Isoenergetic Jamming Transition in Particle-Filled Systems

Christopher G. Robertson and Xiaorong Wang
Bridgestone Americas, Center for Research and Technology,
1200 Firestone Parkway, Akron, Ohio 44317-0001, USA

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A full understanding of the jamming transition remains elusive, but recent advances which draw upon the common features of frustrated systems are encouraging. Herein, we show that, for mixtures of oil and silica particles, the dependence of the dejamming stress on filler volume fraction, ϕ, is consistent with the shape of a reported jamming phase diagram [Trappe *et al.*, Nature (London) **411**, 772 (2001)]. We discover for the first time, however, that the role of ϕ disappears when mechanical energy input, defined as stress multiplied by strain, is used instead of stress as the critical parameter. We also examine literature results for aqueous suspensions of boehmite alumina powders, latex dispersions of polystyrene particles, and carbon black-filled elastomers in order to illustrate the universality of our finding. This study provides evidence for a thermodynamic interpretation of the jamming transition.

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Jamming processes can occur in a variety of systems of diverse characteristic length scales, including quantum spins, molecular structures, colloidal suspensions, polymer-filler composites, granular materials, and even automobile traffic. Jamming and glass-formation processes appear to have interrelated physics [1]. One striking example of the parallel between the jamming of particles and the glass transition is the finding that granular materials subjected to tapping or vibration exhibit diffusive noise which depends on the perturbation intensity in a manner which is qualitatively similar to the non-Arrhenius increase in viscosity as the glassy state is approached during cooling of liquids [2,3]. Indeed, deformation in jammed particle-filled systems, and in other jammed athermal systems such as foams, appears to act as temperature in typical glass-forming liquids. The notion of "effective temperature" has been proposed in these complex materials where solid-to-liquid transitions are driven by the applied stress, strain, or vibration [1–6].

Based on the view of jammed particles and glasses as related materials, Liu and Nagel [7] proposed a jamming phase diagram with axes of temperature, load (stress), and $1/\rho$, where ρ is the density of particles in the system. Indeed, such a phase diagram was demonstrated experimentally for attractive particles by Trappe *et al.* [8], although the experimental shape was concave versus the proposed convex diagram. The density of particles was varied via the volume fraction of filler, ϕ, in the suspending fluid in the study by Trappe and co-workers. In this Letter, we consider the nonlinear oscillatory shear rheology for mixtures of oil and silica particles as a function of ϕ to further study this jamming phase diagram and offer new insights into the nature of the jamming transition.

Mixtures of oil and silica particles were formed by high shear mechanical mixing. The oil used was diisodecyl adipate from The C. P. Hall Company. This oil has a density of 0.918 $\mathrm{g/cm^3}$, a viscosity of 30 cP at 25 °C, and a glass transition temperature of −43 °C. The silica employed was Nan-O-Sil amorphous colloidal silica powder from Energy Strategy Associates, Inc. The silica particles were surface treated with tetrasulfidosilane. The silica powder is made up of spherical particles with diameters in the range from 10 to 500 nm. We determined the average particle diameter to be about 100 nm using microscopy. The density of the silica in the particles has a reported value of 2.1 $\mathrm{g/cm^3}$. Viscoelastic measurements were conducted in oscillatory shear using a Rheometrics ARES strain-controlled rheometer with dual (200 and 2000 g cm) force rebalance transducers. A cone and plate geometry was used to ensure a homogeneous strain field. The plate diameter/cone angle combination used was either 15 mm/0.1 radian or 25 mm/0.02 radian, depending on the filler volume fraction and related compliance of the mixture. After each mixture was loaded between the cone and plate fixtures and the normal force relaxed to zero, oscillatory shear was applied at 30 °C, 0.5 Hz, and 10% strain for 10 min. The material was then allowed to equilibrate at 30 °C, 0.5 Hz, and 0.004% strain before performing a strain sweep from 0.004% to 74%, in logarithmic increments, at $\omega = 3.14$ rad/s ($f = 0.5$ Hz) and 30 °C. The strain during oscillatory shearing was varied according to $\gamma(t) = \gamma^0 \sin(\omega t)$, where γ^0 is the strain amplitude. For simplicity, our use of strain γ in this Letter corresponds to the amplitude value (we do not include the superscript 0). The maximum in-phase stress σ at the point where the strain reaches its maximum value is given by $\sigma = G'\gamma$, where G' is the dynamic storage modulus.

Storage modulus G' and loss modulus G'' are given in Fig. 1 as functions of both strain amplitude and filler volume fraction for the oil-silica mixtures. At low strains, a strain-independent jammed state is observed with solid-like behavior characterized by $G'_0 \gg G''_0$ ($G'/G'' = 20$ to 30). The subscript 0 denotes the zero-strain limiting values. As strain is increased further, a breakup of the jammed state occurs and the material transitions into the liquid state ($G' < G''$). The locus of the jamming transition can be

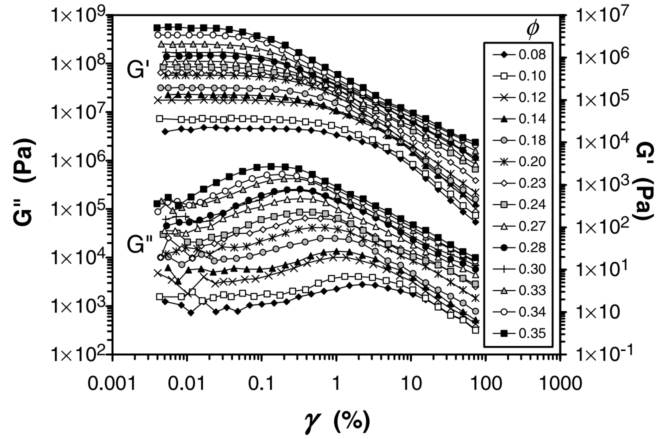

FIG. 1. Strain dependence of dynamic storage and loss moduli at 30 °C and 0.5 Hz for the oil-silica mixtures with the indicated filler volume fractions.

assigned as the extent of deformation where the maximum in the loss modulus $G''_{\max}$ transpires. An essentially equivalent definition of the jamming transition is where G' is reduced by half. It can be observed from Fig. 1 that the critical strain γ_c at the jamming transition decreases with ϕ. In contrast, the critical stress σ_c is an increasing function of ϕ. Mechanical energy, in units of Joule per volume [9], can be defined as stress multiplied by strain, $\sigma\gamma$. It is remarkable to note in Fig. 2 that normalized storage and loss moduli collapse onto universal curves when plotted against $\sigma\gamma$. The extent of vertical normalization is certainly influenced by filler volume fraction, but no horizontal shifting is required to superimpose the results for the entire range of data ($0.08 \leq \phi \leq 0.35$) when plotted versus $\sigma\gamma$ rather than as functions of stress or strain alone. The relationship between the critical stress σ_c at the jamming transition and $1/\phi$ for our oil-silica materials is in agreement with the isothermal plane of the jamming phase diagram reported by Trappe *et al.* [8]. However, when the location of the jamming transition is defined by $\sigma_c\gamma_c$, a constant energy value is found, independent of ϕ. These observations are illustrated in Fig. 3. To our knowledge, this is the first time that the isoenergetic behavior of the jamming transition has been uncovered. This constant mechanical energy required for the solid-to-liquid transition to occur for our particle-filled materials provides evidence for a thermodynamic interpretation of the jamming transition.

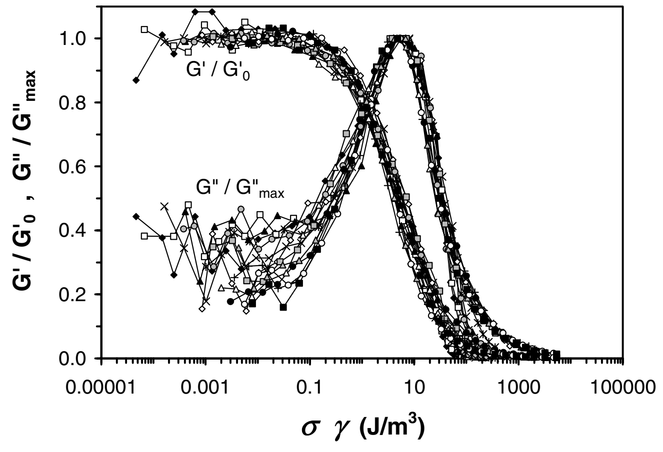

FIG. 2. Normalized dynamic storage and loss moduli at 30 °C and 0.5 Hz plotted versus $\sigma\gamma$ for the oil-silica mixtures. The storage modulus data are vertically scaled by G'_0, the zero-strain limiting value of G', and the loss modulus data are normalized by $G''_{\max}$, the peak value of G''. The symbol legend is the same as that given in Fig. 1.

A notable thermodynamic construction for the out-of-equilibrium jammed state has been developed by Edwards and co-workers [10–13] and successfully applied, for example, to understand the elegant vibrated beads experiments of Nowak *et al.* [14,15]. Edwards's approach defines the jammed solid in terms of granular compactivity and effective temperature. In our oil-silica system, the volume is set by ϕ, and it is expected that the volume does not change appreciably as the mixtures transition between jammed and liquidlike states; hence the concept of compactivity is not of key relevance. The effective temperature from Edwards's thermodynamic description of jammed granular materials was recently shown to be very similar to the effective temperature determined by application of the fluctuation-dissipation relation to a driven, athermal system [16]. Our observation that a critical mechanical energy is necessary to break up a jammed structure may be related to the notion of a critical effective temperature.

One technologically important area where particle jamming processes are manifested is the use of vulcanized elastomers containing fillers such as carbon black and silica in numerous applications which include gaskets, damping materials, and automobile tires. In automobile tires, typical dynamic stresses and strains place the behavior of the tread rubber compounds right in the middle of the jamming transition range. The process of breakup and

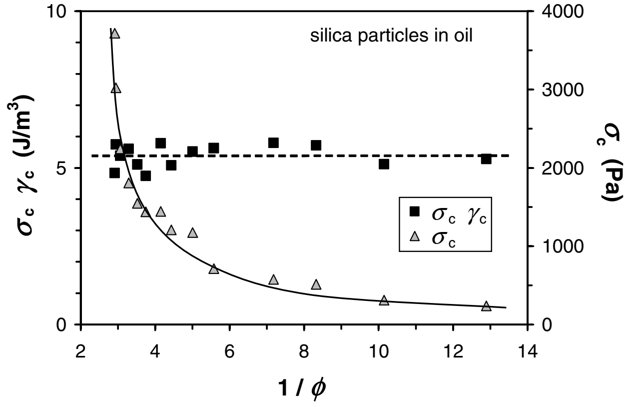

FIG. 3. Critical stress (σ_c) and energy ($\sigma_c\gamma_c$) versus $1/\phi$ for oil-silica mixtures. The lines are included to guide the eye.

reformation of the filler-filler network during deformation of the tread rubber is a significant contributor to hysteresis in tires which impacts vehicle gas mileage. Payne [17] was the first to document the strong reduction in storage modulus and increase in tanδ due to increasing dynamic strain amplitude in elastomers containing fillers, and such nonlinear viscoelasticity in filled rubbers is often called the Payne effect. A sound theoretical model of the Payne effect has yet to emerge. We realize that the Payne effect simply reflects a jamming-unjamming process. In Fig. 4, our analysis of Payne's original data further confirms our assertion that the jamming transition is isoenergetic and independent of filler volume fraction. Although Payne published a later paper [18] which suggested the importance of both stress and strain on the onset of nonlinearity in filled elastomers, this aspect of the Payne effect has been unappreciated in the literature. The results in Figs. 3 and 4 are very similar although the quantity $\sigma_c \gamma_c$ is much greater for the vulcanized natural rubber material containing carbon black compared to our oil-silica mixtures (3000 J/m^3 versus 5 J/m^3). This is not surprising as we expect the critical energy value at the jamming transition to depend on the nature of the liquid or rubbery material surrounding the fillers as well as the shape, size, and interaction forces of the particles. Our own results on carbon black-filled rubbers (not shown) are consistent with our analysis of Payne's data in Fig. 4.

The scaling behavior of various jammed particle-filled materials has been investigated for some time. The low strain dynamic storage modulus G_0' and the yield strain associated with the onset of nonlinearity in viscoelasticity γ_y are commonly described by the following power laws:

$$G_0' \propto \phi^a, \tag{1}$$

$$\gamma_y \propto \phi^{-b}, \tag{2}$$

where a and b are the characteristic exponents. From these reported relationships, we formulate the analogous expression for the yield stress:

$$\sigma_y = G_0' \gamma_y \propto \phi^{a-b}. \tag{3}$$

The stress and strain at the onset of nonlinearity (yielding) are analogous to our definitions of the critical stress and strain at the jamming transition, although they are consistently offset as shown in Figs. 1 and 2. Therefore, we can use the subscripts y and c interchangeably. From Eqs. (2) and (3), the product of stress and strain is found to be proportional to volume fraction to the exponent $a - 2b$:

$$\sigma_c \gamma_c \propto \sigma_y \gamma_y \propto \phi^{a-2b}. \tag{4}$$

Based on our experimental observations that $\sigma_c \gamma_c$ is independent of filler volume fraction, we propose a scaling law between the exponents a and b:

$$\sigma_c \gamma_c \neq f(\phi) \Rightarrow a - 2b \approx 0. \tag{5}$$

Using Eqs. (1) and (2), we determined values of $a = 3.3 \pm 0.2$ and $b = 1.7 \pm 0.1$ for the oil-silica system. Similar parameters of $a = 3.4 \pm 0.3$ and $b = 1.7 \pm 0.1$ were evaluated from Payne's data on carbon black-filled rubber [17]. These exponents support our claim in Eq. (5); this is not surprising given the lack of variation of $\sigma_c \gamma_c$ with respect to ϕ, which we demonstrated earlier in Figs. 3 and 4.

Shih *et al.* investigated aqueous suspensions of two types of boehmite alumina powders, catapal and dispal [19]. The catapal gels yielded scaling exponents of $a = 4.1$ and $b = 2.1$, and the scaling behavior of the dispal gels was characterized by $a = 4.2$ and $b = 2.3$. Weakly aggregating dispersions of polystyrene particles displayed $a = 4.6 \pm 0.3$ and $b = 2.5 \pm 0.3$ according to de Rooij and coworkers [20]. The results of these studies provide further confirmation of our scaling law assertion of $a - 2b \approx 0$. This independence of $\sigma_c \gamma_c$ with respect to ϕ was not recognized by these investigators. We do note that some particle-filled liquid systems which also contain polymeric stabilizers [8,21] do not conform to this isoenergetic behavior. The jammed particle networks in these systems are expected to be less developed, and the dynamics of the adsorbed polymer may also contribute to the nonlinear rheology.

In summary, we observe that silica-oil mixtures, elastomers filled with carbon black, alumina suspensions, and polystyrene particle dispersions all have jamming transitions characterized by $\sigma_c \gamma_c$ values which are independent of particle concentration. These systems differ widely in the strength and type of interparticle forces as well as the shape, average size, and size distribution of the particles. Furthermore, the dispersing fluids are quite diverse, ranging from low molecular weight liquids to crosslinked polymers. The isoenergetic nature of the jamming transition appears to be a universal feature of these systems. We emphasize that a critical mechanical energy, a thermodynamic quantity, appears to control the breakup of a jammed state, and this product of stress and strain is

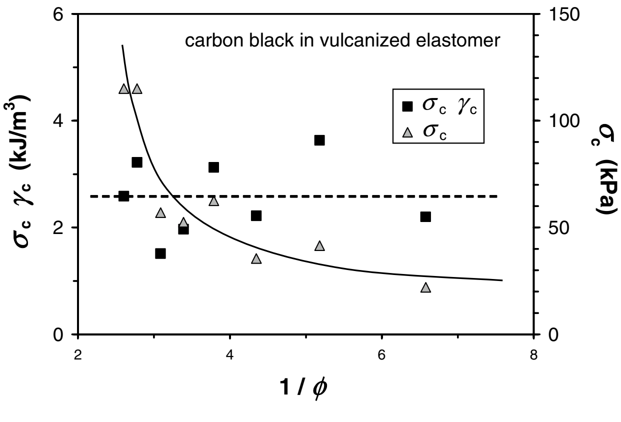

FIG. 4. Critical stress (σ_c) and energy ($\sigma_c \gamma_c$) versus $1/\phi$ for carbon black-filled rubber. The σ_c and γ_c data are taken directly from Table I of Ref. [17], although we divided the reported double strain and stress values by two for consistency with the more traditional definitions. The lines are included to guide the eye.

independent of filler volume fraction. The magnitude of this energy is a function of the elasticity of the jammed fractal structure and the interaction strength between particles. It is noteworthy that this mechanical energy, similar to thermal energy (kT), is theoretically derivable from Hamiltonians, which makes it a natural choice as a parameter in constructing phase diagrams. Based on our findings, the relevance of the σ versus $1/\phi$ plane of the proposed jamming phase diagram [7,8] is not clear.

Our investigation reveals the isoenergetic character of the jamming transition. We observe a critical mechanical energy input, independent of particle density, which is associated with the solid-to-liquid transition in particle-filled systems. This is a new discovery which suggests that the jamming process may be thermodynamic in nature. The jamming of particulate materials is also kinetic [22,23]. The coexistence of kinetic and thermodynamic descriptors of the jamming transition is analogous to observations about the glass transition. The similarities between the phenomenological features of the jamming transition in particulate materials and the glass transition of liquids indicate that large-scale crowding or pinning of particles and molecular cooperativity or caging may be components of a larger unified physical picture of dynamics in frustrated systems.

[1] See contributions in *Jamming and Rheology: Constrained Dynamics on Microscopic and Macroscopic Scales*, edited by A. J. Liu and S. R. Nagel (Taylor and Francis, New York, 2001).

[2] G. D'Anna and G. Gremaud, Phys. Rev. Lett. **87**, 254302 (2001).

[3] G. D'Anna and G. Gremaud, Nature (London) **413**, 407 (2001).

[4] P. Sollich, F. Lequeux, P. Hebraud, and M. E. Cates, Phys. Rev. Lett. **78**, 2020 (1997).

[5] I. K. Ono, C. S. O'Hern, S. A. Langer, A. J. Liu, and S. R. Nagel, Phys. Rev. Lett. **89**, 095703 (2002).

[6] L. Berthier and J.-L. Barrat, J. Chem. Phys. **116**, 6228 (2002).

[7] A. J. Liu and S. R. Nagel, Nature (London) **396**, 21 (1998).

[8] V. Trappe, V. Prasad, L. Cipelletti, P. N. Segre, and D. A. Weitz, Nature (London) **411**, 772 (2001).

[9] The use of proper units for stress ($\mathrm{Pa} = \mathrm{N/m^2}$) and strain (m/m) leads to $\sigma\gamma$ having units of energy density, $\mathrm{J/m^3}$.

[10] A. Mehta and S. F. Edwards, Physica (Amsterdam) **157A**, 1091 (1989).

[11] S. F. Edwards and R. B. S. Oakeshott, Physica (Amsterdam) **157A**, 1080 (1989).

[12] S. F. Edwards, *Current Trends in the Physics of Materials* (North-Holland, Amsterdam, 1990).

[13] S. F. Edwards, in *Granular Matter: An Interdisciplinary Approach*, edited by A. Mehta (Springer, New York, 1994).

[14] E. R. Nowak, J. B. Knight, M. L. Povinelli, H. M. Jaeger, and S. R. Nagel, Powder Technol. **94**, 79 (1997).

[15] E. R. Nowak, J. B. Knight, E. Ben-Naim, H. M. Jaeger, and S. R. Nagel, Phys. Rev. E **57**, 1971 (1998).

[16] H. A. Makse and J. Kurchan, Nature (London) **415**, 614 (2002).

[17] A. R. Payne, J. Appl. Polym. Sci. **6**, 57 (1962).

[18] A. R. Payne, J. Appl. Polym. Sci. **8**, 2661 (1964).

[19] W.-H. Shih, W. Y. Shih, S.-I. Kim, J. Liu, and I. A. Aksay, Phys. Rev. A **42**, 4772 (1990).

[20] R. de Rooij, D. van den Ende, M. H. G. Duits, and J. Mellema, Phys. Rev. E **49**, 3038 (1994).

[21] V. Prasad, V. Trappe, A. D. Dinsmore, P. N. Segre, L. Cipelletti, and D. A. Weitz, Faraday Discuss. **123**, 1 (2003).

[22] L. E. Silbert, D. Ertas, G. S. Grest, T. C. Halsey, and D. Levine, Phys. Rev. E **65**, 051307 (2002).

[23] P. N. Segre, V. Prasad, A. B. Schofield, and D. A. Weitz, Phys. Rev. Lett. **86**, 6042 (2001).