

Reply to “Comment on Test of nonequilibrium thermodynamics in glassy systems: The soft-sphere case”

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We show that Gupta’s Comment is incorrect, since the equilibration process in question is not isothermal, and hence the free energy does not decrease. We furthermore show that our free energy expression [E. La Nave, F. Sciortino, P. Tartaglia, M. S. Shell, and P. G. Debenedetti, Phys. Rev. E **68**, 032103 (2003)] satisfies the second law.

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In the nonequilibrium thermodynamic formalism [1–4], structural glasses are characterized by vibrational and configurational degrees of freedom. The vibrational degrees of freedom are in equilibrium with the heat bath temperature, T . The configurational degrees of freedom are thermalized at a different temperature, $T_e > T$. In the inherent structure (IS) formalism, the free energy of a glass is expressed as [3,4]

$$F^{\text{gl}}(V, T, T_e) = -T_e S_{\text{conf}}(V, E_{\text{IS}}) + E_{\text{IS}} + F_{\text{vib}}(V, T, E_{\text{IS}}), \quad (1)$$

where E_{IS} is the energy of the IS (local minimum of the potential energy surface) explored by the glass, $S_{\text{conf}}(V, E_{\text{IS}})$ is the configurational entropy representing the degeneracy of inherent structures of depth E_{IS} and $F_{\text{vib}}(V, T, E_{\text{IS}})$ is the vibrational free energy of the system constrained in a typical basin of depth E_{IS} . For the limiting case discussed by Gupta in his Comment, for which F_{vib} is not a function of E_{IS} , T_e is given by [3,4]

$$T_e \frac{dS_{\text{conf}}}{dE_{\text{IS}}} = 1. \quad (2)$$

Equilibrium is reached when $T_e = T$. The notion of “equilibrium” or “isothermal process” in glasses is very subtle. Since the out-of-equilibrium glass is characterized by the two temperatures T and T_e , a generalized isothermal process would require coupling of the fast (vibrational) degrees of freedom to a bath at temperature T and coupling of the slow (configurational) degrees of freedom to a bath at temperature T_e .

In his Comment [5], Gupta argues that Eq. (1) is incorrect since it appears to violate the second law of thermodynamics. His argument is incorrect because the equilibration process in question is not isothermal. The second law of thermodynamics states that, during an irreversible equilibration process the total entropy change undergone by a closed and adiabatic system must be positive. It is only in the case of an isothermal process that the second law of thermodynamics is equivalent to stating that the free energy of the system (Helmholtz for isochoric processes; Gibbs for isobaric ones) must decrease, but this is not the case for the equilibration of a glass.

The concept of temperature in glasses is not trivial, depending on the characteristic time of the measurement device [6]. To account for this, a nonequilibrium formalism is introduced in which the system’s slow degrees of freedom (the value of E_{IS} in the IS formalism) are at a configurational temperature T_e different from the fast degrees of freedom (vibrations). Hence, strictly speaking, the equilibration process of the configurational degrees of freedom is not isothermal. In the limiting case discussed in the Comment (E_{IS} independence of the vibrational free energy), it is shown below that the change of total entropy during an adiabatic aging process for the composite system glass and reservoir, calculated from the proposed out of equilibrium thermodynamic formalism [3,4], is strictly positive, and hence it does not violate the second law of thermodynamics.

Consider an infinitesimal step in the equilibration process of the glass, during which the system moves from a typical basin of depth E_{IS} to one of depth $E_{\text{IS}} - dE_{\text{IS}}$, with $dE_{\text{IS}} > 0$. From Eq. (2), this change of energy corresponds to a change in the configurational entropy $dS_{\text{conf}} = -dE_{\text{IS}}/T_e$. Since the composite system (glass and reservoir) is adiabatic, the configurational cooling involves a transfer of energy dE_{IS} to the bath. This produces a change in the entropy of the bath equal to $dS_{\text{bath}} = dE_{\text{IS}}/T$. The total change of entropy in the composite system (configurational degrees of freedom + bath) $dS_{\text{tot}} \equiv dS_{\text{conf}} + dS_{\text{bath}}$ is then given by

$$dS_{\text{tot}} = -\frac{dE_{\text{IS}}}{T_e} + \frac{dE_{\text{IS}}}{T} = dE_{\text{IS}} \left(\frac{1}{T} - \frac{1}{T_e} \right) > 0. \quad (3)$$

As required by the second law, dS_{tot} is strictly positive, since $T_e > T$. This is the only way of satisfying the second law in this situation.

We also note that an increase in the equilibrium liquid’s free energy upon cooling is the usual situation. Consider Eq. (1) with $T = T_e$. Then, for the simple case considered in Gupta’s comment (E_{IS} -independent F_{vib}),

$$\begin{aligned} \frac{dF^{\text{eq}}}{dT} &= -S_{\text{conf}} - T \frac{dS_{\text{conf}}}{dE_{\text{IS}}} \frac{dE_{\text{IS}}}{dT} + \frac{dE_{\text{IS}}}{dT} + \frac{dF_{\text{vib}}}{dT} \\ &= -(S_{\text{conf}} + S_{\text{vib}}) < 0, \end{aligned} \quad (4)$$

where Eq. (2) has been used. If a liquid is suddenly quenched to a lower T , during equilibration the final value of the free

energy has to be larger than the initial one. Also this does not contradict the second law of thermodynamics.

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