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Letter

Excess Entropy Scaling in Active-Matter Systems

S. Arman Ghaffarizadeh and Gerald J. Wang*

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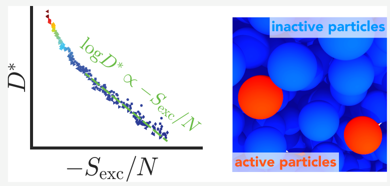
ABSTRACT: Active-matter systems feature discrete particles that can convert stored or ambient free energy into motion. To realize the engineering potential of active matter, there is a strong need for predictive and theoretically grounded techniques for describing transport in these systems. In this work, we perform molecular-dynamics (MD) simulations of a model active-matter system, in which we vary the total fraction of active particles ($0.01 \le \phi \le 0.5$) as well as the degree of activity of the active particles. These simulations reveal a fascinating array of transport phenomena, including activity-enhanced diffusion coefficients. By adapting an existing result for binary (inactive) fluids, we demonstrate the existence of an excess entropy scaling relation in an active system. This relationship is well supported by our MD results and establishes a new connection between transport (dynamics) and structure (statics) in active matter, a promising step for predictive and generalizable models of other transport phenomena in such systems.



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Active-matter systems feature discrete particles that can convert stored or ambient free energy into motion.[1−3] The transport properties of systems containing active particles can differ significantly compared to those of their inactive counterparts (see, e.g., the diffusion coefficient of a self-propelled microswimmer compared to that of a Brownian particle,[4−6] the onset of turbulence in active fluids at Reynolds numbers lower than those in classical turbulence,[7−9] or a variety of collective motion phenomena with no close inactive analogues[10,11]). Advancements over the past decade in methods for synthesizing active particles[12−16] have enabled the realization of numerous active-matter systems, exhibiting a rich array of structural and transport phenomena. One particularly exciting engineering application of active particles is for modifying (and perhaps eventually controlling) the material and transport properties of the (inactive) fluid within which they are suspended, as has been explored in the case of diffusion,[17−19] viscosity,[20] heat transfer properties,[21] and phase behavior.[22−24]

Despite considerable recent progress in microscopic descriptions of the mechanics of active-matter systems,[25−30] an open question looms large: What general principles can be used to predict, or at least roughly estimate, the (activity-modified) transport properties in a system that has been seeded with active particles? Such principles will be critical for the eventual design and control of thermofluid systems using active particles. In this work, within the context of a simple conceptual model of active matter, we seek to answer this question—in particular, "how can we predict the activity-enhanced diffusivity of an inactive fluid with active inclusions?"—by turning to one of the more enigmatic and celebrated characters from the past 50 years of thermodynamics: excess entropy.

In a nutshell, the excess entropy (S_{exc}) of a system is a measure of how far that system's entropy S is from that of its ideal-gas (maximum-entropy) state (at equivalent temperature and density), i.e., $S_{exc} \equiv S - S_{ideal\ gas}$. This quantity is negative by construction; in the limit that the system's temperature approaches infinity, the excess entropy vanishes. Since the pioneering work of Rosenfeld,[31] numerous studies have supplied evidence for remarkable scaling relations that connect excess entropy with transport quantities for (inactive) fluids as wide-ranging as systems of hard spheres,[32] Lennard-Jones fluids,[33,34] supercooled and binary mixtures,[35−37] ionic melts,[38] and hydrocarbons.[39] Recently, Sachin and Joy investigated the validity of excess entropy scaling for a binary glassy liquid consisting exclusively of athermal active particles and found that excess entropy scaling works well provided that the system is not in a strongly supercooled state.[40] This work demonstrates that excess entropy scaling is robust for a system containing only active particles ("active" in this case referring to all particles having significant persistence lengths) and leaves open the question that motivates this work: To what extent does excess entropy scaling work for fluid mixtures of active and inactive particles?

In all of the work described above, excess entropy scaling posits an exponential relationship between (an appropriately scaled form of) the coefficient of self-diffusion D^* and the (per-particle) excess entropy S_{exc}/N:

$$D^* = c_1 \exp\left(-c_2 \frac{S_{exc}}{N k_B}\right) \tag{1}$$

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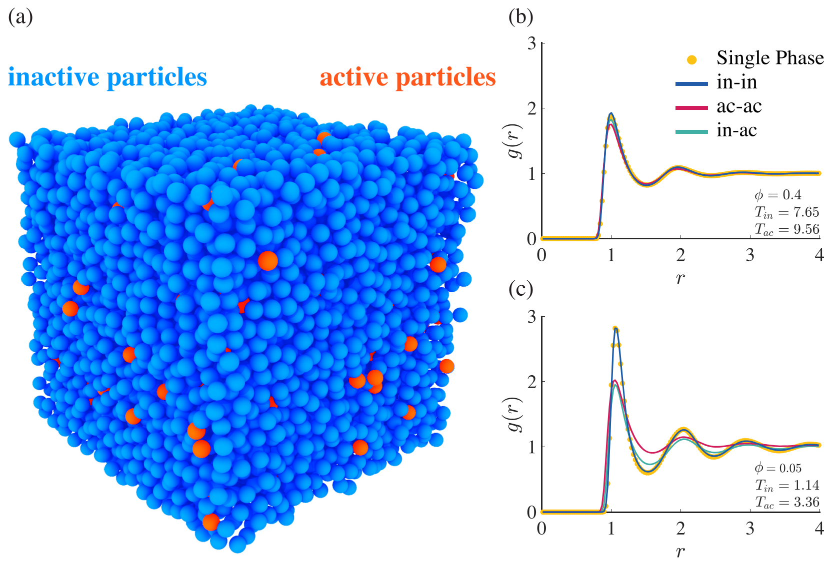

Figure 1. (a) System containing inactive particles (blue) and active particles (red), where $\phi = 0.03$. Partial radial distribution functions (RDFs) showing spatial correlations for inactive–inactive ("in-in"), active–active ("ac-ac"), and inactive–active ("in-ac") particle pairs, for systems with (b) $\phi = 0.4$, $T_{\text{inactive}} = 7.65$, and $T_{\text{active}} = 9.56$ and (c) $\phi = 0.05$, $T_{\text{inactive}} = 1.14$, and $T_{\text{active}} = 3.36$. In panels (b) and (c), the "single-phase" data (gold) are obtained by computing the RDF for a LJ fluid containing a single particle type at the same temperature as the inactive particles in the mixed system.

where c_1 and c_2 are material-specific constants, N is the number of particles, and k_B is Boltzmann's constant. In particular, as the magnitude of the excess entropy increases (via, e.g., a decreased system temperature or increased system density, each of which serves to make a system less well-described as an ideal gas), the scaled self-diffusion coefficient decreases. This scaling (i.e., conversion from a dimensional diffusivity D to its nondimensional counterpart D^*) may be performed using exclusively thermodynamic (macroscopic) observables of the system (e.g., temperature and density), as originally done by Rosenfeld;[31] similarly successful scalings featuring microscopic quantities (e.g., the molecular diameter and the intermolecular collision frequency) also exist, as first suggested by Dzugutov.[41] One of the primary appeals of excess entropy scaling relations is that they represent straightforward connections between transport properties and static structure (which is the only knowledge needed to estimate excess entropy). In addition, these scaling relations open the door to computationally expedient predictions of transport properties via knowledge of a system's microscopic structure. In this work, we address the next logical (and as of yet unanswered) question: Do excess entropy scaling relations for active-matter systems exist, despite the fact that such systems are decidedly out of equilibrium? Below, we study this question using computer simulations (and answer it in the affirmative), within the context of a simple two-temperature model for particle activity.

We consider a system of particles in which each particle is specified as either active or inactive, all of which are of mass m and interact via the Lennard-Jones (LJ) potential[42]

$$u(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{2}$$

where $u(r)$ is the interaction energy of two particles separated by a distance r and ϵ and σ are the energy and length scales of the LJ potential, respectively. In all of the discussion that follows, we report quantities in nondimensional units, normalized against length-scale σ, energy-scale ε, mass-scale m, time-scale $\sqrt{m\sigma^2/\epsilon}$, temperature-scale k_B/ε, density-scale m/σ^3, diffusivity-scale $\sigma^2/(\sqrt{m\sigma^2/\epsilon})$, and entropy-scale k_B.

Each of our simulations consists of 8000 particles placed in a cubic domain with a side length of 21 (yielding a nondimensional density ρ of 0.86), with periodic boundary conditions applied in all three dimensions. In each simulation, a fraction of particles ϕ (ranging from 0.01 to 0.5) are designated as active; the remainder are designated as inactive (Figure 1a).

To simulate active particles, we employ a model first proposed independently by Weber et al.[43] and by Grosberg and Joanny[44] and later characterized in detail by Tanaka et al.[45] This model is grounded in the idea that active particles, by virtue of frequent energy injection (typically originating from a feature of the system that is not explicitly simulated, e.g., light–matter interaction for a photoactive colloid or cellular metabolism for an active animal or person), exhibit motion consistent with a thermodynamic temperature higher than that of inactive particles. In particular, in our simulations, active and inactive particles have initial velocities that are sampled from two distinct Maxwell–Boltzmann distributions: Active (inactive) particle velocities are initialized from a distribution consistent with the temperature T_{active} (T_{inactive}); the "activity" of the active particles follows from the relationship $T_{\text{active}} > T_{\text{inactive}}$. To sustain these initial differences between the two subsets of particles, each population has its initial temperature maintained through application of a Langevin thermostat.[46] In this work, we explore systems that contain only fluid phases (i.e., neither inactive nor active components of any system are in coexistence with a solid LJ phase); as such, and informed by the phase diagram for a Lennard-Jones material,[47] the lowest inactive fluid temperature included in this analysis is 0.7. In total, we study 320 distinct systems, spanning $0.01 \le \phi \le 0.5$, $0.7 \le T_{\text{inactive}} \le 18$, and $0.8 \le T_{\text{active}} \le 21$. We provide comprehensive details about the thermostat used and on the range of systems studied in the Supporting Information.

Employing a time step of 2×10^{-3}, we allow each simulation to run for a time of 8×10^5 to reach steady state, after which

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we record data over a sampling window of 2×10^5. In each simulation, we measure two quantities of critical interest.

(1) Excess Entropy. In this work, we approximate excess entropy S_{exc} via two-particle correlations, which dominate the spatial correlations featuring more than two particles.[48,49] In a system with a single particle type, a form of the (per-particle) excess entropy that is particularly amenable to efficient computation[50] is

$$\frac{S_{exc}}{N} \approx -2\pi\rho \int_0^\infty [g(r) \ln g(r) - g(r) + 1]r^2 \, dr \tag{3}$$

where $\rho \equiv N/V$ is the number density, N is the number of particles, V is the system volume, and $g(r)$ is the radial distribution function (RDF). In our case (featuring two particle types, namely, inactive particles and active particles), and in analogy to the work of Samanta et al.,[52] we compute the excess entropy contribution from particle type i as

$$\frac{S_{exc,i}}{N} = -2\pi \sum_j \rho_j \int_0^\infty [g_{ij}(r) \ln g_{ij}(r) - g_{ij}(r) + 1]r^2 \, dr \tag{4}$$

where index j runs over both particle types and g_{ij} refers to the radial distribution function between type i and type j (see, e.g., Figure 1b,c). Note that $\rho_{active} + \rho_{inactive} = \rho$. The total excess entropy is then calculated as a weighted average of the component excess entropies

$$S_{exc} = \phi S_{exc,active} + (1 - \phi)S_{exc,inactive} \tag{5}$$

This form of writing the excess entropy, decomposed by particle type, is inspired by analogy to the work of Hoyt et al. on metallic alloys,[51] also featuring multiple particle types (which are, of course, both inactive).

(2) Coefficient of Self-Diffusion. To calculate the self-diffusion coefficient of particle type i (as a reminder, i can refer either to active particles or to inactive particles), we measure the mean-square displacement (MSD) of that type as

$$\mathrm{MSD}_i = \langle |\mathbf{r}^2(t)| \rangle_i = \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle_i \tag{6}$$

where the angle brackets indicate an average computed over all particles of type i, $\mathbf{r}$ is the displacement vector, and t denotes the length of the measurement window. Using the Einstein relation, the self-diffusion coefficient for particle type i (in three spatial dimensions) is defined as

$$D_i = \lim_{t \to \infty} \frac{\mathrm{MSD}_i}{6t} \tag{7}$$

In our analyses, we extract D_i by performing a least-squares regression to a (zero-intercept) line for the MSD versus time data.

For each system, we compute an overall (and scaled) self-diffusion coefficient as

$$D^* = \left(\frac{D_{active}}{\chi_{active}}\right)^{\phi} \left(\frac{D_{inactive}}{\chi_{inactive}}\right)^{1-\phi} \tag{8}$$

where the form of the scaling factor χ_i is also inspired by previous work[51,52] on binary systems:

$$\chi_i = 4 r_{peak}{}^4 g_{ii}(r_{peak}) \rho_i \sqrt{\frac{\pi T_i}{m_i}} + \chi_{cross} \tag{9}$$

and

$$\chi_{cross} = 4 r_{peak}{}^4 g_{ij}(r_{peak}) \rho_j \sqrt{\frac{\pi T_{ave}(m_{inactive} + m_{active})}{2 m_{inactive} m_{active}}} \tag{10}$$

where r_{peak} refers to the location of the first peak in the radial distribution function (for dense LJ systems at nondimensional densities below unity, this is generally within a few percent of $2^{1/6}$, the equilibrium separation distance between two LJ atoms) and $T_{ave} \equiv \phi T_{active} + (1 - \phi)T_{inactive}$ is a weighted temperature used only for the cross term χ_{cross}. As a reminder, throughout this work, we study systems in which $m_{active} = m_{inactive}$ and work in a set of units such that both are unity. At this junction, for the sake of comparison, there are two distinctions worth noting.

(a) In contradistinction to previous studies of inactive systems,[37,51,52] in which all components exist at the same thermodynamic temperature, eq 8 depends upon two distinct temperatures (T_{active} and $T_{inactive}$, via χ_{active} and $\chi_{inactive}$, respectively).

(b) In contradistinction to previous studies of active systems,[40] in which all particles exhibit the same degree of activity (i.e., the same persistence length) in any given system, eq 8 features two distinct degrees of activity (via, again, two distinct temperatures).

We find that over a wide range of system conditions, our model active-matter system is described very well by the classic result for excess entropy scaling. In particular, in Figure 2, we demonstrate that the relationship between (scaled) diffusion coefficient D^* and (negative per-particle) mixture excess entropy $-S_{exc}/N$ is described well by an exponential function, especially when $-S_{exc}/N > 1.5$. In other words, for the purpose of modeling diffusion in an active fluid using excess entropy scaling (at least at the level of complexity of the two-temperature model for activity), it is sufficient to think of the system as a binary mixture of active and inactive components. To the best of our knowledge, this is the first instance in which the scaling proposed by Hoyt et al. has been used for a mixture

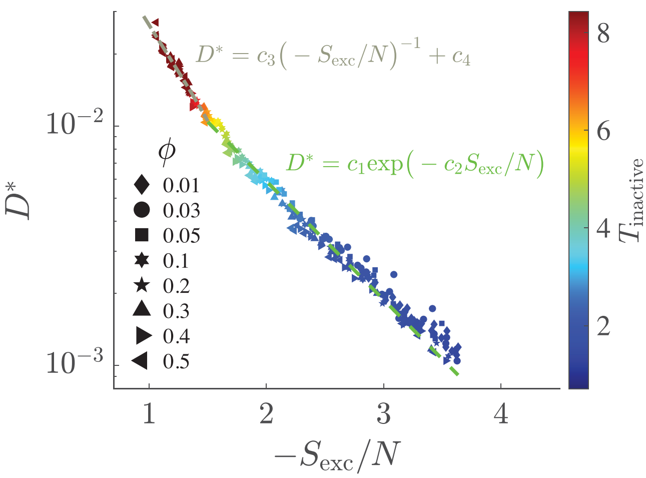

Figure 2. Scaled diffusion coefficient D^* (Equation 8) as a function of mixture excess entropy (eq 5). The color of the marker indicates the inactive particle temperature, and the marker symbol indicates the fraction of active particles. When $-S_{exc}/N > 1.5$, the data agree with the classic exponential model [where $c_1 = 0.058$ and $c_2 = -1.14$ obtained via fitting (green dashed line)]; when $-S_{exc}/N < 1.5$, the data agree with a model that varies inversely with $-S_{exc}/N$ [where $c_3 = 0.048$ and $c_4 = -0.021$ obtained via fitting (gray dashed line)].

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of two components with different levels of activity (instead of two components with different particle diameters[37,40,51,52]).

Intriguingly, for relatively low magnitudes of the excess entropy (i.e., for systems that are under thermodynamic conditions relatively close to the ideal gas), we observe that D^* deviates above the exponential curve. Motivated by the results of Krekelberg et al.,[37] we find that in this relatively low-magnitude region ($-S_{\mathrm{exc}}/N < 1.5$, in our case), the data are fairly well-described by a model that varies inversely with the excess entropy.

Having verified the existence of an excess entropy scaling relation for an active system, it is only natural to wonder whether this result empowers us to develop a (quasi)predictive scheme (informed by a relatively small number of simulations) to understand how the addition of active particles affects the diffusivity of an inactive fluid. Such a scheme would be especially useful in any engineering effort that entails the tailoring or control of the properties of the base fluid (potentially even on demand, via modifications of T_{active} or ϕ). To this end, we make use of the excess entropy scaling result and invert eq 8 to obtain

$$D_{\mathrm{inactive}} = \left[c_1 \exp\left(-c_2 \frac{S_{\mathrm{exc}}}{N}\right) \left(\frac{D_{\mathrm{active}}}{\chi_{\mathrm{active}}}\right)^{-\phi} \right]^{1/(1-\phi)} \chi_{\mathrm{inactive}} \tag{11}$$

In Figure 3, we show that for systems with $-S_{\mathrm{exc}}/N > 1.5$ (i.e., for systems where the classical excess entropy scaling result works well), values for D_{inactive} computed using eq 11, which requires no explicit measurements of transport for the inactive fluid (beyond the small number of simulations needed to extract c_1 and c_2), are in reasonable agreement with the D_{inactive} values directly measured via the Einstein relation. Although this is not a truly predictive approach (in particular, eq 11 requires knowledge of the underlying radial distribution functions as well as the diffusivity of the active particles), it is nevertheless a promising demonstration that the core scientific result in this work may potentially enable a new pathway for modeling activity-modified fluid transport properties.

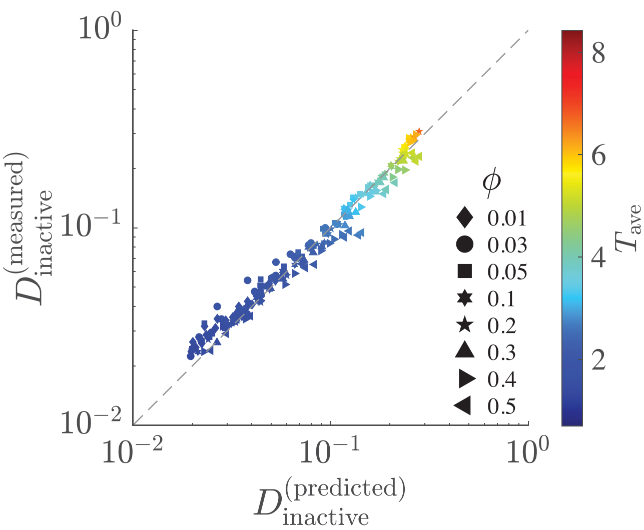

Figure 3. For systems with $-S_{\mathrm{exc}}/N > 1.5$, parity plot comparing values of D_{inactive} obtained from eq 11 (horizontal axis) with values of D_{inactive} obtained from direct measurement within each simulation (vertical axis). The color of the marker indicates the inactive particle temperature, and the marker symbol indicates the fraction of active particles. The line of parity is denoted with black dashes.

In summary, we have explored the question of whether excess entropy scaling can capture activity-modified diffusion in a fluid containing active inclusions. Using computer simulations, we have answered this question in the affirmative, within the context of a simple model for active matter, namely, a two-temperature model in which active particles are maintained at a temperature higher than that of the surrounding inactive particles. In particular, we have shown that the classical excess entropy scaling result (an exponential relationship between scaled diffusivity and excess entropy) works well if one analogizes an active system (which fundamentally consists of two distinct particle types with two distinct levels of activity) to a binary mixture. We have also demonstrated that knowledge of the excess entropy scaling relation for an active-matter system enables a (quasi)predictive model for activity-modified transport properties of the base fluid, a useful basis for any future work that targets the rational design and control of fluids laden with active particles.

Our results naturally raise several fascinating questions for future study, which we briefly mention. Our work is situated in the context of a relatively simple (and well-characterized) model for activity. Does the same hold for more complex models of active, self-propelling, and/or swimming particles? Our result considers only Brownian and interparticle forces acting on each particle. Would the addition of hydrodynamic interactions alter this picture, as is known to be the case for inactive systems?[53] From an engineering perspective, it is worthwhile to build upon our final result and develop a more fully predictive model for activity-modified fluid transport properties (potentially making use of data-driven approaches to overcome limitations in predicting the radial distribution functions needed for the two-point-correlation approximation). Finally, from a fundamental perspective, it is worth asking about the extent to which we should expect active materials to generally obey excess entropy scaling relationships (including for other transport phenomena besides diffusion). To this end, it may be especially helpful to consider various first-principles rationalizations that have been offered for excess entropy scaling (e.g., the concept of hidden scale invariance in so-called "Roskilde-simple fluids"[33]) and examine the extent to which they hold in active-matter systems. On this front, we are especially buoyed by recent work by Saw et al., which reported on approximate scale invariance in a variety of systems out of thermal equilibrium.[54]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.2c01415.

Discussion of the two-temperature model, additional characterization of active systems, and further details about simulations and analysis (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Gerald J. Wang − *Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States;* orcid.org/0000-0002-0631-011X; Email: gjwang@cmu.edu

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Author

S. Arman Ghaffarizadeh − *Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States;* orcid.org/0000-0002-6894-074X

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.jpclett.2c01415

Notes

The authors declare no competing financial interest.

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