Comment on "Test of nonequilibrium thermodynamics in glassy systems: The soft-sphere case"

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In this Comment, I show that the free energy expression for a glass proposed by La Nave *et al.* [Phys. Rev. E **68**, 032103 (2003)] cannot be correct since it violates the second law of thermodynamics.

Using the inherent structure (IS) formalism of the potential energy landscape, La Nave *et al.* [1] have recently proposed expressions for the free energy, F, for the equilibrium liquid and the out-of-equilibrium glassy states. The expression for the liquid state is (see the first paragraph of [1]; see also Eq. (1) of [2])

$$F^{(\text{liq})}(V,T) = -TS_{\text{conf}}(V, E_{\text{IS}}(V,T)) + E_{\text{IS}}(V,T)$$
$$+ F_{\text{vib}}(V, T, E_{\text{IS}}(V,T)). \qquad (1)$$

A glassy state is assumed to be a nonequilibrium state in which the vibrational degrees of freedom are in equilibrium with the heat bath temperature, T, but the configurational degrees of freedom are not in equilibrium with the heat bath and correspond to a different temperature, T_e. T_e is variously referred to as the configurational, or fictive, or effective temperature of the glass. The free energy of such a glass is expressed as (see Eq. (1) of [1])

$$F^{(\text{gl})}(V,T,T_e) = -T_e S_{\text{conf}}(V, E_{\text{IS}}(V,T_e)) + E_{\text{IS}}(V,T_e)$$
$$+ F_{\text{vib}}(V, T, E_{\text{IS}}(V,T_e)). \qquad (2)$$

In these expressions, $E_{\text{IS}}(V,T)$ is the average energy of IS explored by the system of volume V at the heat bath temperature T. $S_{\text{conf}}(V, E_{\text{IS}})$ is the configurational entropy representing the degeneracy of inherent structures of depth, E_{IS}. $F_{\text{vib}}(V, T, E_{\text{IS}})$ is the vibrational free energy of an average basin of depth E_{IS}. Equation (2) reduces to Eq. (1) for the equilibrium liquid for which $T_e = T$.

The purpose of my Comment is to point out that Eq. (2) is inconsistent with the second law of thermodynamics. To show this, I consider structural relaxation of a glass of configurational temperature T_e when it is placed in contact with a heat bath of temperature T (where $T < T_e$). During relaxation, the glass will begin to explore basins of energy other than $E_{\text{IS}}(T_e)$. After a sufficiently long time, the glass will equilibrate to the liquid state at the temperature T and T_e becomes equal to T. According to the second law of thermo-

dynamics, the free energy of the system must decrease during such a relaxation process and requires that

$$\Delta F(V,T,T_e) < 0, \qquad (3)$$

where

$$\Delta F(V,T,T_e) \equiv F^{(\text{liq})}(V,T) - F^{(\text{gl})}(V,T,T_e). \qquad (4)$$

It follows, from Eqs. (1)–(4), that (suppressing the V dependence from now on)

$$\Delta F(T,T_e) = -TS_{\text{conf}}(E_{\text{IS}}(T)) + T_e S_{\text{conf}}(E_{\text{IS}}(T_e)) + E_{\text{IS}}(T)$$
$$- E_{\text{IS}}(T_e) + \Delta F_{\text{vib}}(T,T_e). \qquad (5)$$

To present my argument in the simplest form, I consider the limiting case when F_{vib} is same for all basins. This assumption is not critical for the arguments and conclusions that follow. With this assumption, $\Delta F_{\text{vib}}(T,T_e) = 0$ and Eq. (5) reduces to

$$\Delta F(T,T_e) = -TS_{\text{conf}}(E_{\text{IS}}(T)) + T_e S_{\text{conf}}(E_{\text{IS}}(T_e))$$
$$+ E_{\text{IS}}(T) - E_{\text{IS}}(T_e). \qquad (6)$$

Expanding $S_{\text{conf}}(E_{\text{IS}}(T_e))$ about its values at T, one obtains

$$S_{\text{conf}}(E_{\text{IS}}(T_e)) = S_{\text{conf}}(E_{\text{IS}}(T)) + (E_{\text{IS}}(T_e) - E_{\text{IS}}(T))(1/T) + \cdots. \qquad (7)$$

Here I follow the arguments of Ruocco *et al.* [3] in substituting T^{-1} for $(dS_{\text{conf}}/dE_{\text{IS}})_T$ in the above equation. Substituting Eq. (7) in Eq. (6), and keeping only terms of first order in $(T_e - T)$, one obtains

$$\Delta F(T,T_e) = (T_e - T)S_{\text{conf}}(E_{\text{IS}}(T))$$
$$+ ((T_e/T) - 1)[E_{\text{IS}}(T_e) - E_{\text{IS}}(T)] + \cdots. \qquad (8)$$

Since $E_{\text{IS}}(T)$ is a monotonically increasing function of T [4], it follows from Eq. (8) that $\Delta F(T,T_e)$ is > 0 whenever $T_e > T$. This is a violation of the second law as expressed by Eq. (3)

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[1] E. La Nave, F. Sciortino, P. Tartaglia, M. S. Shell, and P. G. Debenedetti, Phys. Rev. E **68**, 032103 (2003).

[2] F. Sciortino and P. Tartaglia, Phys. Rev. Lett. **86**, 107 (2001).

[3] G. Ruocco, F. Sciortino, F. Zamponi, C. DeMichelle, and T.

Scopigno, J. Chem. Phys. **120** 10666 (2004) (See comment no. 44 of this paper).

[4] E. La Nave, F. Sciortino, P. Tartaglia, C. DeMichele, and S. Mossa, J. Phys.: Condens. Matter **15**, S1085 (2003).