Notes

Can the Prigogine-Defay Ratio Exceed Unity at T_2? Comment on a Paper by DiMarzio, Gibbs, Fleming, and Sanchez

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Davies and Jones (DJ), in a definitive treatment of the thermodynamics of the glass transition,[1] have shown that the combination of thermodynamic quantities known as the Prigogine-Defay ratio r

$$r = \Delta C_p \Delta\beta / TV(\Delta\alpha)^2 \qquad (1)$$

will be equal to 1 if the excess properties of the liquid are determined by a single ordering parameter, but if more than one are needed, $r \geq 1$. DiMarzio in a recent paper[2] has offered a proof that under the DJ assumptions r must equal 1 on the glass transition line $T_2(P)$, regardless of the number of ordering parameters. He concludes that the fact that experimentally $r > 1$ on $T_2(P)$ implies that the order parameter treatment of DJ is itself inapplicable to the glass transition. DiMarzio's proof has been criticized by myself[3] and Gupta and Moynihan.[4]

In a paper in this journal,[5] DiMarzio et al. have extended the Gibbs–DiMarzio theory (GD) of the glass transition[6] to include the effect of pressure. As they point out, GD is a two ordering parameter theory, with the parameters the fraction of flexed bonds f and the number of holes n_0. They examine the value of r on the transition line, $T_2(P)$, on which the entropy S vanishes, and conclude it is 1 there, apparently confirming DiMarzio's conclusion.

Their analysis proceeds somewhat as follows: at $T_2(P)$, $S(f,n_0)$ becomes zero. On further isobaric cooling the state reached at T_2 remains the equilibrium one; there are no further changes in f and n_0, and α_g and $C_{p,g} = 0$. If the transition had been observed under a higher pressure, S would have become zero at a different pair of values of f and n_0. If the glass below $T_2(P)$ undergoes an isothermal compression, the equilibrium values of f and n_0 will change, although $S(f,n_0)$ will remain equal to zero. The compressibility of the glass, β_g, will therefore not vanish. DiMarzio et al. calculate β_g and show correctly that

$$r_{\mathrm{EQ}} = C_{p,l}[\beta_l - \beta_g(\mathrm{EQ})]/TV[\alpha_l]^2 = 1 \qquad (2)$$

where the symbol EQ denotes that the equilibrium behavior of the glassy phase is being used.

However DJ assumes, contrary to the above analysis, that the values of the order parameters must freeze in at $T_2(P)$ and not change in the glassy state. Such an assumption is entirely consistent with the spirit of GD,[6] and its extensions,[5,7] all of which assert a relation between the configurational entropy S and the relaxation time τ such that τ becomes infinite when $S = 0$. It follows that the *experimentally* observed properties of the glass (exptl) will not be those of equilibrium, but rather those of constant f and n_0. Specifically, isothermal compression of the glass will lead to no change of n_0 in an experiment of finite duration, and $\beta_g(\mathrm{EXP})$ must vanish. It follows that to apply DJ we must examine

$$r_{\mathrm{exptl}} = C_{p,l}\beta_l/TV[\alpha_l]^2 \qquad (3)$$

By comparison of eq 2 and 3, together with the recognition that $\beta_l > \beta_g(\mathrm{EQ}) > 0$, it follows immediately that $r_{\mathrm{exptl}} > 1$.

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References and Notes

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Some Insights into the Order Parameter Theory of Glasses. A Response to a Comment by Goldstein

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The significance of DiMarzio's contribution to order parameter theory is somewhat different than Goldstein implies.[1] Over a period of 12 years, three publications[2–4,] have stressed the usefulness of order parameter theory for glasses, but only when one works with equations that describe their time-dependent behavior. These equations are[2,3]

$$\frac{\mathrm{d}z_i}{\mathrm{d}t} = \sum_j L_{ij}\frac{\partial G}{\partial z_j} \qquad (1)$$

where z_i are the order parameters, t is the time, $\partial G/\partial z_j$ are the forces conjugate to z_j, and L_{ij} are kinetic coefficients which are expressible as integrals over autocorrelation functions of the $\dot{z}_i$. For a given temperature and pressure history $(T(t), P(t))$ eq 1 can be used to evaluate $z_i(t)$. The L_{ij} are functions of T and P and have the same kind of discontinuity as the underlying thermodynamic transition. Thus, if the system displays a first-order transition, then the L_{ij} are discontinuous functions of T and P; for a second-order transition the L_{ij} are continuous, but their T,P derivatives are discontinuous; if there is no transition, then L_{ij} and all of its derivatives are continuous. These facts allow us to decide strictly on the basis of kinetic measurements whether the glass transition is basically kinetic or thermodynamic in origin.[3] Two important questions about eq 1 are: what are physically meaningful z_i, and can a complete set be found? In a simple version[4] of the entropy theory (Gibbs–DiMarzio theory) of glasses the amount of flexibility, f, and the number of holes n_0 of a crude lattice model provide a complete set and offer the hope of evaluation of the corresponding L_{ij}.

The above formulation does not mean to imply that eq 1 is the final word. First, eq 1 as it stands is an equation for average values of the z_i and fluctuations about the average values may well be important, especially near a transition. For this reason, one should add a fluctuating term to the right-hand side of eq 1 and thereby cast it into a vector analogue of the Langevin equation.[5] Second, the matrix product of L_{ij} with $\partial G/\partial z_j$ can be generalized to a folding operation to allow for memory effects.[6] Third, the equations may be nonlinear.[7] Nevertheless, eq 1 constitutes a necessary first step in the path to a correct order parameter description of glasses.

The statement that the Prigogine-Defay ratio r equals 1 for