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Comment on "Critical exponent for glassy packing of rigid spheres and disks"

Moorad Alexanian
Department of Physics, University of North Carolina at Wilmington, Wilmington, North Carolina 28403-3297

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S. Jasty, M. Al-Naghy, and M. de Llano recently presented [Phys. Rev. A **35**, 1376 (1987)] an argument to justify the weak divergence of the pressure at random close packing for a classical continuous system with hard cores. Their analysis is based on the behavior of the equilibrium canonical partition function at random close packing. Therefore this approach is erroneous owing to the nonequilibrium nature of the glassy state.

In a recent article,[1] an attempt is presented to justify the conjecture that the pressure P of a system of hard disks or hard spheres has an algebraic singularity at the Bernal density ρ_B and so

$$P/\rho_B kT \rightarrow D(1-\rho/\rho_B)^{-\alpha} \quad \text{as } \rho \rightarrow \rho_B , \tag{1}$$

with $D > 0$ and $0 < \alpha < 1$. The argument used in Sec. II of Ref. 1 is based on the nonvanishing of the equilibrium canonical partition function $Q(N,V,T)$ at ρ_B and on the expansion of $Q(N,V,T)$ about $\rho = \rho_B$. Now it is well known that a classical continuous system of hard disks or hard spheres possesses a thermodynamic limit owing to the stability and the temperedness of the hard-core potential.[2] Therefore, in the thermodynamic limit, the equilibrium partition function $Q(N,V,T)$ gives rise to a unique[2] pressure P, which is a continuous, decreasing function of the specific volume $v = \rho^{-1}$. Accordingly, in the thermodynamic limit, the equilibrium partition function $Q(N,V,T)$ yields the two equilibrium branches of the equation of state joined by a straight tie-line which corresponds to the first-order Kirkwood transition. In addition, P possesses[3] a simple pole at the density ρ_0 of closest packing (stable crystalline phase). Accordingly, the pressure P is finite for $0 \leq \rho < \rho_0$. Therefore,[3] for arbitrarily large N,

$$Q(N,V,T) \rightarrow Q(N,Nv_B,T)e^{CN(1-v_B/v)} \quad \text{as } v \rightarrow v_B , \tag{2}$$

where $v_B^{-1} = \rho_B < \rho_0$ and C is a pure number. Note that (2) yields, with the aid of Eqs. (1) and (2) of Ref. 1, the expected finite pressure $P/kT \rightarrow Cv_B^{-1}$ as $v \rightarrow v_B$. Therefore Eq. (11) of Ref. 1 is erroneous for two reasons. Firstly, only two terms in the expansion of the exponential function in (2) are kept. This leads to the wrong Helmholtz free energy per particle f in the thermodynamic limit, defined by Eq. (2) of Ref. (1), viz., f independent of v and so $P = 0$. [This result can also be corroborated directly from the formulas of Ref. 1, since according to Eq. (12), an intensive pressure requires that $B/A = O(N)$ and $\beta = O(N^{-1})$ as $N \rightarrow \infty$. However, this latter behavior implies the contradictory result, which follows from Eqs. (2) and (11) of Ref. 1, that f is independent of v.] Clearly, all the terms in the exponential function in (2), an infinite number, must be kept. Secondly, $\beta N \rightarrow 1$ as $N \rightarrow \infty$ since the pressure P, which is defined after the thermodynamic limit is taken [see Eqs. (1) and (2) of Ref. 1], does not diverge at $v = v_B$. Therefore, $\alpha = 0$ in Eq. (12).

Now on rapid cooling, the equilibrium liquid may bypass crystallization and solidify continuously into a glass—via the (metastable) supercooled liquid phase. Experimentally, therefore, a (nonequilibrium) glass may be obtained as an extension of the equilibrium fluid branch. Nonetheless, metastable states cannot be derived from the equilibrium partition function after the thermodynamic limit has been taken. Consequently, knowledge of the equilibrium partition function only is of no avail in the study of a metastable or a nonequilibrium state. However, partial knowledge of P, for instance, in the form of the first few virial coefficients, may be used to generate a nonequilibrium pressure, as is done in Ref. 1 via Padé approximants. Also, knowledge of the thermodynamic pressure of a supercooled liquid or an amorphous solid—for instance, via molecular-dynamics computer simulations—yields a partition function which is different from that of the stable crystalline solid phase.[3,4] Therefore, if an algebraic singularity is assumed in a (nonequilibrium) thermodynamic pressure P at an amorphous close-packing density $\rho_1 < \rho_0$, then

$$P/\rho_1 kT \rightarrow B(1-\rho/\rho_1)^{-\mu} \quad \text{as } \rho \rightarrow \rho_1 , \tag{3}$$

with $B > 0$ and $\mu > 0$. However, the value of μ can be restricted if one invokes[3] the finiteness of the heat capacity as $\rho \rightarrow \rho_1$. Now

$$\frac{C_P}{Nk} - \frac{3}{2} = -\left[\frac{P^2}{NkT}\right]\left[\frac{\partial V}{\partial P}\right]_T \rightarrow B\mu^{-1}\left[1-\frac{\rho}{\rho_1}\right]^{-\mu+1} \quad \text{as } \rho \rightarrow \rho_1 . \tag{4}$$

Therefore, if C_P is finite, then[3] $0 < \mu \leq 1$. Clearly, the case $\mu = 1$ cannot be excluded. The behavior (3) with $0 < \mu < 1$ results from a nonequilibrium partition function $Q_{\text{ne}}(N,V,T)$ which, for arbitrarily large N, gives[3]

$$Q_{\mathrm{ne}}(N,V,T)\to Q_{\mathrm{ne}}(N,Nv_1,T)\exp\left[\frac{BN}{1-\mu}\left[1-\frac{v_1}{v}\right]^{1-\mu}\right] \quad \text{as } v\to v_1\ , \qquad (5)$$

with $Q_{\mathrm{ne}}(N,Nv_1,T)\neq 0$. Note again that all the terms in the infinite series for the exponential function are essential for the occurrence of the singularity in (3). Finally, the behavior (3) with $\mu=1$ corresponds[3] to the case when $Q_{\mathrm{ne}}(N,Nv_1,T)=0$, viz.,

$$Q_{\mathrm{ne}}(N,V,T)\to f(N,T)\left[1-\frac{v_1}{v}\right]^{BN} \quad \text{as } v\to v_1\ ,$$

where $f(N,T)$ is independent of v.

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[1] S. Jasty, M. Al-Naghy, and M. de Llano, Phys. Rev. A **35**, 1376 (1987).

[2] D. Ruelle, *Statistical Mechanics: Rigorous Results* (Benjamin, New York, 1969).

[3] M. Alexanian, Phys. Rev. A **31**, 4018 (1985).

[4] M. Alexanian and S. K. Bose, Ann. N.Y. Acad. Sci. **484**, 297 (1986).