# Comments on a paper entitled "Prigogine–Defay ratio for systems with more than one order-parameter"

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KF and has a comparable splitting at 100 K. Although several crystals were grown with different initial europium [0.11, 0.13, and 0.25%] concentrations, the observed intensity for this symmetry site was quite small in all of them. Therefore values for the spin-Hamiltonian parameters could not be determined.

In sodium fluoride we only observed a broad line with a $g$ value ~ 2 in crystals grown with different initial europium (0.14, 0.25, and 0.27%) concentrations. No hyperfine structure superimposed on the broad line was observed. A similar spectrum has been reported for $Eu^{2+}$ in LiCl and LiBr single crystals.[4] Although different heat treatments were carried out in order to observe a different EPR spectrum in NaF, all of them were unsuccessful.

Recently, we found a linear dependence of the form $b_2^0 = B - Ar$ (where $r$ is the nearest neighbor distance) for the orthorhombic symmetry sites of $Eu^{2+}$ in the alkali chlorides and bromides series.[4] Although for the alkali iodides the same systematic behavior, ($b_2^0$ decreases as lattice size increases) was observed,[5] it was not possible to distinguish clearly between a linear dependence of the form $b_2^0 = [C - Dr]$ and that predicted by the point charge model calculation ($b_2^0 \propto r^{-3}$). From the results of Table I, it is possible to observe that, apparently, the same systematic behavior was found in the alkali fluorides. How-

ever, no conclusion can be stated about the functional dependence of $b_2^0$ with $r$, until the $S$-ground state splitting of $Eu^{2+}$ can be measured in NaF.

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# COMMENTS

# Comments on a paper entitled "Prigogine–Defay ratio for systems with more than one order parameter"

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A recent paper by Gupta and Moynihan[1] claims to show that order-parameter theory (OPT) can be used to prove that the Prigogine–Defay ratio $r = \Delta C_p \Delta \kappa / TV(\Delta \alpha)^2$ is greater than 1. They also claim to show that a previous paper[2] in which the relation $r = 1$ is derived is in error. This comment is a response to the Gupta–Moynihan paper.

It must be observed at the outset that the OPT being discussed in this comment and in Ref. 1 and 2 has little to do with that of Landau–Ginzberg (LG) OPT. In the LG type treatments the behavior of a real thermodynamic transition is elucidated. See for example work by De Gennes[3] on liquid crystals or by Griffiths[4] on tricritical points. However, in the OPT of this discussion it is imagined that the order parameters are kinetically "frozen in" as one lowers the temperature and that the glass transition, which appears superficially to be a thermodynamic second-order transition in the Ehrenfest

sense, is really kinetic in nature. In the simplest view of order parameter theory (SOPT) it is imagined that the freezing in occurs abruptly. Above the transition line the order parameters $Z_i$ are free to relax to whatever values which will minimize the free energy, while below the transition line they attain a time independent value $Z_{0i}$.[5] SOPT can be viewed only as a very crude approximation to the more general time dependent order-parameter theory (TOPT).[2,6,7]

It is important to note that a misstatement has been made in Ref. 1 with respect to comments I allegedly made about the validity of OPT. A correct paraphrasing of my comments is as follows. (1) SOPT necessarily implies $r = 1$. (2) If experimentally $r > 1$ then the experimental material is not described by SOPT, but rather one needs a kinetic modification (TOPT). This kinetic modification has been discussed in detail previously.[2,6,7] (3) SOPT has no predictive value.

Support for this statement can be seen from the fact that no new insights have to date been obtained from the SOPT approach. Statements (2) and (3) are corollaries of (1). The discussion of some specific points raised in Ref. (1) follows. Consider, first, Fig. 1 of Ref. (1). I remind the reader that, both in Ref. 1 and Ref. 8, the statement has been made that if the transition for volume ocurred along the same line as the transition for entropy then indeed $r = 1$. One can indeed show that the $T(P)$ line for volume is the same as that for entropy, provided only that $dT/dP$ is nonzero and finite. For the entropy $T(P)$ line we have $dT/dP = TV\alpha/\Delta C_p$. Thus provided $\Delta C_p \neq 0$ we have $\Delta\alpha \neq 0$. Now consider the volume changes along the *same* $T(P)$ line. We have $dT/dP = \Delta\kappa/\Delta\alpha$ and $\Delta\kappa$ is nonzero because $\Delta\alpha$ is nonzero. The following generalization of the above obviously holds. If one of the three quantities $\Delta C_p$, $\Delta\alpha$, $\Delta\kappa$ is nonzero along a $T(P)$ line then each of the other two is also nonzero along this line. It also follows that $r = 1$ along this line.[9] It is necessary in the above argument to realize that both $\Delta S = 0$ and $\Delta V \neq 0$ simultaneously is impossible along a $T(P)$ line because of the relation $d(\Delta G) = 0$. Similarly $\Delta S \neq 0$ and $\Delta V = 0$ are not both simultaneously possible.

Consider next Eq. (4) of Ref. 1. The authors imply that I maintain Eq. (4) is valid for all $Z_i$, $T$, and $P$ at equilibrium. In point of fact I claimed it to be true only for an aribtrarily selected point on the transition line $T(P)$.[2] It is not even necessary for Eq. (4) to be true at every point on the transition line simultaneously. A symmetric matrix can be diagonalized at a given point by a choice of new $Z_i$ variables or equivalently, a general quadratic form can be cast into a sum of squares. However, a symmetric matrix cannot be diagonalized simultaneously at all $Z_i$, $T$, and $P$ points by a transformation of variables unless the associated curvature tensor vanishes identically.[10] The impact of Eq. (6) of Rev. 1 is thereby diminished because it need be valid only *at a point, on the transition line, for transformed $Z_i$ variables*. The burden of proof now lies with Gupta and Moynihan to show the relevance of this restricted observation to glasses. Furthermore, the formula for entropy and volume are *not* given by the two equations immediately above Eq. (5) of Ref. 1, but rather, there are additional terms as described in Eqs. (2.2)–(2.3) of Ref. 2. When taking higher order derivatives these additional terms contribute. Thus Eq. (5) does not logically follow from Eq. (4). However, for the case of chemical equilibrium $V = \partial G/\partial P$, $S = -\partial G/\partial T$ are valid and Eq. (6) does logically follow from Eq. (4) if we decide to identify the extents of reaction with order-parameters.

We now consider Eq. (21) of Ref. 1. As observed in Ref. 2, it is not necessary to have each of the $Z_i$ a con-

stant on the line of tangency. All that is needed is one equation $g(Z_i) = 0$ relating them. This has been stressed in Ref. 7. In fact it is the relationship $g(Z_i) = 0$ which defines the transition line. It is interesting to note that a simple version[7] of the entropy theory of glasses[11] results in an equation $S_c(f, n_0) = 0$ which defines the transition line. Here $S_c$ is the configurational entropy, $f$ is a quantity relating to the flexibility of the molecules and $n_0$ relates to volume. The theory predicts on the basis of a Flory–Huggins lattice model that a polymer system undergoes a thermodynamic second-order transition. One might hope, at least, to understand the kinetics of glasses by studying the time dependent behavior of $f$ and $n_0$.

My main disappointment with the Gupta–Moynihan paper is that they ignore my main contribution[2,6,7] which is the observation that Onsager-like equations are applicable to the time variation of order-parameters in glasses and concentrate instead on my proof that $r = 1$ even though this proof was qualified by the condition that a $T(P)$ line exists [see the paragraph after Eq. (2.25) of Ref. 2].

Finally, I wish to make the observation that if one proceeds from very slow experiments to experiments so fast that one can consider the system adiabatic then $r = C_P\Delta\kappa/TV(\Delta\alpha)^2 = (1 - C_v/C_P)^2 < 1$.

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[9] A way out of this difficulty is to assume that no $T(P)$ line exists. If this is done, however, it must first be shown that an ensemble of temperature–pressure histories $[T(t), P(t)]$ exist ($t$ is time) for which there is meaning associated with the idea that the transition occurs at a point. In particular, it must be shown that if a certain $[T(t), P(t)]$ results in a transition that $[T(t), P(t) \pm \theta P_0]$ does not result in a transition $[(0 < \theta \leq 1)]$.

Another related point is that $\alpha$, $\kappa$, $C_p$ are independent quantities. It is therefore conceptually impossible for us to determine them at a point $(T_1, P_1)$ by making measurements on one line containing the point. At least two lines passing through the point are required.

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