

# Monte Carlo study of a bond-diluted $q$ -state clock model: A simple representation for the glass transition

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The idea of local bond ordering is discussed further as a representation for the glass transition: in a supercooled liquid, the local ordering of bonds can lead to substantial lowering in the configurational energy in the absence of long-range structural ordering or crystallization. This concept is developed in the context of a model system using quantities such as a bond energy order parameter and the corresponding response function, the bond susceptibility, which provides a theoretical identification for the calorimetric glass transition temperature. Thermodynamic properties of the two-dimensional model system are investigated by means of Monte Carlo simulation. These simulations exhibit local bond ordering at the intermediate temperature range uncorrelated with any type of long-range structural ordering whether conventional or  $xy$  type, implying stronger mechanical properties such as the viscosity for the structurally disordered system.

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## I. INTRODUCTION

The problem of the glass transition is a classic one in physics and materials science. Viewpoints break down into considerations of an underlying thermodynamic phase transition,<sup>1,2</sup> and kinetic explanations of an arrested liquid.<sup>3</sup> Discussions have approached the glass transition in terms of the fragmentation of small structural units,<sup>4</sup> the agglomeration of clusters through chemical bonds,<sup>5</sup> and correlations between different metastable equilibrium states representing distinct configurations or arrangements of the liquid molecules.<sup>6</sup> Furthermore, the effects of frustration arising from the local ordering of bonds in a supercooled liquid, have been discussed in a two-order-parameter description of liquids.<sup>7</sup> Here we would like to introduce a representation for the glass transition, which incorporates some of these ideas in a simple form.

To begin we recall some of the basic structural features of typical covalently bonded glass-forming materials such as silica. Vitreous silica is made up of  $\text{SiO}_4$  tetrahedra similar to quartz the crystalline phase of silica. Thus, molecular structure for the two different phases of silica, i.e., vitreous and crystalline, are alike with major exception of the  $\text{Si}_1$ - $\text{Si}_2$  next-nearest-neighbor (NNN) distance which may be also specified by the Si-O-Si bond angle. The statistical distribution of Si-O-Si bond angles as determined by Mozzi and Warren for vitreous silica is shown in Fig. 1.<sup>8</sup> From the bond angles distribution it becomes clear that  $\text{Si}_1$ - $\text{Si}_2$  distances vary moderately which is in fact the primary source of the topological disorder. The distribution is characterized by a half-width-half-maximum (HWHM) of about  $17^\circ$  and a most probable value of  $144^\circ$ . Clearly the variation in Si-O-Si bond angles (or  $\text{Si}_1$ - $\text{Si}_2$  distances) is significant enough to suppress the long-range order (LRO) characterizing the crystalline phase, and yet small enough to maintain the medium-range order (MRO) characteristic of vitreous silica which extends to about a nanometer or two. We note that the ordering in nearest-neighbor (NN) distances, and moderation in the variation of NNN distances is well maintained in spite of the

fact that vitreous silica is devoid of long-range structural order. Similar structural properties are also observed in various other covalent network materials such as  $\text{GeO}_2$ ,  $\text{B}_2\text{O}_3$ , etc.

This observation regarding the existence of medium-range order in glass is striking enough to indicate a strong role for the local ordering of bonds, i.e., relaxation of bonds into their low-lying energy states, in a proper microscopic representation for the glass transition. The local ordering of bonds can be viewed as being brought about by the cooperative rearrangement of a molecular group as suggested in the theory of Adam and Gibbs.<sup>1</sup> The basic idea is that a supercooled liquid does not need to undergo long-range structural ordering in order to achieve metastable equilibrium. In fact the cooperative rearrangements of the molecular groups can lead to substantial lowering in the configurational energy of an entire sample through reduced bond energies at the local level. This is perhaps the primary reason for the ordering of

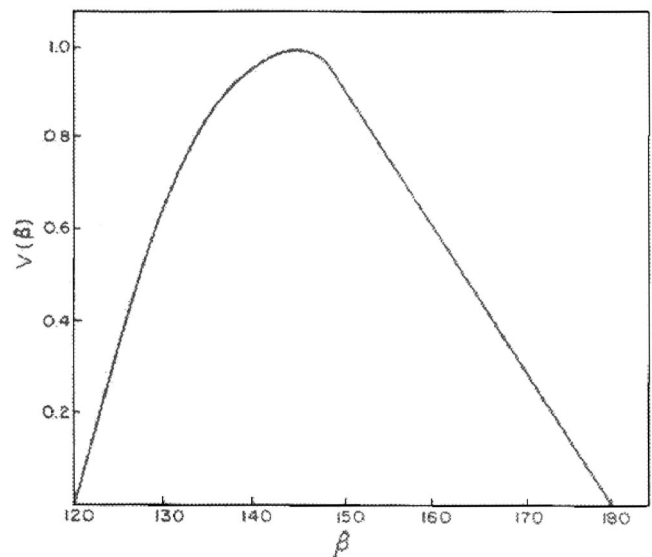


FIG. 1. Statistical distribution of Si-O-Si bond angles in vitreous silica (Ref. 8).

NN distances, and moderation in the variation of NNN distances or alternatively the bond angle degrees of freedom in glassy materials as may be seen in Fig. 1.

A model for the glass transition incorporating small structural units or fragments was proposed by Suzuki *et al.*<sup>4</sup> In the fragmentation model, noncrystalline solids are assumed to be assemblies of pseudomolecules—a pseudomolecule being a cluster of atoms having a disordered lattice in which there are no definite defects such as undercoordinated or overcoordinated atoms. As the temperature increases, bond breaking intensifies at the boundaries of the clusters where bonds tend to be weak. The bond breaking mechanism arising from the thermal excitation of electrons from bonding to antibonding energy states causes the noncrystalline solid to fragmentize with the average fragment size decreasing as the temperature increases. Consequently material begins to show viscous flow when the average fragment size reaches a critical small value. The fragmentation model has some success with describing the temperature dependence of viscosity and the variation in glass transition temperature with the heating rate for *a*-Si.<sup>4</sup> The origin of pseudomolecules in the cooling process, however, is not addressed in the fragmentation model.

Attempts have been made to incorporate frustration arising from local bond ordering in a supercooled liquid, through the introduction of a local order parameter describing the energetically favored local arrangements of the liquid molecules which are not consistent with the crystallographic symmetry favored by density ordering or crystallization characterized by density as the order parameter. In the two-order-parameter description of liquids due to Tanaka,<sup>7</sup> the frustration arises from competition between density ordering and local bond ordering, explaining why some molecules crystallize easily without vitrification while others easily form glasses without crystallization. This model emphasizes that the introduction is necessary of a bond order parameter, in addition to the density, in order to have a complete thermodynamic description of the liquid state and in particular the supercooled glass-forming liquids.

In accord with the two-order-parameter description of liquids,<sup>7</sup> we present a microscopic representation for the glass transition, called the bond-ordering representation, that is general enough to be applicable to various types of glass-forming liquids with widely differing bonding schemes and chemical compositions. The focus of the bond-ordering representation is the bonds linking neighboring atoms rather than the atomic arrangements. In other words a bond is treated as a distinct object possessing internal degrees of freedom or energy states. The energy state of a bond is of course governed by the separation and relative orientation of the participating atoms. The term “bond ordering” refers to local process of relaxation of bonds into their low-lying energy states, facilitated by the cooperative rearrangement of a molecular group. Bond ordering may be thereby viewed as a form of ordering in energy space. The important point that we would like to bring home, however, is that such an ordering is achievable without need for any type of long-range structural ordering. To this end we present results from Monte Carlo (MC) simulation of a model system described

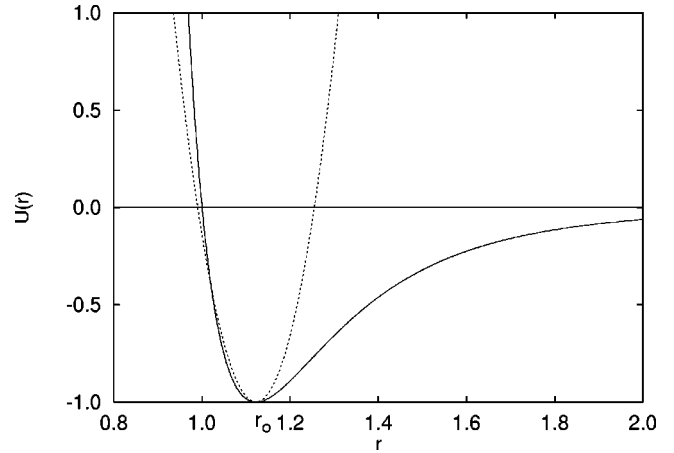


FIG. 2. Lennard-Jones or 6-12 potential typical of a two-body interaction as a function of distance or separation  $r$ . The upright parabola shown as dotted curve is the corresponding harmonic approximation.

by a Hamiltonian which couples the coordinates of ions to the electronic states of electrons as for a typical covalently bonded network material. Simulation results make clear the possibility of the local ordering of bonds, i.e., relaxation into low-lying energy states of the bonds, uncorrelated with any type of long-range structural ordering whether conventional or *xy* type. Bond ordering, or the strengthening of bonds, naturally implies stronger mechanical properties such as the viscosity for the disordered system. This is in view of the fact that a system which is bond ordered, resides in deeper minima of the potential energy hypersurface and needs to overcome higher potential energy barriers hindering viscous flow.

The rest of this paper is organized as follows. In Sec. II, we derive the model Hamiltonian and describe the meaning of bond dilution implied therein. In Sec. III, we give mathematical definitions for various structural and bond-related thermodynamic functions of interest. In Sec. IV, the thermodynamic functions are given their physical interpretations and a theoretical identification is presented for the calorimetric glass transition temperature based on variation with temperature of a bond-related response function that is defined in Sec. III. Simulation procedure and the thermodynamic results are discussed in Sec. V. Section VI contains the concluding remarks and a summary of the main ideas presented in this paper.

## II. MODEL SYSTEM

In this section we introduce a lattice model that is a bond-diluted version of the  $q=8$  state clock model, the thermodynamic properties of which are then investigated by means of MC simulation. The potential energy function  $U(r)$ , for a typical two-body interaction (e.g., Lennard-Jones potential shown in Fig. 2), may be expanded in the displacement  $x = r - r_0$  from the equilibrium separation

$$U(r) = U(r_0) + \frac{U''(r_0)}{2!}x^2 + \frac{U'''(r_0)}{3!}x^3 + \dots, \quad (1)$$

where, the coefficients are evaluated at the equilibrium separation  $r_0$ . Dropping the constant term which plays no role and in harmonic approximation, we have

$$U(r) \cong \frac{U''(r_0)}{2} x^2. \quad (2)$$

For many-body system, we consider a system of atoms defined on a square lattice and interacting through NN coupling. The displacement of an atom from its equilibrium lattice site is specified by a vector  $\mathbf{R}_i$ . The deviation from equilibrium separation for a NN pair is approximated by

$$x \approx |\mathbf{R}_i - \mathbf{R}_j|, \quad (3)$$

where  $\mathbf{R}_i$  and  $\mathbf{R}_j$  represent the displacements of the atoms from their equilibrium lattice sites labeled  $i$  and  $j$ , respectively. This approximation is justified in the light of the following arguments. Denoting the Bravais lattice vectors of the NN sites labeled  $i$  and  $j$  by  $\mathcal{R}_i$  and  $\mathcal{R}_j$ , respectively, the deviation  $x$  from equilibrium separation is then given by

$$\begin{aligned} x = r - r_0 &= |(\mathcal{R}_i + \mathbf{R}_i) - (\mathcal{R}_j + \mathbf{R}_j)| - |\mathcal{R}_i - \mathcal{R}_j| \\ &= |(\mathcal{R}_i - \mathcal{R}_j) + (\mathbf{R}_i - \mathbf{R}_j)| - |\mathcal{R}_i - \mathcal{R}_j| \\ &\leq |\mathcal{R}_i - \mathcal{R}_j| + |\mathbf{R}_i - \mathbf{R}_j| - |\mathcal{R}_i - \mathcal{R}_j| = |\mathbf{R}_i - \mathbf{R}_j|. \end{aligned} \quad (4)$$

Equation (3) is therefore an approximation of  $x$  in terms of an upper bound  $|\mathbf{R}_i - \mathbf{R}_j|$ . In order to have a more tractable system one may also introduce the idealizing constraint that all the atomic displacements are of the same magnitude  $|\mathbf{R}|$

$$|\mathbf{R}_i| = |\mathbf{R}|, \quad \forall \mathbf{R}_i. \quad (5)$$

With these approximations Eq. (2) yields

$$U(r) = |\mathbf{R}|^2 U''(r_0) [1 - \hat{\mathbf{R}}_i \cdot \hat{\mathbf{R}}_j]. \quad (6)$$

Denoting the coupling strength by  $J = |\mathbf{R}|^2 U''(r_0)$ , we therefore get the following Hamiltonian for a system of atoms interacting through NN coupling:

$$\tilde{\mathcal{H}} = -J \sum_{\langle i,j \rangle} \hat{\mathbf{R}}_i \cdot \hat{\mathbf{R}}_j = -J \sum_{\langle i,j \rangle} \cos \left[ \frac{2\pi}{q} (s_i - s_j) \right]. \quad (7)$$

This is clearly of the same mathematical form as the  $q$ -state clock model,<sup>9,10</sup> when the displacement or site degrees of freedom are taken to be discrete. In Eq. (7),  $q$  is the number of possible orientations, and  $s_i = 1, 2, \dots, q$ , is an integer characterizing the orientation of the site variable  $\hat{\mathbf{R}}_i$ . As a way of illustration two typical configurations of such a system are displayed in Fig. 3.

The more realistic Hamiltonian that we employed for our MC simulation work, also involves a coupling between the ionic coordinates and the electronic state of the bond

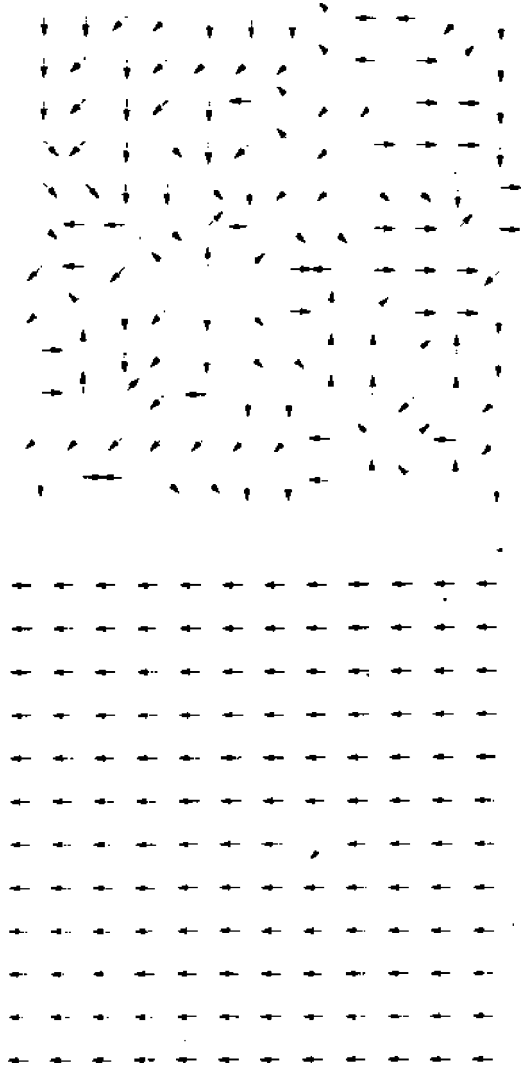


FIG. 3. Two snapshots of the system typifying a disordered (up) and a significantly ordered (down) configurations.

$$\begin{aligned} \mathcal{H} &= -J \sum_{\langle i,j \rangle} (\hat{\mathbf{R}}_i \cdot \hat{\mathbf{R}}_j + 1) n_{ij} \\ &= -J \sum_{\langle i,j \rangle} \left( \cos \left[ \frac{2\pi}{8} (s_i - s_j) \right] + 1 \right) n_{ij}, \end{aligned} \quad (8)$$

where  $s_i = 1, 2, \dots, 8$ , and  $n_{ij} = 0, 1$ . Here  $s_i$  is an integer label for the displacement of an atom from its designated equilibrium lattice site. The coefficient  $n_{ij}$  ( $= 0, 1$ ) may be regarded as the bond electron occupation number for a bond linking a NN pair. That is a given bond may or may not be broken depending on whether the corresponding bond electron occupation number  $n_{ij}$ , takes on the values 0 or 1, respectively. The value taken by each  $n_{ij}$  depends on the total number of electrons made available to the system (as input to the simulation code), and the relative value of NN interactions for a given configuration of the system. The available electrons are treated at zero temperature: that is for every configuration of the system, NN pairs are sorted out in the ascending order of (configurational) energy and are assigned a bond electron

in that order. Hence, NN pairs with lower configurational energy are more likely to have a bond electron. The introduction of the constant in the Hamiltonian, ensures that no bonding state is higher in energy than the antibonding state characterized by  $n_{ij}=0$ . The choice of  $q=8$ , for the number of possible orientations of a site variable, while closely approximates a circle also helps simplify the simulation by allowing only a limited number of moves.

Interesting results are obtained with a bond electron (hole) concentration of about 60% (40%), as we report later in this paper. The choice of bond dilution or hole concentration (i.e., 40%), is consistent with the fact that for the system to be fluid one requires a large concentration of holes or broken bonds, however, in order to maintain the condensed phase attributes of the system, the hole concentration must not exceed the limitation set by the bond percolation threshold that is 50% for a square lattice. As we shall see in Sec. V, the overall effect of holes is to suppress the  $xy$ -like phase transition that is believed to occur for the  $q$ -state clock models with  $q>4$ , and instead one observes evidence for the local ordering of bonds. The local ordering of bonds naturally implies stronger mechanical properties such as the viscosity for the structurally disordered system. This is in view of the fact that a bond-ordered system is low in configurational energy and resides in deeper minima of the potential energy hypersurface, hence needs to overcome higher potential energy barriers hindering viscous flow.

### III. THERMODYNAMIC FUNCTIONS

In Sec. I, we defined bond ordering as that process involving the relaxation of bonds into their low-lying energy states, brought about by the cooperative rearrangement of a molecular group. There are a few thermodynamic functions relevant to our discussion, that are defined in this section and are considered in the context of the glass transition phenomena.

#### A. Bond order parameter

Previous work has suggested the need for a bond order parameter characterizing energetically favored local arrangements of the liquid molecules.<sup>7</sup> Here we introduce a bond energy order parameter as a thermodynamic variable that characterizes the degree of bond order prevailing in a physical system at a given temperature. The bond order parameter is assumed to be large when bonds are in their low-lying energy states, as for a bond-ordered low temperature phase (e.g., glass), and negligible when bonds are distributed among all possible energy states with uniform probability which is the case when the thermal energy is far in excess of the typical binding energy.

In order to construct an expression for the bond order parameter pertaining to the model system, every NN pair of atoms is characterized by a bond variable  $\hat{\mathbf{B}}_{ij}$ , the purpose of which is to characterize the configurational energy of the pair  $\epsilon_{ij} = -J(\hat{\mathbf{R}}_i \cdot \hat{\mathbf{R}}_j)$ , given by the scalar product of the site variables. The unitary vector  $\hat{\mathbf{B}}_{ij}$  may be specified by an angular variable  $\phi_{ij}$  that is given by  $\phi_{ij} = \pi \epsilon_{ij} / J$ , where  $-J \leq \epsilon_{ij} \leq J$ , and so,  $-\pi \leq \phi_{ij} \leq \pi$ . An expression that fulfills all the

requirements of an extensive bond order parameter defined over the entire system is the following:

$$\langle M_b \rangle = \left\langle \left| \sum_{\langle i,j \rangle}^{2N} \hat{\mathbf{B}}_{ij} \right| \right\rangle, \quad (9)$$

where angular braces stand for ensemble average,  $N$  is the total number of atoms or sites in the system, and  $\hat{\mathbf{B}}_{ij} = [\cos \pi(\hat{\mathbf{R}}_i \cdot \hat{\mathbf{R}}_j), -\sin \pi(\hat{\mathbf{R}}_i \cdot \hat{\mathbf{R}}_j)]$ . The intensive bond order parameter  $\langle m_b \rangle$  is given by

$$\langle m_b \rangle = \langle M_b \rangle / 2N, \quad (10)$$

where, the normalization factor corresponds to  $2N$  NN pairs contained in the system given periodic boundary condition, and so,  $0 \leq \langle m_b \rangle \leq 1$ .  $\langle m_b \rangle$  is a bond order parameter in the manner of energy, as it characterizes the configurational energy of the system. A property of bond order parameter  $\langle m_b \rangle$  is that it vanishes only for thermal energies far in excess of the binding strength  $J$ , where all possible energy states are equally likely in accordance with the Boltzmann probability factor. That is,  $\lim_{\beta J \rightarrow 0} \langle m_b \rangle = 0$ , where  $\beta = (k_B T)^{-1}$ , and  $k_B$  is Boltzmann constant. This important property should also serve to distinguish  $\langle m_b \rangle$  from bond-orientational order parameter characterizing  $xy$  type transition in 2D.

#### B. Bond susceptibility

Bond susceptibility is the response function associated with bond order parameter  $\langle M_b \rangle$ , and its thermodynamically conjugate field  $H_b$  which may be referred to as the bond ordering field. The bond ordering field  $H_b$  is introduced primarily for pedagogic reasons; however, in view of the two-order-parameter description of liquids,<sup>7</sup>  $H_b$  should be regarded as the field favoring the local ordering of bonds as opposed to the one favoring global density ordering or crystallization. That is, in a liquid there always exist two competing orderings: (i) global density ordering that results in crystallization and, (ii) local bond ordering that leads to the glass transition.<sup>7</sup>

With this background the change in the Gibbs free energy  $G(T, H_b)$  in an infinitesimal bond ordering process may be expressed as

$$dG = -S dT - \langle M_b \rangle dH_b. \quad (11)$$

The bond susceptibility, apart from a normalization, is defined by

$$\chi_b = \left( \frac{\partial \langle M_b \rangle}{\partial H_b} \right)_{T, H_b=0} \quad (12)$$

$$= - \left( \frac{\partial^2 G}{\partial H_b^2} \right)_{T, H_b=0}. \quad (13)$$

The free energy  $G(T, H_b)$  is of course defined in terms of the partition function in the presence of the bond ordering field

$$\exp(-\beta G) = \text{Tr} \exp[-\beta(\mathcal{H} - H_b M_b)], \quad (14)$$

where, the trace denotes a sum over all microstates, and  $M_b = |\sum_{\langle i,j \rangle}^{2N} \hat{\mathbf{B}}_{ij}|$ . From Eqs. (13) and (14), one may readily obtain a fluctuation-dissipation equation expressing the bond susceptibility in terms of the equilibrium fluctuations of the bond parameter

$$\chi_b = [\langle M_b^2 \rangle - \langle M_b \rangle^2] / 2Nk_B T. \quad (15)$$

Equation (15) for the bond susceptibility is properly normalized to the number of NN pairs  $2N$ , for a system of size  $N$  with periodic boundary condition, and may be employed to calculate bond susceptibility in an equilibrium MC simulation. A detailed derivation of Eq. (15) is given in the Appendix.

Bond susceptibility is the response function measuring the tendency for relaxation of bonds into their low-lying energy states brought about by cooperative rearrangement of a molecular group, and is intimately related to the correlation length associated with the bond variables  $\hat{\mathbf{B}}_{ij}$  which is in fact the characteristic length associated with relaxation in a cooperatively rearranging region. Furthermore, it provides the basis for a theoretical identification of the calorimetric glass transition temperature that is presented in Sec. IV.

### C. Structural order parameter and susceptibility

The structural order parameter is a measure of the conventional LRO a system may possess. For the model system we are considering, the displacement of an atom from its designated equilibrium lattice site is characterized by the unitary vector  $\hat{\mathbf{R}}_i$  which may be specified by the angle that it makes with a fixed axis in the plane of the system  $\theta_i = 2\pi s_i/8$ , where  $s_i = 1, 2, \dots, 8$ . The extensive structural order parameter defined over the entire system may be therefore expressed as

$$\langle M_s \rangle = \left\langle \left| \sum_{i=1}^N \hat{\mathbf{R}}_i \right| \right\rangle, \quad (16)$$

where  $\hat{\mathbf{R}}_i = [\cos \theta_i, \sin \theta_i]$ . The intensive (or normalized) structural order parameter is given by

$$\langle m_s \rangle = \langle M_s \rangle / N, \quad (17)$$

where the normalization factor is chosen such that,  $0 \leq \langle m_s \rangle \leq 1$ .

The analogy between structural order parameter and magnetization of a magnetic system,<sup>9,10</sup> is rather obvious. In fact we can use this analogy to express the structural susceptibility in terms of the equilibrium fluctuations in the structural order parameter, as follows:

$$\chi_s = [\langle M_s^2 \rangle - \langle M_s \rangle^2] / Nk_B T, \quad (18)$$

where  $M_s = |\sum_{i=1}^N \hat{\mathbf{R}}_i|$ . The structural susceptibility is the response function describing the tendency for structural ordering and is intimately related to the correlation length associated with the site variables  $\hat{\mathbf{R}}_i$ .<sup>9,10</sup>

## IV. INTERPRETATION

### A. Theoretical identification for $T_g$

Following the previous discussion one can trace the physical origin of MRO characteristic of the vitreous state in the local ordering of bonds, which becomes most intense at some particular temperature. This brings us to another identification for the calorimetric glass transition temperature  $T_g$  that in particular applies to fragile and intermediate class of the glass-forming liquids.

In the glass transition temperature regime, the bond susceptibility of a supercooled liquid reaches a maximum. This implies that one should also expect a peak (or a maximum) in the specific heat because of the large energy fluctuations associated with the strong fluctuations in the number of bonds in each energy state. This may be understood in view of the fact that for a system at constant temperature the specific heat varies directly as the mean square fluctuation in the internal energy<sup>9,10</sup>  $C \sim \langle (\mathcal{H} - \langle \mathcal{H} \rangle)^2 \rangle / T^2$ . Hence, the anomalous peak in the experimentally measured specific heat of various fragile and intermediate glass-forming liquids such as  $\text{As}_2\text{Se}_3$ ,  $\text{B}_2\text{O}_3$ , etc.,<sup>11,12</sup> can be regarded as a result of the strong fluctuations in the number of bonds in each energy state, occurring at the glass transition. Hence, we propose a theoretical identification for calorimetric  $T_g$  as that particular temperature corresponding to the maximum of bond susceptibility of a supercooled liquid. We need to point out that for the laboratory systems, the specific heat peak anomaly is not observed in a cooling process. We believe that this is because, given the large structural relaxation times for a liquid in the glass transition temperature regime and rapid laboratory cooling rates, the structure of the liquid simply does not find the time necessary for it to relax into low-lying configurational energy states and as a result the specific heat peak anomaly is suppressed. However, once the liquid is cooled, and then reheated, the bonds have already found the necessary time for them to relax into their low-lying energy states as a result of which the specific heat peak anomaly is observed in the heating process.

Having given an explanation for the specific heat peak anomaly at the glass transition, we also briefly consider the unexpected linear behavior of the specific heat at very low temperatures.<sup>13</sup> There is evidence that the low temperature anomalous properties of amorphous materials, e.g., the deviation of the specific heat from Debye- $T^3$  behavior, arise mainly from two-level systems and not from the multilevel vibrational degrees of freedom associated with the atoms.<sup>14,15</sup> The energy gaps  $\Delta$  of the two-level systems are supposed to vary with a uniform probability in some range  $0 \leq \Delta \leq \Delta_0$ , where  $\Delta_0 \approx 1$  K. In our view these low energy excitations may be attributed to the bond ordering process at very low temperatures. In structurally disordered systems, whether supercooled liquid or glass, bonds continuously relax into more stable internal energy states with lowering of the temperature. At very low temperatures certain number of bonds may be seen to act like two-level systems with varying energy gaps. Bond ordering process is therefore a possible explanation for the low temperature anomalous specific heat of the amorphous materials.

### B. Order parameter for glass

We would like to address at this point a possible order parameter for the glass transition, the temperature variation of which may be used as a distinguishing criterion between fragile and strong behaviors in supercooled liquids. This is simply the bond order parameter if one is considering, strictly, a liquid-glass transition.

Many of the theories describing glass transition phenomena assume that there is a single parameter which characterizes glass. This assumption is believed to be inaccurate.<sup>16</sup> Prigogine and Defay have shown that in general the ratio of the discontinuities in second-order thermodynamic function, isothermal compressibility  $\Delta\kappa$ , heat capacity at constant pressure  $\Delta C_p$ , and coefficient of thermal expansion  $\Delta\alpha$

$$R = \frac{\Delta\kappa\Delta C_p}{TV(\Delta\alpha)^2} \quad (19)$$

is equal to unity if a single order parameter characterizes the underlying thermodynamic transition, but if more than one order parameter is involved, then  $R > 1$ .<sup>17</sup> The latter seems to describe most glasses. We therefore consider a two order parameter description of glass, which involves two of the thermodynamic parameters described earlier, namely, the structural order parameter  $\langle m_s \rangle$  and the bond order parameter  $\langle m_b \rangle$ . We require for the amorphous solids, or glass, that the structural LRO vanishes while the bond order parameter remains significantly large. The requirement of the vanishing of the structural LRO is meant to characterize the liquidlike attributes of the amorphous systems. Yet large values for bond order parameter is a solidlike attribute implying stronger mechanical properties such as the viscosity, and should serve to distinguish glass from the liquid phase.

Clearly in the case of strong glass formers such as silica characterized with strong and directional covalent bonds, the values for bond order parameter above and below the glass transition must be quite comparable. This is because the typical binding energy of a Si-O bond in vitreous silica is an enormous 0.45 eV that is equivalent to several thousand K, hence silica tends to maintain its structure at temperatures which are low compared to that binding energy. On the other hand, in the case of fragile systems the liquid undergoes substantial bond ordering in the supercooled temperature range mainly due to the weak and nondirectional nature of their van der Waals' or ionic bonds. As a result the bond order parameter is expected to vary rather significantly for the fragile class over the supercooled range of temperature. Originally the labels strong and fragile were introduced to refer to the ability of a liquid to withstand changes in MRO with temperature.<sup>18</sup> In the context of the bond-ordering representation, these labels will be referring to the ability of a liquid to withstand changes with temperature in bond order parameter  $\langle m_b \rangle$ . It is worthwhile to mention that in the bond-ordering picture, an ideal glass may be characterized as being maximally bond-ordered which should also imply the least possible configurational energy for the amorphous structure. This interpretation of ideal glass in terms of the bond order parameter is also consistent with the one emerging from the

potential energy landscape consideration in which the ideal glass is characterized with least amount of configurational energy.<sup>19</sup>

The viscous behavior of supercooled liquids when cooled toward glass transition may be also interpreted in terms of the bond-ordering representation or more precisely the temperature variation of the bond order parameter. Fragile liquids undergo significant bond ordering through the supercooled temperature regime leading to a strongly temperature-dependent effective potential energy barrier for the viscous flow. For that reason one may argue that the viscosity in the fragile limit is seen to vary in a highly non-Arrhenius manner, as opposed to the Arrhenius-like behavior of the viscosity exhibited by strong glass-forming liquids.

### V. MONTE CARLO SIMULATION

Simple clock models have been investigated analytically,<sup>20,21</sup> and by computer simulation.<sup>9,10</sup> Previous Monte Carlo works have examined the behavior of the two-dimensional simple clock systems with various values of the parameter  $q$ . The important results are that for  $q \leq 4$  the system exhibits one second-order transition, but for  $q > 4$  two Berezinskii-Kosterlitz-Thouless (BKT) transitions<sup>22,23</sup> are present. As  $q$  increases the lower transition temperature ( $\sim 1/q^2$ ) approaches zero leaving just one BKT transition for the continuous or  $xy$  model. The upper transition temperature is believed to have a value approximately equal to that of the BKT transition point for the  $xy$  model, i.e.,  $0.89J/k_B$ .<sup>24</sup>

Our model Hamiltonian, represented by Eq. (8), is in fact a bond-diluted version of the  $q=8$  state clock model, involving NN interactions with bonding and antibonding electronic states. For our purpose the eight possible states of a site variable must be interpreted as the possible displacements of an atom from its designated equilibrium lattice site, with all the site variables being in the same clock-state if the system were in a fully ordered configuration (Fig. 3).

#### A. Procedure

The standard MC importance sampling,<sup>25</sup> was used to simulate the behavior of the system on  $L \times L$  square lattices with periodic boundary condition. We performed simulations on lattices of size  $L=12, 20, 32,$  and  $50$ . In every case the system was initialized in a random configuration suitable for high temperature regime where it is known to be disordered. Starting with initial value  $2.0J/k_B$ , the temperature was lowered in steps of  $0.05J/k_B$ . At every temperature the system was allowed to equilibrate through several hundred Monte Carlo steps per site (MCS). The data points were then acquired by averaging over 40 000 MCS. The data were accumulated in several bins and binned averages were used to obtain error estimates for the calculated average values. For most cases, the estimated statistical error is less than 2% of the calculated average value. In order to test our simulation code, we simulated the  $q=6$  state clock model (in the absence of bond dilution) and compared our results with the extensive literature available on the subject.<sup>9,10</sup> Good agreement was obtained.

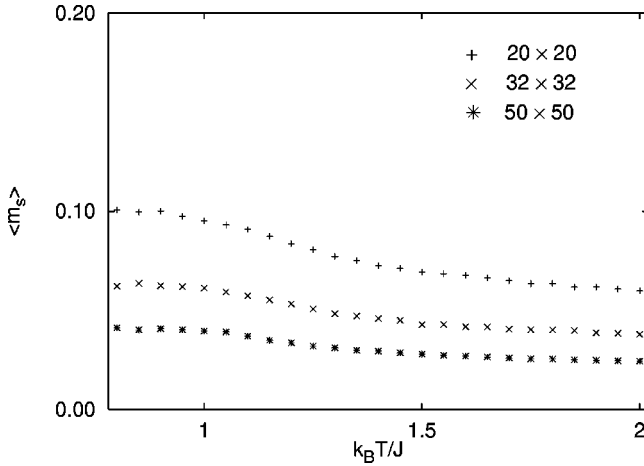


FIG. 4. Structural order parameter as a function of temperature for three system sizes.

The thermodynamic functions have been already discussed and given explicit mathematical definitions in Sec. III. In addition, the specific heat is obtained from equilibrium fluctuations in the internal energy

$$C = [\langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2] / 2Nk_B T^2. \quad (20)$$

The bond-related quantities, i.e., bond order parameter  $\langle m_b \rangle$ , bond susceptibility  $\chi_b$ , internal energy  $E$ , and the specific heat  $C$ , are normalized to the number of NN pairs  $2N$  for systems of size  $N=L^2$  with periodic boundary condition. On the other hand the structural properties, i.e., structural order parameter  $\langle m_s \rangle$  and structural susceptibility  $\chi_s$ , are normalized to the system size  $N$ . As a note on the calculation of the internal energy, the NN pairs were sorted out in ascending order of energy at every time step and were given a bond electron in that order. Our results correspond to an annealed hole (bond electron) concentration of 40% (60%).

### B. Thermodynamic parameters

Figure 4 contains the temperature variation of the struc-

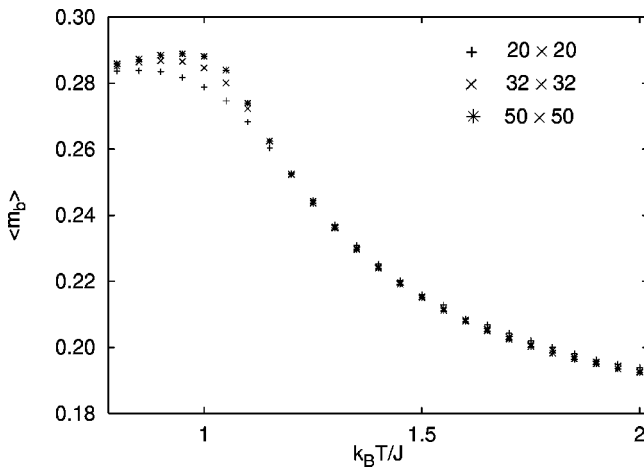


FIG. 5. Variation of bond order parameter with temperature. There appears a sharp variation due to local ordering of bonds.

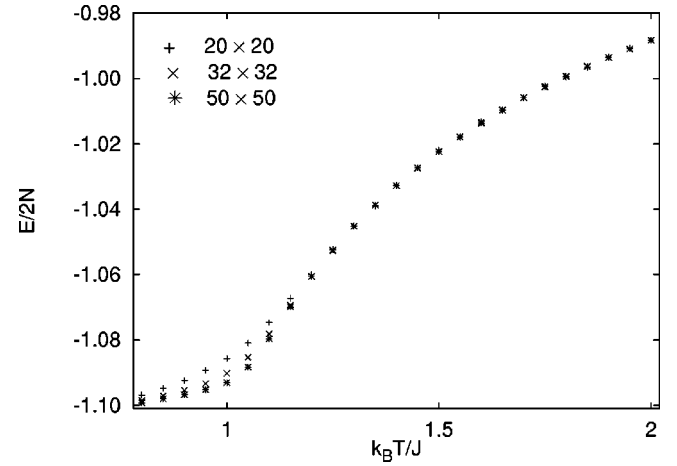


FIG. 6. Internal energy as a function of temperature.  $E$  is measured in units of coupling strength  $J$ .

tural order parameter  $\langle m_s \rangle$  for three different system sizes  $L=20, 32,$  and  $50$ . Clearly there is no indication of conventional structural ordering for the range of temperatures shown. The finite size effects on structural order parameter are evident, implying the vanishing of the order parameter for the systems of large enough size.

Figure 5 shows the bond order parameter  $\langle m_b \rangle$  as a function of temperature. There is no significant effect due to the system size on  $\langle m_b \rangle$ . Evidently the system undergoes moderate bond ordering with lowering of the temperature. This is in absence of conventional structural ordering as may be seen from Fig. 4 representing the temperature variation of the structural order parameter. The internal energy is shown in Fig. 6, exhibiting a sharp descend with decreasing temperature because of the local ordering of bonds.

### C. Response functions

Figure 7 shows the temperature variation of the structural susceptibility. The structural susceptibility is seen to be non-singular throughout the range of temperature shown, hence

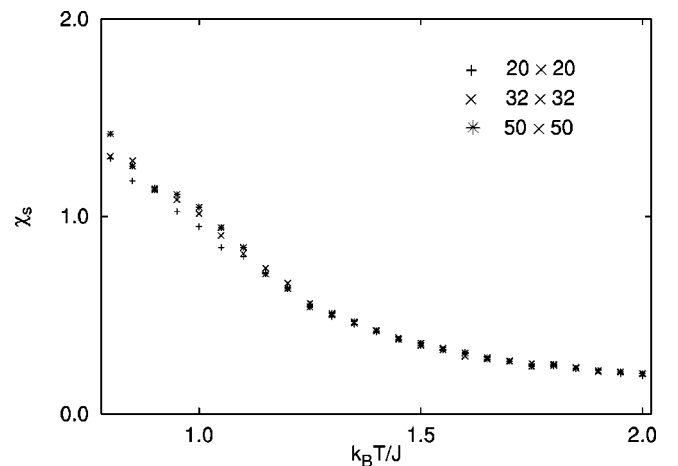


FIG. 7. Variation of structural susceptibility with temperature. Clearly there is no indication of long-range structural ordering in the temperature range shown.

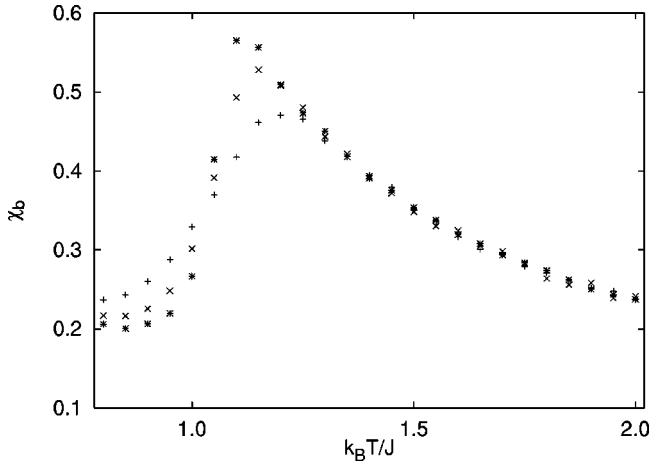


FIG. 8. Bond susceptibility as a function of temperature for three system sizes:  $20^2$  (+),  $32^2$  ( $\times$ ), and  $50^2$  (\*).

ruling out long-range structural ordering whether conventional or  $xy$  type. We need to point out that in the case of conventional ordering the structural order parameter deviates from zero at the transition point and stays finite for all temperatures below the transition point. But in the case of  $xy$  type ordering, the structural order parameter remains zero in the thermodynamic limit, even though the correlation length and the structural susceptibility diverge at the transition and stay infinite for temperatures below the transition.<sup>24</sup> There is a slight undulation at around  $1.0J/k_B$  that we believe is due to fluctuations arising from the local ordering of bonds, as is evident in Fig. 5 representing the temperature variation of the bond order parameter.

The bond susceptibility is shown in Fig. 8 displaying a peak followed by a sharp fall in the quantity as the tempera-

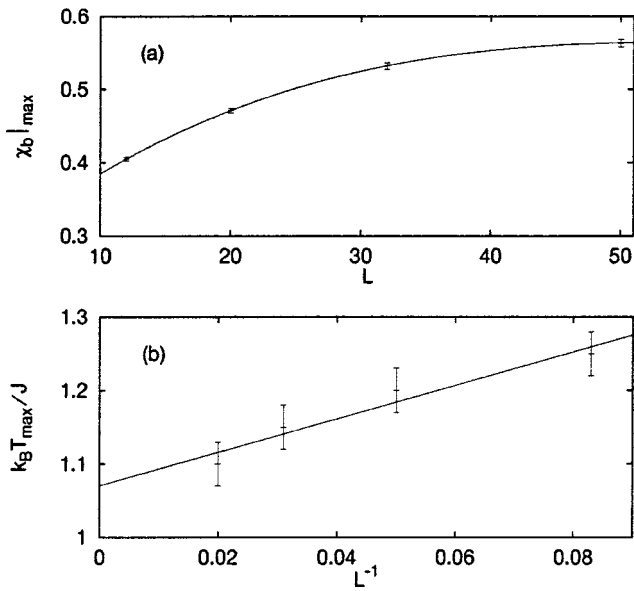


FIG. 9. (a) Variation of the peak value of bond susceptibility with lattice size  $L$ . Solid curve is drawn to guide the eye. (b) Temperature corresponding to the peak value of bond susceptibility as a function of  $L^{-1}$ . Solid line represents least-squares fit to the data points.

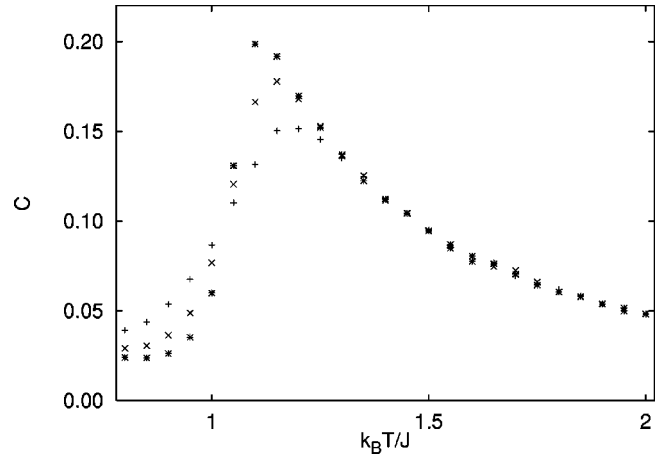


FIG. 10. Specific heat as a function of temperature for three system sizes:  $20^2$  (+),  $32^2$  ( $\times$ ), and  $50^2$  (\*).

ture decreases. While there is a slight size dependence to the height of the peaks, this tendency is seen to disappear for large enough lattices. This may be seen from Fig. 9(a), where the variation of the peak height with the lattice size is displayed. The temperature corresponding to the maximum of bond susceptibility, is estimated to be  $1.07J/k_B$  in the thermodynamic limit or the limit of the infinite lattice size. This estimate is obtained by a linear extrapolation of the data points as a function of  $L^{-1}$ , displayed in Fig. 9(b).

Figure 10 represents the variation of the specific heat with temperature. There appears to be some size dependence to the height of the peaks. This size dependence disappears for large enough system sizes as may be seen in Fig. 11(a) where the variation of the peak height for the specific heat with the lattice size is displayed. In fact even for the simple clock models with  $q > 4$  (in the absence of bond dilution), the spe-

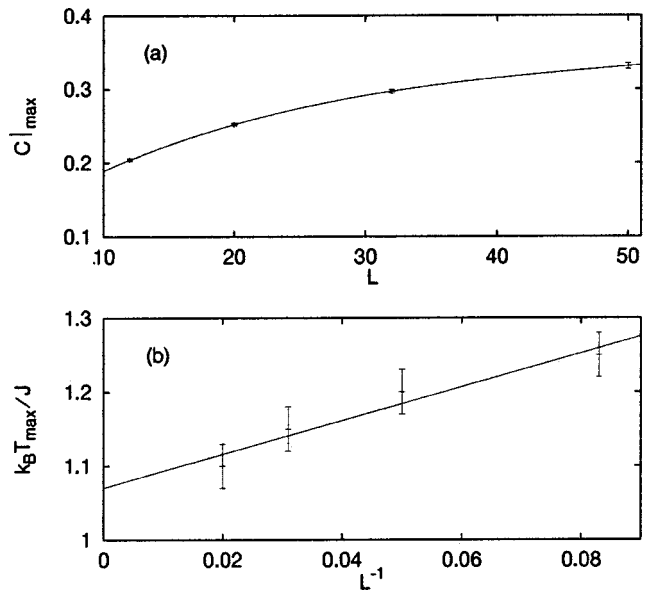


FIG. 11. (a) Variation of the peak value of specific heat with lattice size  $L$ . Solid curve is drawn to guide the eye. (b) Temperature corresponding to the peak value of specific heat as a function of  $L^{-1}$ . Solid line represents least-squares fit to the data points.



cific heat is found to be a smooth function of temperature free of any singular behavior such as a divergence.<sup>9</sup> The temperature corresponding to the maximum of the specific heat is estimated to have a value equal to that of the bond susceptibility in the thermodynamic limit, i.e.,  $1.07J/k_B$ , as may be seen from Fig. 11(b).

#### D. Discussion

Perhaps the most interesting feature of the simulation results, is the conspicuous peak in the bond susceptibility seen in Fig. 8, that is an indication of the local ordering of bonds, uncorrelated with any type of long-range structural ordering. This becomes evident from the structural order parameter and the structural susceptibility seen in Fig. 4 and Fig. 7, respectively. Unlike the behavior observed for the simple clock models in the absence of bond dilution, the structural susceptibility does not exhibit singular behavior in the intermediate temperature range hence ruling out long-range structural ordering whether conventional or  $xy$  type. The smooth behavior of the structural susceptibility can be of course understood in view of the large concentration of annealed holes, or bond dilution.

In the temperature range where the bond susceptibility displays a maximum, one also observes a maximum in the specific heat, shown in Fig. 10, which should be attributed to the large energy fluctuations associated with the local ordering of bonds. Indeed experimental measurements of the heat capacity for covalently bonded fragile systems such as  $As_2Se_3$ ,  $B_2O_3$ , etc., indicate similar peaks at the glass transition, which therefore suggest a bond-ordering nature for the glass transition in such systems.

In the bond-ordering temperature range, the bond order parameter is seen to increase rapidly with the decreasing temperature (Fig. 5). The internal energy, on the other hand, is seen to display a sharp descend with lowering of the temperature as may be seen in Fig. 6. This behavior along with the nonsingular behavior of the structural susceptibility testifies to the earlier assertion that a system may undergo substantial bond ordering and hence largely reduce its internal energy, in the absence of long-range structural ordering.

#### VI. SUMMARY

In the context of a model system, a bond energy order parameter is introduced for supercooled liquids, the temperature variation of which serves to distinguish between fragile and strong liquids. The variation with temperature of the bond susceptibility provides a theoretical identification for the calorimetric glass transition temperature as the temperature corresponding to the maximum of the bond susceptibility of a supercooled liquid. This identification has a distinct advantage in having its foundation in the bond energy order parameter characterizing viscous liquids.

MC simulation results of the model system indicate bond ordering at the intermediate temperature range that is uncorrelated with any type of structural ordering whether conventional or  $xy$  type, and thus make clear the possibility of the local ordering of bonds in the absence of long-range struc-

tural ordering. The local ordering of bonds must also result in the ordering of NN distances and moderation in the variation of NNN distances, and hence may be regarded as the physical origin of the local structural order or the medium-range order seen in the glassy materials.

#### APPENDIX: DERIVATION OF FLUCTUATION-DISSIPATION EQUATION FOR BOND SUSCEPTIBILITY

The change in the Gibbs free energy in an infinitesimal bond ordering process is expressed as

$$dG = -S dT - \langle M_b \rangle dH_b. \quad (A1)$$

The bond susceptibility apart from a normalization will therefore be given by

$$\chi_b = \left( \frac{\partial \langle M_b \rangle}{\partial H_b} \right)_{T, H_b=0} \quad (A2)$$

$$= - \left( \frac{\partial^2 G}{\partial H_b^2} \right)_{T, H_b=0}. \quad (A3)$$

The partition function  $Z$  in the presence of the field  $H_b$  is given by

$$Z = \text{Tr} \exp[-\beta(\mathcal{H} - H_b M_b)], \quad (A4)$$

where, the trace denotes a sum over all microstates,  $\beta = (k_B T)^{-1}$ , and  $M_b = |\sum_{\langle i,j \rangle}^{2N} \hat{\mathbf{B}}_{ij}|$ . The Gibbs free energy  $G(T, H_b)$  is of course given by the partition function

$$G = -\frac{1}{\beta} \ln Z. \quad (A5)$$

On substituting this expression for the Gibbs free energy into Eq. (A3), we get

$$\chi_b = \beta \left[ \frac{\partial}{\partial \beta H_b} \left( \frac{\partial \ln Z}{\partial \beta H_b} \right) \right]_{\beta, H_b=0}. \quad (A6)$$

On carrying out the partial differentiation with temperature held constant, and then equating  $H_b$  to zero, we get

$$\chi_b = \beta \left[ \frac{\text{Tr} M_b^2 \exp[-\beta(\mathcal{H} - M_b H_b)]}{Z} - \frac{\{\text{Tr} M_b \exp[-\beta(\mathcal{H} - M_b H_b)]\}^2}{Z^2} \right]_{H_b=0} \quad (A7)$$

$$= \beta \left[ \frac{\text{Tr} M_b^2 \exp(-\beta \mathcal{H})}{\text{Tr} \exp(-\beta \mathcal{H})} - \left( \frac{\text{Tr} M_b \exp(-\beta \mathcal{H})}{\text{Tr} \exp(-\beta \mathcal{H})} \right)^2 \right] \quad (A8)$$

$$= \beta [\langle M_b^2 \rangle - \langle M_b \rangle^2] \quad (A9)$$

$$= \beta \langle (M_b - \langle M_b \rangle)^2 \rangle. \quad (\text{A10})$$

The fluctuation-dissipation result expressed in Eq. (A9) as

well as Eq. (A10), relates the bond susceptibility of the system with the equilibrium fluctuations in the bond order parameter in the absence of the bond ordering field, or  $H_b = 0$ .

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<sup>1</sup>G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).

<sup>2</sup>J. H. Gibbs and E. A. DiMarzio, J. Chem. Phys. **28**, 373 (1958).

<sup>3</sup>W. Götz and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992); E. Leutheusser, Phys. Rev. A **29**, 2765 (1984).

<sup>4</sup>M. Suzuki, Y. Masaki, and A. Kitagawa, Phys. Rev. B **53**, 3124 (1996).

<sup>5</sup>R. Kerner and M. Micoulaut, J. Non-Cryst. Solids **210**, 298 (1997).

<sup>6</sup>M. Mézard and G. Parisi, Phys. Rev. Lett. **82**, 747 (1999).

<sup>7</sup>H. Tanaka, J. Chem. Phys. **111**, 3163 (1999); **111**, 3175 (1999).

<sup>8</sup>R. L. Mozzi and B. E. Warren, J. Appl. Crystallogr. **2**, 164 (1969).

<sup>9</sup>M. S. S. Challa and D. P. Landau, Phys. Rev. B **33**, 437 (1986).

<sup>10</sup>J. Tobochnik, Phys. Rev. B **26**, 6201 (1982); **27**, 6972 (1983).

<sup>11</sup>C. T. Moynihan *et al.*, J. Phys. Chem. **78**, 2673 (1974).

<sup>12</sup>A. J. Easteal *et al.*, J. Am. Ceram. Soc. **60**, 134 (1977).

<sup>13</sup>R. C. Zeller and R. O. Pohl, Phys. Rev. B **4**, 2029 (1971).

<sup>14</sup>P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. **25**, 1 (1972).

<sup>15</sup>W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972); *Amorphous*

*Solids: Low-Temperature Properties* (Springer-Verlag, Berlin, 1981).

<sup>16</sup>S. R. Elliott, *Physics of Amorphous Materials* (Longman Scientific, London, 1990).

<sup>17</sup>I. Prigogine and R. Defay, *Chemical Thermodynamics* (Longman Greens, London, 1954).

<sup>18</sup>C. A. Angell, J. Non-Cryst. Solids **131**, 13 (1991); **102**, 205 (1988).

<sup>19</sup>C. A. Angell, Science **267**, 1924 (1995).

<sup>20</sup>J. V. José, L. P. Kadanoff, S. Kirkpatrick, and D. R. Nelson, Phys. Rev. B **16**, 1217 (1977).

<sup>21</sup>S. Elitzur, R. B. Pearson, and J. Shigemitsu, Phys. Rev. D **19**, 3698 (1979).

<sup>22</sup>J. Kosterlitz and D. Thouless, J. Phys. C **6**, 1181 (1973); J. Kosterlitz, *ibid.* **7**, 1046 (1974).

<sup>23</sup>V. L. Berezinskii, Sov. Phys. JETP **32**, 493 (1971).

<sup>24</sup>J. Tobochnik and G. V. Chester, Phys. Rev. B **20**, 3761 (1979); R. Gupta and C. F. Baillie, *ibid.* **45**, 2883 (1992).

<sup>25</sup>K. Binder and D. W. Heermann, *Monte Carlo Simulation in Statistical Physics* (Springer-Verlag, Berlin, 1997).