive particle concentration fixed, and *vice versa*.

This facilitates an important consideration in both experiments and simulations about which variables are held fixed

and varied. Depending on the ensemble of variables that are held fixed (active swimmer density, composition, *etc.*), the theory predicts in general different phase boundaries. To produce a phase diagram in a simulation, one typically fixes the overall swimmer composition x_a and swimmer Pe_R, and varies the total area fraction ϕ or *vice versa*. This corresponds to a global dense/dilute-phase separation based upon fluctuations in the total particle density, which is well described by the mechanical instability criterion $(\partial \Pi^{act}/\partial \phi)_{x_a,T_s,Pe_R} = 0$, as shown by the red solid curve in Fig. 5.

In the experiments of Kümmel *et al.*,[21] the active swimmer area fraction ($\phi_a = 0.01$) and Péclet number $\left(Pe \equiv U_0\sqrt{\tau_R/D_0} = 20\right)$ were held fixed, and the passive particle area fraction (ϕ_d) was varied. The ensemble of variables that we fix and vary must therefore be considered when we predict of the phase behavior of active mixtures. It is likely that one can conduct an experiment or simulation where the phase behavior agrees with the thermodynamic spinodal $\det(\partial^2 f/\partial\phi_i\partial\phi_j) = 0$ (red dashed curve in Fig. 5). There remains much more to the phase portrait than the existing studies and our mechanical theory have revealed.

7 Conclusions

We developed a simple mechanical theory to address an important question in active matter: do active particles thermally equilibrate, and if so, what is the quantity that gets shared upon collisions? We found that the swimmers' activity $k_sT_s \equiv \zeta U_0{}^2\tau_R/2$ does not have the same properties of the thermal energy k_BT. The swimmers' capability to have run lengths $U_0\tau_R$ small or large compared to their size a (and other length scales in the problem) distinguishes them from passive Brownian particles whose step size is smaller than any other length scale in the system.

We discovered that for $Pe_R \equiv a/(U_0\tau_R) \ll 1$ the quantity that gets shared upon collisions is Pe_R, not the scale k_sT_s. This was seen in the simple mixing experiment in Fig. 1 and from analyzing the motion of a passive particle as a probe to measure the kinetic activity of the swimmers (k_sT_s). The notion of the swimmers' energy k_sT_s and/or Pe_R being shared *via* collisions is an interesting concept that may facilitate further theoretical and experimental studies.

Another fundamental difference between an active system and a classical fluid was found by observing the motion of a passive particle in a sea of active swimmers. Even after undergoing many collisions with swimmers, the passive bath particle ceases to move (aside from its translational Brownian motion) if the swimmers are removed because of the damping by the solvent. In contrast, a passive bath particle placed inside a classical molecular or colloidal solution keeps its k_BT activity even when the other particles are removed. Because the swimmers must continuously collide into the passive bath particle to impart information about their kinetic activity, there is no "thermal equilibration" that takes place in an active suspension.

To understand the temperature and phase behavior of active matter, we studied a mixture of active and passive Brownian particles. Our theory applies more generally to a mixture of active systems with different activities. In fact, we showed that a passive Brownian particle behaves equivalently to a "swimmer" with $Pe_R \to \infty$, so the active/passive mixture corresponds to a limiting case of a mixture of active systems with different activities. A swimmer that takes small steps and reorients rapidly is indistinguishable from a purely Brownian particle if it is placed behind an osmotic barrier. For a mixture of active particles with different, finite Pe_R, we would simply write the swim and collisional pressures for each individual species $Pe_R^{(1)}$, $Pe_R^{(2)}$, *etc.* The total active pressure of the system is a sum of the contributions from all species, as in eqn (1).

By understanding the dependence of the active swimmer composition x_a and the total area fraction ϕ in each of the active pressure contributions, we obtained an explicit equation of state for the active/passive mixture. The key principle in deriving the equation of state was that a swimmer imparts the same displacement whether it collides into another swimmer or a passive particle. We found that the swim pressure decreases with increasing area fraction and is the destabilizing term that leads to a phase separation in active systems. In contrast, the interparticle (collisional) pressure increases monotonically with the area fraction and helps to stabilize the suspension from phase separation. The competition between these two effects is determined by the reorientation Péclet number, $Pe_R \equiv a/(U_0\tau_R)$. The spinodal specifies the regions in the phase diagram where these two opposing effects cancel precisely, and these regions were identified in the $Pe_R - \phi$ space for our mixture.

We corroborated our theory with recent simulations[20] and experiments[21] of active/passive mixtures. Our simple model may be a useful tool for predicting phase behavior in both experiments and simulations, as many regions of phase space are difficult to explore because of experimental and computational challenges of covering the parameter space.

We found that different stability conditions give rise to different phase boundaries, facilitating considerations in simulations about which variables are held fixed and varied. The derivative of our active pressure with respect to the total area fraction predicts accurately the global dense/dilute phase transitions observed in simulations. To predict the local phase separation within the dense or dilute phase (as in immiscible polymer mixtures), a different stability criterion is required. Finally, we extended the mechanical theory to determine the nonequilibrium chemical potential and free energy for a mixture of active and passive species.

Extension of our theory to 3D and for different particle size ratios is straightforward. In 3D the characteristic activity scale becomes $k_sT_s \equiv \zeta U_0{}^2\tau_R/6$ instead of $\zeta U_0{}^2\tau_R/2$ due to the extra degree of freedom. For a mixture of particles with different sizes a and b, the pair-distribution function adjusts to different collision pairs $g_{aa}(\phi)$, $g_{ad}(\phi)$, etc because now the particle–particle separation at contact is different. For a polydispersed active system, the large clusters are no longer crystalline and are less stable than those in a monodisperse system. Therefore the two-phase region in Fig. 5 shrinks and shifts to smaller Pe_R.

In our model we neglected hydrodynamic interactions between the particles, which may contribute additional terms such as the

"hydrodynamic stresslet"[30] to the active pressure. We also did not consider the effects of polar order and alignment of the swimmers, which are not necessary for phase-separating systems.

Appendix

A. Micromechanical equations of motion

The active particle dynamics are governed by the N-particle Langevin equation

$$0 = -\zeta \boldsymbol{U} + \boldsymbol{F}^{\mathrm{swim}} + \boldsymbol{F}^{\mathrm{P}} + \sqrt{2\zeta^2 D_0}\boldsymbol{\Lambda}_{\mathrm{T}} \tag{A1}$$

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = \sqrt{\frac{2}{\tau_{\mathrm{R}}}}\Lambda_{\mathrm{R}} \tag{A2}$$

where $\boldsymbol{U}$ is the translational velocity, ζ is the hydrodynamic drag factor, $\boldsymbol{F}^{\mathrm{swim}} \equiv \zeta \boldsymbol{U}_0 = \zeta U_0 \boldsymbol{q}$ is the self-propulsive swim force, U_0 is the swim speed, θ specifies the swimmers' direction of motion $\boldsymbol{q} = (\cos\theta, \sin\theta)$, $\boldsymbol{F}^{\mathrm{P}}$ is the interparticle force between the particles to enforce no overlap, $\boldsymbol{\Lambda}_{\mathrm{T}}$ and Λ_{R} are unit random normal deviates, τ_{R} is the orientation time of the swimmer, and D_0 is the Stokes–Einstein–Sutherland translational diffusivity. The passive Brownian particles are governed by the same equation but without the self-propulsive force:

$$0 = -\zeta_{\mathrm{d}} \boldsymbol{U}_{\mathrm{d}} + \boldsymbol{F}^{\mathrm{P}} + \sqrt{2\zeta_{\mathrm{d}}{}^2 D_0}\Lambda_{\mathrm{T}}, \tag{A3}$$

where the subscript "d" indicates a passive particle. For simplicity in this work we considered spherical particles with the same size for active and passive particles so that $\zeta = \zeta_{\mathrm{d}}$. The left-hand side of eqn (A1) and (A3) is zero since inertia is negligible for colloidal suspensions. A more detailed discussion concerning the origin of the swim force and the role of hydrodynamic interactions is available elsewhere.[17]

B. Limits of active free energy

To gain further insight into the free energy, we analyze the limits of f^{act} for our mixture system for large and small concentrations of active swimmers relative to passive particles. Expanding the active free energy for small $\varepsilon = \phi_{\mathrm{d}}/\phi_{\mathrm{a}} = (1 - x_{\mathrm{a}})/x_{\mathrm{a}}$, we find in the limit of large active concentration

$$\begin{aligned} f^{\mathrm{act}} &= f^{\mathrm{act}}(\phi_{\mathrm{a}}, \phi_{\mathrm{d}} = 0, T_{\mathrm{s}}, \mathrm{Pe}_{\mathrm{R}}) + f'(\phi_{\mathrm{a}}, T_{\mathrm{s}}, \mathrm{Pe}_{\mathrm{R}})\phi_{\mathrm{d}} \\ &\quad + \frac{k_{\mathrm{B}}T}{\nu}\phi_{\mathrm{d}} \log\left(\frac{\phi_{\mathrm{d}}}{\phi_{\mathrm{a}}}\right) + \mathcal{O}(\varepsilon^2), \end{aligned} \tag{B1}$$

where $\nu \equiv \pi a^2$ is the projected area of a particle and the first term on the right is the active free energy for a purely active system:[5]

$$\begin{aligned} f^{\mathrm{act}}(\phi_{\mathrm{a}}, \phi_{\mathrm{d}} = 0, T_{\mathrm{s}}, \mathrm{Pe}_{\mathrm{R}}) &= \frac{k_{\mathrm{s}}T_{\mathrm{s}}}{\nu}\phi_{\mathrm{a}}\left[\log\phi_{\mathrm{a}} - \phi_{\mathrm{a}}\left(\frac{\phi_{\mathrm{a}}}{10} + 1\right)\right. \\ &\quad \left. -4\mathrm{Pe}_{\mathrm{R}}\phi_0 \log(\phi_0 - \phi_{\mathrm{a}})\left(\frac{1}{\pi} + \frac{4}{3}\mathrm{Pe}_{\mathrm{R}}\right)\right] \\ &\quad + \frac{k_{\mathrm{B}}T}{\nu}\phi_{\mathrm{a}} \log\phi_{\mathrm{a}}, \end{aligned} \tag{B2}$$

and the second term in eqn (B1) is

$$\begin{aligned} f'(\phi_{\mathrm{a}}, T_{\mathrm{s}}, \mathrm{Pe}_{\mathrm{R}}) &= \frac{k_{\mathrm{s}}T_{\mathrm{s}}}{\nu}\left[-\phi_{\mathrm{a}}\left(\frac{\phi_{\mathrm{a}}}{5} + 1\right)\right. \\ &\quad \left. - 4\mathrm{Pe}_{\mathrm{R}}\phi_0\left(\log(\phi_0 - \phi_{\mathrm{a}}) - \frac{\phi_{\mathrm{a}}/\phi_0}{1 - \phi_{\mathrm{a}}/\phi_0}\right)\left(\frac{1}{\pi} + \frac{4}{3}\mathrm{Pe}_{\mathrm{R}}\right)\right] \\ &\quad + \frac{k_{\mathrm{B}}T}{\nu}\log\phi_{\mathrm{a}}. \end{aligned} \tag{B3}$$

Expanding the swim pressure for small $\varepsilon' = \phi_{\mathrm{a}}/\phi_{\mathrm{d}} = x_{\mathrm{a}}/(1 - x_{\mathrm{a}})$, we find in the limit of small active concentration

$$\begin{aligned} f^{\mathrm{act}} &= f^{\mathrm{osm}} + f''(\phi_{\mathrm{d}}, T_{\mathrm{s}}, \mathrm{Pe}_{\mathrm{R}})\phi_{\mathrm{a}} \\ &\quad + \frac{1}{\nu}(k_{\mathrm{B}}T + k_{\mathrm{s}}T_{\mathrm{s}})\phi_{\mathrm{a}} \log\left(\frac{\phi_{\mathrm{a}}}{\phi_{\mathrm{d}}}\right) + \mathcal{O}(\varepsilon'^2), \end{aligned} \tag{B4}$$

where the first term on the right is the osmotic pressure of a purely Brownian suspension:

$$f^{\mathrm{osm}} = \frac{k_{\mathrm{B}}T}{\nu}\phi_{\mathrm{d}}[\log\phi_{\mathrm{d}} - \phi_0 \log(\phi_0 - \phi_{\mathrm{d}})], \tag{B5}$$

and the second term in eqn (B4) is

$$\begin{aligned} f''(\phi_{\mathrm{d}}, T_{\mathrm{s}}, \mathrm{Pe}_{\mathrm{R}}) &= \frac{k_{\mathrm{B}}T}{\nu}[\log\phi_{\mathrm{d}} + 2\phi_0 \log(\phi_0 - \phi_{\mathrm{d}})] \\ &\quad + \frac{k_{\mathrm{s}}T_{\mathrm{s}}}{\nu}\left[\log\phi_{\mathrm{d}} - \phi_{\mathrm{d}}\left(\frac{\phi_{\mathrm{d}}}{10} + 1\right) - \frac{8}{\pi}\mathrm{Pe}_{\mathrm{R}}\phi_0 \log(\phi_0 - \phi_{\mathrm{d}})\right]. \end{aligned} \tag{B6}$$

The influence of the swim pressure and swimmers' interparticle collisions are present in the correction term.

C. Mechanical derivation of the chemical potential for multicomponent systems

The number density of an N_{c}-component system§ satisfies the conservation equation

$$\frac{\partial n}{\mathrm{d}t} + \sum_{i=1}^{N_{\mathrm{c}}} \nabla_i \cdot \boldsymbol{j}_i = 0, \tag{C1}$$

where $\boldsymbol{j}_i = n_i\boldsymbol{u}_i = n_i\langle\boldsymbol{u}\rangle + \boldsymbol{j}_i^{\mathrm{rel}}$ is the particle flux of species i, $\boldsymbol{j}_i^{\mathrm{rel}} = n_i(\boldsymbol{u}_i - \langle\boldsymbol{u}\rangle)$ is the flux of species i relative to the suspension average velocity $\langle\boldsymbol{u}\rangle$, which is defined as $\langle\boldsymbol{u}\rangle = \sum_{i=1}^{N_{\mathrm{c}}} \phi_i\boldsymbol{u}_i + (1 - \phi)\boldsymbol{u}_{\mathrm{f}}$, and $\boldsymbol{u}_i$ and $\boldsymbol{u}_{\mathrm{f}}$ are the number averaged velocity of swimmer species i and fluid at a continuum point, respectively. The total volume (or area) fraction of the particles is $\phi = \sum_{i=1}^{N_{\mathrm{c}}} \phi_i$. Incompressibility requires the suspension-average velocity (particles plus the fluid) to satisfy $\nabla\cdot\langle\boldsymbol{u}\rangle = 0$.

§ There are $N_{\mathrm{c}} + 1$ total components, including the solvent.

We apply an averaged macroscopic mechanical momentum balance to obtain an expression for $\boldsymbol{j}_i^{\mathrm{rel}}$. Following the standard Irving–Kirkwood approach, we obtain

$$0 = -\sum_{i=1}^{N_c} n_i \zeta_i (\boldsymbol{u}_i - \langle \boldsymbol{u} \rangle) + \nabla \cdot \boldsymbol{\sigma}^{\mathrm{act}}, \tag{C2}$$

where $\boldsymbol{\sigma}^{\mathrm{act}} = \boldsymbol{\sigma}^{\mathrm{swim}} + \boldsymbol{\sigma}^{\mathrm{P}}$ is the active stress and the left-hand side is zero since inertia is negligible for colloidal systems. Using the relative flux $\boldsymbol{j}_i^{\mathrm{rel}} = n_i(\boldsymbol{u}_i - \langle \boldsymbol{u} \rangle)$ we arrive at a relationship between the active particle flux and gradients in the active stress:

$$\sum_{i=1}^{N_c} \zeta_i \boldsymbol{j}_i^{\mathrm{rel}} = \nabla \cdot \boldsymbol{\sigma}^{\mathrm{act}}. \tag{C3}$$

We did not rely upon the notion of a thermodynamic chemical potential or the free energy to arrive at this expression.

We can use our mechanical derivation to define a non-equilibrium chemical potential by analogy to the quantity whose gradient would drive a flux:

$$\boldsymbol{j}_i^{\mathrm{rel}} = -\frac{n_i}{\zeta_i(1-\phi)} \nabla \mu_i^{\mathrm{act}}, \tag{C4}$$

where again $\phi = \sum_{j=1}^{N_c} \phi_j$. This definition is analogous to that of a thermodynamic system where the relative flux is driven by gradients in the thermodynamic chemical potential. Substituting eqn (C4) into eqn (C3) and using the definition $\Pi^{\mathrm{act}} \equiv -\mathrm{tr}\,\boldsymbol{\sigma}^{\mathrm{act}}/2$, we arrive at

$$\sum_{i=1}^{N_c} n_i \frac{\partial \mu_i^{\mathrm{act}}}{\partial \phi} = (1-\phi) \frac{\partial \Pi^{\mathrm{act}}}{\partial \phi}. \tag{C5}$$

For a two-component (active and passive) system, we have $n_{\mathrm{a}}(\partial \mu_{\mathrm{a}}^{\mathrm{act}}/\partial \phi) + n_{\mathrm{d}}(\partial \mu_{\mathrm{d}}^{\mathrm{act}}/\partial \phi) = (1 - \phi_{\mathrm{a}} - \phi_{\mathrm{d}})\partial \Pi^{\mathrm{act}}/\partial \phi$, as given in the main text.

This relationship between the chemical potential and pressure is equivalent for a system of passive Brownian particles and active swimmers with small τ_{R}. We thus interpret μ^{act} as a natural definition and extension of the chemical potential for nonequilibrium systems.

Comparison to thermodynamics. From equilibrium thermodynamics,[14] the chemical potential of species i for a multicomponent system is given by

$$\mu_i = \nu \left(\frac{\partial f}{\partial \phi_i} - \Pi \right), \tag{C6}$$

where ν is the volume (or area) of a particle. The free energy is related to the osmotic pressure by

$$\phi_{\mathrm{a}} \frac{\partial f}{\partial \phi_{\mathrm{a}}} + \phi_{\mathrm{d}} \frac{\partial f}{\partial \phi_{\mathrm{d}}} = f + \Pi. \tag{C7}$$

Taking the density derivative of both eqn (C6) and (C7) and combining the results, we obtain

$$n_{\mathrm{a}} \frac{\partial \mu_{\mathrm{a}}}{\partial \phi} + n_{\mathrm{d}} \frac{\partial \mu_{\mathrm{d}}}{\partial \phi} = (1 - \phi_{\mathrm{a}} - \phi_{\mathrm{d}}) \frac{\partial \Pi}{\partial \phi}, \tag{C8}$$

which is identical to eqn (16) of the main text, a result obtained using a mechanical derivation.

Therefore the mechanical derivations of the stress, momentum balance, and flux are in full agreement with thermodynamics.

Acknowledgements

SCT is supported by the Gates Millennium Scholars fellowship and the National Science Foundation Graduate Research Fellowship under Grant No. DGE-1144469. This work is also supported by NSF Grant CBET 1437570.

References

1 S. Ramaswamy, *Annu. Rev. Condens. Matter Phys.*, 2010, **1**, 323–345.
2 J. Toner, Y. Tu and S. Ramaswamy, *Ann. Phys.*, 2005, **318**, 170–244.
3 S. C. Takatori, W. Yan and J. F. Brady, *Phys. Rev. Lett.*, 2014, **113**, 028103.
4 X. Yang, M. L. Manning and M. C. Marchetti, *Soft Matter*, 2014, **10**, 6477–6484.
5 S. C. Takatori and J. F. Brady, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2015, **91**, 032117.
6 I. Theurkauff, C. Cottin-Bizonne, J. Palacci, C. Ybert and L. Bocquet, *Phys. Rev. Lett.*, 2012, **108**, 268303.
7 J. Palacci, S. Sacanna, A. P. Steinberg, D. J. Pine and P. M. Chaikin, *Science*, 2013, **339**, 936–940.
8 G. S. Redner, M. F. Hagan and A. Baskaran, *Phys. Rev. Lett.*, 2013, **110**, 055701.
9 J. Bialké, H. Löwen and T. Speck, *Europhys. Lett.*, 2013, **103**, 30008.
10 J. Stenhammar, A. Tiribocchi, R. J. Allen, D. Marenduzzo and M. E. Cates, *Phys. Rev. Lett.*, 2013, **111**, 145702.
11 X.-L. Wu and A. Libchaber, *Phys. Rev. Lett.*, 2000, **84**, 3017–3020.
12 D. Loi, S. Mossa and L. F. Cugliandolo, *Soft Matter*, 2011, **7**, 10193–10209.
13 M. E. Cates and J. Tailleur, *Europhys. Lett.*, 2013, **101**, 20010.
14 M. Doi, *Soft Matter Physics*, Oxford University Press, Oxford, United Kingdom, 2013.
15 Y. Fily, S. Henkes and M. C. Marchetti, *Soft Matter*, 2014, **10**, 2132–2140.
16 S. C. Takatori and J. F. Brady, *Soft Matter*, 2014, **10**, 9433–9445.
17 W. Yan and J. F. Brady, *Soft Matter*, 2015, **11**, 6235–6244.
18 W. Russel, D. Saville and W. Schowalter, *Colloidal Dispersions*, Cambridge University Press, 1992.
19 J. F. Brady, *J. Chem. Phys.*, 1993, **98**, 3335–3341.
20 J. Stenhammar, R. Wittkowski, D. Marenduzzo and M. E. Cates, *Phys. Rev. Lett.*, 2015, **114**, 018301.
21 F. Kümmel, P. Shabestari, C. Lozano, G. Volpe and C. Bechinger, *Soft Matter*, 2015, **11**, 6187–6191.
22 J. Stenhammar, D. Marenduzzo, R. J. Allen and M. E. Cates, *Soft Matter*, 2014, **10**, 1489–1499.
23 T. Speck, J. Bialké, A. M. Menzel and H. Löwen, *Phys. Rev. Lett.*, 2014, **112**, 218304.

24 A. Wysocki, R. G. Winkler and G. Gompper, *Europhys. Lett.*, 2014, **105**, 48004.
25 A. P. Solon, J. Stenhammar, R. Wittkowski, M. Kardar, Y. Kafri, M. E. Cates and J. Tailleur, *Phys. Rev. Lett.*, 2015, **114**, 198301.
26 R. G. Winkler, A. Wysocki and G. Gompper, *Soft Matter*, 2015, **11**, 6680–6691.
27 R. B. Griffiths and J. C. Wheeler, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1970, **2**, 1047–1064.
28 P. I. Freeman and J. S. Rowlinson, *Polymer*, 1960, **1**, 20–26.
29 L. Landau and E. Lifshitz, *Theory of Elasticity*, Butterworth-Heinemann, 3rd edn, 1986, vol. 7.
30 D. Saintillan and M. J. Shelley, *Phys. Fluids*, 2008, **20**, 123304.