

to, but not the immediate products of the gene. Physiological controls can be exerted in the hierarchy of events from DNA to the functional enzyme species at several different levels. We are presently examining such possibilities, in the hope of arriving at an unequivocal answer.

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### Structure of Water

Narten and Levy (1) argue that multi-"phase" models of water structure have not been adequately enough specified to allow a valid test against diffraction data, whereas they represent the one-"phase" model of Narten, Danford, and Levy (2) as an adequately specified model. I wish to point out that in fact the Narten-Danford-Levy model is just as inadequately specified as are existing multi-"phase" models. The Narten-Danford-Levy model describes the average structure around any water molecule on the basis of an arrangement of neighbors such as that in ice I, modified by the possible presence of molecular vacancies and interstitial molecules. The model also includes a Gaussian smearing (followed by a continuum) of interatomic distances, which corresponds to the possibility of distortions from the ice-I-like arrangement, in an instantaneous view of the local structure. Since the model is based on ice I, it is reasonable to assume that in an instantaneous picture ("snapshot") of the liquid structure, it will be possible to find numerous local regions having the ice-I-like molecular arrangement—that is, regions in which the distortions are not so large as to destroy the hydrogen-bonding topology of ice I. Narten and Levy have not given an actual probability for the occurrence of such ice-I-like regions in their model, but the only illustration of the model [figure 3 in (1)] is a picture of such a region. These regions must occur in all possible spatial orientations, to conform to the isotropy of the liquid. As we go from an ice-I-like region in one orientation to an adjacent one in another orientation, we must traverse a connecting zone containing some kind of structural

discontinuity or distortion from the ice-I-like molecular arrangement. A complete specification of the liquid structure must include a description of these connecting zones. Narten and Levy have not shown that their particular model description of the average structure around each molecule contains an internally consistent instantaneous description of ice-I-like regions and of connecting regions between them. To demonstrate internal consistency, one would have to show that regions that are ice-like in structure can actually be connected to one another throughout the liquid by means of regions that are distorted from the ice-like structure in the ways allowed by the Narten-Danford-Levy description, and with the probabilities of distortion that are required by the assumed Gaussian smearings plus continuum.

The need for a demonstrably valid description of the connecting zones between differently oriented ice-I-like regions in the Narten-Danford-Levy model is quite the same as the need for a corresponding description of connecting zones between the various "phase" regions of a multi-"phase" model. In both cases, it corresponds to imposing conditions 8 and 9 (1, p. 449), which Narten and Levy put forward as applicable only to the multi-"phase" models. Insofar as Narten and Levy represent their model as a rigorous space average or time average of the water structure, or both, and yet do not demonstrate that the model is a self-consistent description that includes the connecting zones between different ice-like regions, their description is not really a structure *model* at all, but instead is simply the *assumed result* of an averaging procedure applied to a structure the necessary details of which have not been specified. It follows that the Narten-Danford-Levy model of water structure is in no essential way better specified than existing multi-"phase" models are. In several discussions (for example, 3) of the radial distribution function for water, based on multi-"phase" concepts, Gaussian smearings have been applied to the atomic positions of the different "phases" in a way essentially the same as that of Narten, Danford, and Levy. It has not been demonstrated that such a treatment accounts better for the connecting zones in the one-"phase" Narten-Danford-Levy model than in the multi-"phase" models.

I wish to point out also that Narten

and Levy (1, p. 453) did not correctly represent the ideas that I expressed in a discussion of water structure (3) based on ice polymorphism. I suggested that liquid water is a mixture of molecular arrangements not only of the three types represented by ices I, II, and III, but of many diverse kinds, of which the various ice structures are only illustrative examples. In calculating a radial distribution function containing contributions only from structures based on ices I through III, my purpose was only to show by actual example that combinations of ice-like phases could account for the main features of the observed radial distribution function, which other authors had tried to explain with structural models that either ignored ice polymorphism or overlooked the real features of the dense ice polymorphs (4). I pointed out (3) that the contributions from the connecting zones between ice-like regions would have to be included in any complete treatment of the radial distribution function.

To include these zones in a calculation of the radial distribution function would require a detailed knowledge of the structure, which we lack. This lack is a handicap not only for model testing but also for a rational discussion of the structural basis of many important properties of water (such as fluidity and diffusion) that depend more on the non-ice-like than on the ice-like features of the structure (3). The importance of this aspect of water structure gives us added reason not to rely heavily on models that do not incorporate the non-ice-like features of water structure in a demonstrably valid way. The molecular vacancies and interstitial molecules of the Narten-Danford-Levy model are clearly valid possible features of liquid structure, and there is little doubt that such features do occur to some extent in the water structure. However, they would be just as stabilizing for a crystalline phase of the ice-I type as for a liquid (5), and it therefore seems unlikely that the presence of these features is the *essential* non-ice-like or noncrystalline aspect of the structure of liquid water. Until it is shown that, in liquid-structure models based on crystal structures, the Gaussian smearing feature (plus continuum) is capable of describing in a valid, internally consistent way the complete three-dimensional structure including the connecting regions between crystal-like regions, there is no

reason to assume that this smearing feature properly represents the essential noncrystalline aspect of the liquid structure.

Narten and Levy (*I*, p. 451) state that "stretching of hydrogen bonds from 2.76 angstroms in the solid to an average of 2.82 angstroms in the liquid near the melting point accounts for most of the heat (1.4 kilocalories) necessary to melt one mole of ice." If correct, this would have important implications for the energy storage mechanism in water. For example, it would imply that the interstitial molecules in the Narten-Levy model could be present with very little increase in energy, in contrast to the increase of about 8 kcal mole<sup>-1</sup> expected from experimental evidence on the interactions between nonhydrogen-bonded water molecules (6). Narten and Levy do not indicate the basis for their calculation of the energy of H-bond stretching, but their stated result is in conflict with calculations based on the compressibility of ice (6, 7) which give an energy contribution of 0.09 to 0.14 kcal mole<sup>-1</sup> for the stated increase in bond length. Most discussions of the heat of fusion and heat capacity of water trace the energy storage mainly to bond bending and bond breakage rather than to bond stretching (for example, 3, 8).

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  2. A. H. Narten, M. D. Danford, H. A. Levy, *Discuss. Faraday Soc.* **43**, 97 (1967).
  3. B. Kamb, in *Structural Chemistry and Molecular Biology*, A. Rich and N. R. Davidson, Eds. (Freeman, San Francisco, 1968), p. 507.
  4. Narten and Levy (*I*, p. 452) refer to the proposal by C. M. Davis and T. A. Litovitz [*J. Chem. Phys.* **42**, 2563 (1965)] of a water model involving "a structure similar to ice II," but in fact the "structure II" of Davis and Litovitz bears practically no relation to actual ice II or to any other known polymorph of ice.
  5. This is shown clearly in a calculation by Narten, Danford, and Levy (2, p. 105) of the entropy and enthalpy of water on the basis of the mixing entropies of the vacancies and interstitial molecules in their model.
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  9. Division of Geological Sciences, Contribution No. 1722. I thank D. Eisenberg and L. Pauling for helpful discussions, and A. H. Narten and H. A. Levy for kindly sending me in advance their reply to this commentary.
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Our critical examination of proposed models for liquid water (*I*) was confined to models for which radial distribution functions have been, or can be, calculated. Kamb (2) compared linear combinations of radial distribution curves calculated for ices I, II, and III with curves derived from diffraction data. On the basis of this comparison, he concluded that the principal features of the radial distribution function of liquid water can be accounted for by the presence in the liquid of the various ice-like molecular arrangements. We pointed out that such a comparison would be meaningful only if large clusters of the various structures were present in the liquid, and that large clusters are ruled out by data from small-angle x-ray scattering. We regret not having pointed out that Kamb's incomplete presentation was intended only for qualitative support of his ideas on ice polymorphism and water structure. We did not discuss these ideas in more detail because they cannot be tested with the x-ray data and were thus outside the stated scope of our article.

Kamb points out that in a one-"phase" model of a macroscopically isotropic liquid the local structure must have different orientations in different regions. However, the conclusion that these regions must be linked by a "connecting zone containing some kind of structural discontinuity or distortion" does not necessarily follow. It is, on the contrary, plausible to visualize gradual, continuous transitions from one region to another of different orientation, so that one cannot distinguish a "connecting region" from any other local environment. In the ice-I model (3) it is assumed that this situation obtains. As Kamb points out, no proof is offered that this hypothesis is self-consistent, but, on the other hand, neither has it been shown to be self-contradictory. The problem seems to be of a topological nature; a systematic method for detailed study of the hypothesis would be enlightening.

In contrast, no such hypothesis is tenable in a multi-"phase" model. By definition such a model contains qualitatively different local arrangements; the connecting zones between them, whether gradual or abrupt, must be different in local arrangement from the regions that are connected. The dis-

tance spectrum for such regions must therefore be included in a valid comparison with the radial distribution function.

The "crystalline" nature of the ice-I model is limited to short-range order. The absence of long-range correlation, visualized as the accumulated result of continuous, small variations in instantaneous local environment, is certainly one "essential noncrystalline aspect of the liquid structure" which is possessed by the model. (Kamb's repeated use of the terms "Gaussian smearing and continuum" can be misleading because they are formal descriptions of an aspect of the atomic correlation function, not of the atomic positions themselves.) Other features of the model that give it a noncrystalline nature, as Kamb recognizes, are random occupancy of cavities and random network vacancies.

The fact that a crystalline phase having a structure resembling the ice-I model for water has not been found does not preclude the existence of this configuration in the liquid. Such a hypothetical solid would melt, presumably with a very small latent heat and density change, and need have no region of thermodynamic stability. All actual solid phases that coexist with the liquid melt with first-order transitions involving relatively large energy increase. This energy must be stored in structural features that distinguish the liquid from the solid (not merely in stretched hydrogen bonds, as we implied). Direct information on the positions of hydrogen atoms in liquid water would be of great value in a discussion of these questions and may well become available through more refined neutron and x-ray diffraction studies.

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