Structural Transition in a Fluid of Spheroids: A Low-Density Vestige of Jamming

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A thermodynamically equilibrated fluid of hard spheroids is a simple model of liquid matter. In this model, the coupling between the rotational degrees of freedom of the constituent particles and their translations may be switched off by a continuous deformation of a spheroid of aspect ratio t into a sphere ($t = 1$). We demonstrate, by experiments, theory, and computer simulations, that dramatic nonanalytic changes in structure and thermodynamics of the fluids take place, as the coupling between rotations and translations is made to vanish. This nonanalyticity, reminiscent of a second-order liquid-liquid phase transition, is not a trivial consequence of the shape of an individual particle. Rather, free volume considerations relate the observed transition to a similar nonanalyticity at $t = 1$ in structural properties of jammed granular ellipsoids. This observation suggests a deep connection to exist between the physics of jamming and the thermodynamics of simple fluids.

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The thermodynamics of a fluid of simple spheres is well-known and almost completely understood [1,2]. However, the constituents of real matter are typically nonspherical. Their translational degrees of freedom are coupled to their rotations [3]. A system of spheroids, ellipsoids of revolution, is arguably the simplest model of matter, where such a coupling exists. This model has recently been realized in colloidal and granular matter experiments, providing an important insight onto the local bulk structure of fluids [4,5] and jammed packings [6]. While a very good agreement between experiment and theory has been achieved for the fluids [5,7], these studies dealt with only one specific particle aspect ratio, $t = 1.6$. The dependence of the fluid structure on the aspect ratio of the constituent particles has not been tested, so that the fundamental role played in these fluids by rotational degrees of freedom remains unknown. The understanding of jammed packings of ellipsoids is incomplete, as well. Many common order metrics are minimized for the, so-called, "maximally random jammed" (MRJ) packings [8]. Yet, it remains unclear, how the various protocols of compression, commonly starting from a fluidlike initial state, explore the available phase space and whether any fundamental physical reason exists for the convergence of many common compression protocols towards packings with densities close to that of the MRJ state [8–13].

In this work, we study the dependence of the bulk structure in fluids of ellipsoids on the aspect ratio $t = a/b$ of the constituent particles, where a and b are the polar and the equatorial diameters, respectively. We combine experiments, theory, and Monte Carlo (MC) simulations, to explore the fundamental role of the rotational degrees of freedom in these fluids, in the vicinity of the so-called "sphere point" ($t = 1$), where the coupling between rotations and translations vanishes. We demonstrate that the critical dependence of this coupling on $\epsilon \equiv |t - 1|$, for $\epsilon \to 0$, gives rise to a dramatic nondifferentiable variation of some structural and thermodynamic fluid properties. Strikingly, a similar nonanalytic behavior has been observed for the densities of jammed amorphous zero-temperature packings of frictionless ellipsoids [6,8,14], ellipses, and spherocylinders. Our observations suggest that vestiges of the jamming transition are present in thermodynamically equilibrated fluids, down to very low densities. We speculate that such vestiges may possibly be responsible for the jamming of many common fluid compression protocols near the so-called "random close packing" (rcp) of spheres, where particle volume fraction is ~0.64.

To resolve the local structure in fluids of ellipsoids, we employ ellipsoidal colloids, suspended in an organic solvent. Classical light, x-ray, or neutron scattering techniques, providing very precise structural information for spherically isotropic particles, do not allow the structure to be resolved in systems of ellipsoids; the separation between the form factor and the structure factor is a major challenge for moderate t, due to the coupling between particle positions and orientations [15,16]. To overcome this obstacle, we carry out real-space experiments, employing direct confocal microscopy [17]. We prepare our colloidal ellipsoids by a uniaxial stretching of PMMA (polymethymethacrylate) spheres [27–30], 2.4 ± 0.04 μm in diameter, as described elsewhere [4,5]. The particles are fluorescently labeled with Nile red for confocal microscopy and sterically stabilized by a poly-12-hydroxystearic acid (PHSA) monolayer [4,5,11]. We suspend the ellipsoids in a mixture of decahydronaphthalene and tetrachloroethylene (mass ratio of 1:1.1), where their rotational and positional degrees of freedom are thermalized by the Brownian motion. This solvent mixture matches the density and the refractive index of the colloids, eliminating particle sedimentation and allowing confocal imaging deep into the bulk of the suspensions. The particle stretching procedure damages the PHSA monolayer [4,5,30]. For $t \lesssim 1.7$, the monolayer was replenished by readsorption of PHSA from a concentrated solution [30]. For higher aspect ratios, this procedure is insufficient and particle stabilization is achieved by introduction of the AOT (dioctyl sodium sulfosuccinate, Sigma-Aldrich 98%) micelles into the suspension. The AOT micelles charge the particles, but also screen long-range Coulomb repulsions [5,31], so that the interactions become quasihard at high AOT concentrations [32]. The coherent physical behavior observed in this work for the AOT- and the PHSA- stabilized particles, at different particle aspect ratios t and volume fractions ϕ, suggests that the chemical details of the stabilizing mechanism do not matter for our current purposes. In particular, as the AOT-stabilized colloids are prolate and almost spherical, they may be regarded as simple hard spheroids, the axes of which are slightly inflated beyond their geometrical size to account for the Coulomb charging [5,7].

As a quantitative characterization of the fluid structure, we obtain the radial distribution function $g(r)$ of the particle centers, resolved by the confocal microscopy [4,5]. $g(r)$ measures the probability for two particle centers within the fluid, to be separated by a distance r. In dense fluids, $g(r)$ exhibits oscillations, which correspond to the liquid coordination shells forming around each particle, several periods of such oscillations are clearly seen in Fig. 1. Note the excellent match between the experimental data (scatter) and the theoretical calculation (solid curves), which is based on the classical Percus-Yevick (PY) approximation [33]. This agreement has been achieved with only one adjustable parameter, which is the inflation of particle axes due to the Coulomb repulsions [5]. The amount of inflation was different for the AOT- and the PHSA-stabilized particles, yet stayed the same for different particle concentrations and aspect ratios. Importantly, once the amount of particle inflation is chosen, the volume fraction and the aspect ratio of the colloids are adjusted accordingly, with no additional free parameters, as detailed elsewhere [5]. A similar agreement with the experiment is achieved for the MC simulations of hard ellipsoids, which also perfectly match the PY data [17]. Interestingly, the $g(r)$ oscillations become less pronounced for larger t (Fig. 1), with the correlations in particle positions being lost in favor of the local orientational correlations.

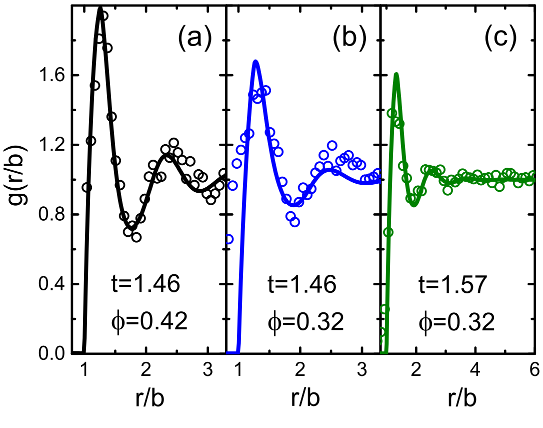

FIG. 1. Good agreement is observed between the PY-theoretical (solid curves) and the experimental (scatter) radial distribution functions $g(r)$. The data in sections (a), (b), and (c) are shown for several different particle aspect ratios t and volume fractions ϕ (see legend). The r values are normalized by the equatorial axis b of the ellipsoids. Note, the effective axes of the ellipsoids are slightly increased compared to the geometric ones, due to the charge effects (see text); the ϕ and t in the legends have been rescaled accordingly, to account for particle "inflation".

To further explore the emergence of local orientational correlations, we study the $g(r)$ for a much denser set of t values near the sphere point. Clearly, the experimental studies become increasingly challenging for a vanishing ϵ. However, the observed agreement between MC simulations, PY theory, and experiments justifies our choice to explore the critical behavior at $\epsilon \to 0$ solely by means of theory and simulation.

The most prominent feature of the $g(r)$ is its principal peak position r_p. To explore the variation of r_p with the particle aspect ratio at a constant particle volume, we normalize r_p by $L \equiv (ab^2)^{1/3}$. Strikingly, r_p/L exhibits a nonanalytic behavior at the sphere point [scatter in Fig. 2(a)], where its derivative is discontinuous. This nonanalyticity is present for different ϕ and shows up for both PY- (solid symbols) and MC- (open symbols) derived values. Importantly, this cusplike feature at $t = 1$ is not an intrinsic geometrical property of an individual ellipsoid; for example, the radius of gyration of an individual ellipsoid is smooth for all t. Remarkably, the gull wing shape of r_p/L resembles the simulated variation, as a function of t, of the particle volume fraction ϕ_j in MRJ packings of the (nonfrictional) ellipsoids [6,8]. This resemblance is not just a coincidence. The most probable separation between adjacent particles r_p must be related to the free volume available for the particles in the fluid. The fraction of free volume in a fluid, measured with respect to the most disordered jammed state (the MRJ), is $\Delta\phi = 1 - \phi/\phi_j$. This $\Delta\phi$ has also a similar gull wing shape and a cusp at $t = 1$ [Fig. 2(b)], validating our choice of MRJ as a reference state for the free volume calculation. Indeed, the free volume calculated with respect to the densest crystalline packing of the ellipsoids [8] does not exhibit such a cusp and random sequential addition (RSA) of ellipsoids produces dilute packings [34], not allowing the fluid free volume to be measured with respect to RSA.

We justify the observed nonmonotonic variation of r_p/L in fluids by simple phenomenological arguments [17]. For

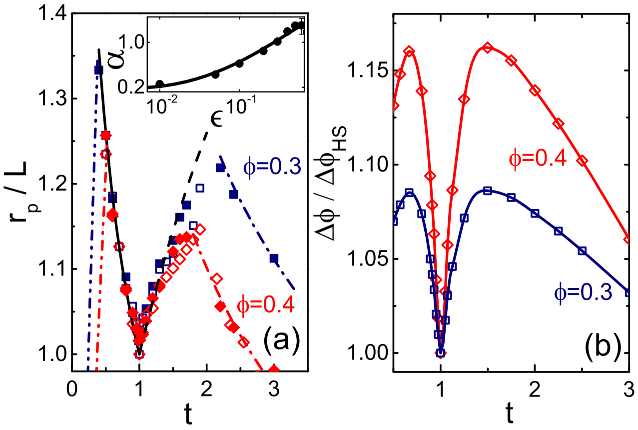

FIG. 2. (a) The separation between the nearest neighbors r_p is minimal for the spheres, with a gull wing shape exhibited as a function of t. The r_p values are normalized by $L = (ab^2)^{1/3}$, to keep the volume of the spheroids constant for all t. Data obtained by MC simulations (open symbols) and PY theory (solid symbols), for two different ϕ (see labels) stay in a very good agreement with our phenomenological predictions. Dashed and solid lines represent $r_p/L = t^{1/3}$ and $t^{-1/3}$, respectively, while dash-dotted and dash-double-dotted curves stay for $(0.77/\phi)^{1/2}t^{-1/3}$ and $(0.77/\phi)t^{2/3}$ (see text). The gull wing shape and the cusp at $t = 1$, exhibited by r_p/L, resemble the behavior of the free volume $\Delta\phi(t)$, shown in (b), where $\Delta\phi_{\mathrm{HS}} \equiv \Delta\phi(t = 1)$ is the free volume in a fluid of hard spheres at the same density. Averaging over all moderate-t data sets from section (a) minimizes the statistical noise; the resulting $\alpha \equiv r_p/L - 1$ (solid symbols in the inset, on a log-log scale) are perfectly matched [35] by $(\epsilon + 1)^{1/3} - 1 + \delta$ (solid curve), where $\delta = 0.0175$ is the accuracy of r_p/b determination.

large t, the orientational degrees of freedom dominate. While a true long-range nematic order is missing for these ϕ values, long particle axes are locally parallel. Thus, an ellipsoid of a geometric volume $\pi ab^2/6$ occupies, on average, a (roughly) ellipsoidal volume $\pi a r_p^2/6$ encompassing the particle [36]. Assuming that the volume fraction of the encompassing ellipsoids is ∼0.77, the densest packing in this range [8] of t, we obtain $r_p/L = (0.77/\phi)^{1/2}t^{-1/3}$, which perfectly matches our r_p/L, for both ϕ values (dash dotted lines in Fig. 2). A similar argument for the oblate particles at $t \ll 1$, where the volume of the encompassing ellipsoid is $\pi r_p b^2/6$, yields the dash-dot-dotted lines in Fig. 2(a). At the opposite limit $t \approx 1$, the orientations of nearly spherical particles are almost random, since the coupling between rotations and translations is very weak [37,38]. Therefore, the effective volume occupied by an oblate spheroid is a sphere of diameter b, which is the corresponding solid of revolution. In a fluid of such effective spheres, the first peak position [1,2] is $r_p = b$, so that $r_p/L = t^{-1/3}$. Once again, this prediction [solid line in Fig. 2(a)] perfectly matches our data. Finally, a short prolate spheroid, revolving freely about one of its equatorial axes, occupies an (oblate) spheroidal volume: $v_o = \pi a^2 b/6$. If such volumes are packed closely together, the separation between their centers scales as $\sim v_0^{1/3} \sim bt^{2/3}$. Identifying this separation with r_p, we obtain $r_p/L \sim t^{1/3}$. Recalling that $r_p/L = 1$ for the spheres, we obtain $r_p/L = t^{1/3}$. This relation is shown by dashes in Fig. 2(a), in a perfect agreement with both PY- and MC-generated data. Furthermore, we average the PY- and MC-r_p/L values for both ϕ in Fig. 2(a), demonstrating a perfect agreement with the proposed phenomenological expressions for oblate and prolate particles [35] of moderate t [inset to Fig. 2(a)]; for this agreement to be achieved, the average resolution of our r_p/L values $\delta = 0.0175$ had to be taken into account, dictated by the r/b-step size of the PY- and MC- $g(r)$ data being 0.015 and 0.02, respectively. Remarkably, our phenomenological arguments demonstrate that in contrast with the packings of pennies or pancakes, oblate spheroids do not tend, at moderate t, to orient in parallel to each other. Similarly, the prolate spheroids exhibit a significant freedom of rotation for $t \lesssim 2$. Thus, in contrast with the common intuition, the nonanalytic behavior at $t = 1$ is not caused by a different mutual orientation of the adjacent particles for $t \to 1^+$ and $t \to 1^-$. Moreover, the fact that our phenomenological arguments reproduce the behavior of r_p/L in fluids, and the similar shape of r_p/L and $\Delta\phi$ (Fig. 2), suggest that analogous arguments may possibly be employed to describe the local microscopic structure in jammed granular packings.

To explore the role of particle anisotropy for the fluid structure beyond the first coordination shell, we use the $g(r)$ to define a positional order parameter [39]: $\tau \equiv \int_0^\infty |g(r) - 1|^2 r^2 dr$, where r is in units of L. By definition, $\tau = 0$ for an ideal gas, where all correlations are missing. At a given ϕ, the strongest positional correlations occur for the spheres, where the orientations are completely disordered [see Fig. 3(a)]. The coupling to rotations increases for larger ϵ, resulting into a dramatic *decrease* of positional correlations measured by τ. Strikingly, τ exhibits a nonanalytic behavior at $t = 1$, as clearly demonstrated by both the PY and the MC methods. Remarkably, while the PY approach employs the classical Berne and Pechukas approximation to calculate the pair potentials [33], no such approximation is used in the MC simulations; thus, the agreement between the PY theory and the simulations strongly supports the validity of our results. Also, the experimental τ (solid symbols) match correctly the theoretical trends. As expected, for moderate t, τ increases with the particle volume fraction. In particular, for the spheres, $\tau_{\mathrm{HS}} \equiv \tau(1)$ diverges as $(0.64 - \phi)^{-1.75\pm.08}$ [Fig. 3(b)]. The divergence of τ, obtained for the equilibrium fluids, complements the previously reported [9] divergence of the *metastable* fluid equation of state at $\phi = 0.64$, which has been highly controversial [13] because of the ambiguity of the metastable fluid branch. The observed behavior suggests that a

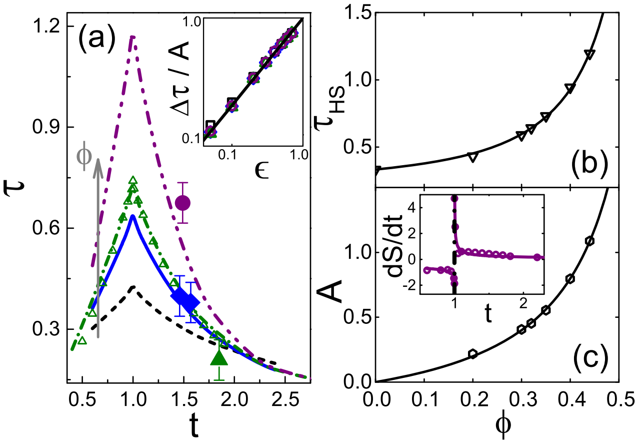

FIG. 3. (a) The strength of short-range positional correlations τ is a nonanalytic function of the particle aspect ratio t. The data are shown for $\phi = 0.20, 0.32, 0.35, 0.44$ (from bottom to top, see ϕ arrow), where rhombi, triangles, and circles correspond to $\phi = 0.32$, 0.35, and 0.44, respectively. A very good agreement is shown for the PY theory (lines), the MC simulations (open triangles), and the experiment (solid symbols); note, the experimental symbols have been shifted by a factor of 1.5, to compensate for possible inaccuracies of particle tracking. The inset demonstrates a collapse of τ for all ϕ; the corresponding normalization factors $A(\phi)$ are shown in (c). $\Delta\tau$ is the (absolute value of the) excess τ, compared to that of the hard spheres (τ_{HS}) at the same ϕ; the latter is shown in (b) to diverge towards $\phi \approx 0.64$. The inset in (c) demonstrates a discontinuity at $t = 1$ in the derivative dS/dt of the excess translational entropy, as in a second-order phase transition; here dS/dt is obtained for $\phi = 0.44$ and normalized by $-2\pi k_B \rho L^3$ for nondimensionalization.

deep relation exists between the local structure in fluids and the onset of jamming, where a global percolating force network forms [10,13].

The observed nonanalyticity of τ and r_p at $t = 1$ suggests that some other properties of the fluid may also be singular at the sphere point, as in the case of a phase transition. To directly test the fluid thermodynamics, we calculate the excess translational entropy (relative to an ideal gas at the same density), approximated [40,41] by: $S \approx -2\pi k_B \rho \int [g(r) \ln g(r) - g(r) + 1] r^2 dr$, where k_B is the Boltzmann factor and ρ is the particle number density. As expected, the derivative dS/dt is discontinuous at the sphere point [inset to Fig. 3(c)], reminiscent of a second-order transition. Furthermore, we observe that the critical scaling of $\Delta\tau \equiv |\tau(t) - \tau_{\mathrm{HS}}|$ allows the $\Delta\tau$ for all ϕ to be collapsed together [inset to Fig. 3(a)], indicating that $\Delta\tau = A(\phi)\epsilon^{3/4}$; here $A(\phi)$ is a function of ϕ only, diverging as $|\phi - 0.64|^{-1.24\pm.04}$ [Fig. 3(c)]. The observed divergence of $A(\phi)$ is caused by the divergence of $\tau_{\mathrm{HS}}(\phi)$ and does not necessarily imply a divergence of $\tau(t > 1)$. Indeed, studies of granular packings of ellipsoids [6,8], demonstrate that the jamming in these systems occurs at a higher ϕ.

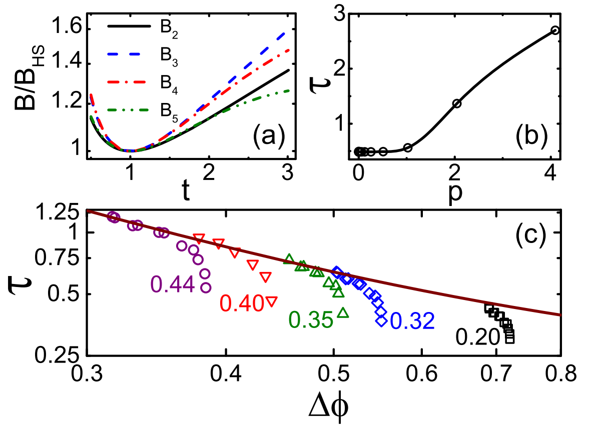

FIG. 4. (a) The second–fifth virial coefficients of the ellipsoids [42] (see legend) exhibit a smooth variation with t near the sphere point, indicating that the nonanalytic behavior of $\tau(t)$ and $S(t)$ is caused by higher-order terms of the virial expansion, as in the critical phenomena. (b) Not all types of spherical anisotropy are the same. In fluids of dipolar spheres [17], interacting through a truncated Lennard-Jones potential [5], τ is a smooth function of the dipole magnitude p, down to $p = 0$, where rotational anisotropy completely vanishes; p is in the Lennard-Jones units [17]. (c) The magnitude of translational correlations τ in fluids of ellipsoids is fully determined, for small ϵ, by the free volume in the fluid, with respect to the MRJ packing of the corresponding ellipsoids. For larger ϵ, nonuniversal deviations from this scaling (solid curve) are observed. Labels indicate the ϕ value of each data set; the data were obtained by PY calculations.

The nondifferentiability of τ at $t = 1$, precluding series expansion, demonstrates that the rotational anisotropy, missing for the simple spheres, qualitatively changes the fluid structure. Interestingly, the virial coefficients of the ellipsoids [42], in contrast with $\tau(t)$, exhibit a smooth variation in the vicinity of the sphere point [Fig. 4(a)], indicating that the nonanalyticity of τ is caused by a complex collective behavior in the fluid, rather than being a trivial property of the particle geometry. Moreover, we observe a continuous variation of τ in molecular dynamics simulations of a dipolar fluid [17], as the magnitude of the dipole is taken continuously to zero [Fig. 4(b)]. Thus, the emergence of different types of spherical anisotropy influences the fluid structure in a different manner.

Finally, it is highly appealing to regard a fluid of ellipsoids as simply an expanded jammed packing. In such case, the only relevant parameter is $\Delta\phi$. Our τ values, plotted for all different ϕ and t as a function of $\Delta\phi$ [Fig. 4(c)] demonstrate that a common scaling (solid curve) can be found, matching all data at small ϵ. However, for larger ϵ, the data significantly deviate from the common curve, indicating that $\Delta\phi$ is no longer the only important parameter; other related manifestations of nonuniversality have been recently detected [43]. This behavior is reminiscent of a critical scaling near the classical phase transitions, where a universal behavior applies at the critical point, yet deviations may be observed when the system is further away from the criticality.

In conclusion, we demonstrate that a nonanalytic behavior of structural and thermodynamic fluid properties occurs at the sphere point, reminiscent of a second-order phase transition. We relate this transition to the emergence of a coupling between translations and rotations at $t = 1$, which is also responsible for similar nonanalyticities in structural properties of jammed granular packings of ellipsoids [6,8,14], ellipses [44], and spherocylinders [45]. Moreover, fingerprints of such nonanalyticities seem also to show up in critical temperatures and concentrations of liquid-vapour transitions in attractive liquids [46], emphasizing the importance of the simpler athermal systems studied in our present work. We describe some aspects of the observed liquid-liquid transition by phenomenological free volume arguments, suggesting that the MRJ packing of ellipsoids plays a role of a ground state for these fluids. Future theoretical and experimental research, directly probing the orientational degrees of freedom in these systems, should provide a deeper insight onto the physics of fluids and random granular packings, providing a better understanding of the ground states of matter.

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