LETTER TO THE EDITOR

A polychromatic correlated-site percolation problem with possible relevance to the unusual behaviour of supercooled H₂O and D₂O†

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Abstract. We introduce a new polychromatic correlated-site percolation problem, which has the novel feature that the partitioning of the sites into different species arises from a purely random process—that of random bond occupancy. A particular case of this percolation problem is shown to be of possible relevance in providing a physical mechanism which may contribute to the unusual properties displayed by liquid H₂O and D₂O under conditions of supercooling below the melting temperature.

1. Introduction

The unusual behaviour of liquid H_2O and its isotope D_2O has been appreciated for some time. Recently, it has become increasingly clear—especially from the concerted efforts of Angell and co-workers—that under conditions of supercooling these two liquids display additional anomalous properties (see e.g. the recent review of Angell (1979)). For example, as the temperature is decreased below the melting temperature, T_M, various static response functions such as the isothermal compressibility $K_T(T)$, constant-pressure specific heat $C_P(T)$, and thermal expansivity $\alpha(T)$ become larger at an increasingly rapid rate, while the mass density $\rho(T)$ decreases rapidly (Angell 1979). In fact, Angell has postulated the existence of a thermodynamic singularity at a temperature T_s, with $T_s = -45\,°C$ for H_2O at a pressure P of 1 atm.

Thus far, no satisfactory physical mechanism underlying these unusual liquid phenomena has been found. However, information obtained on supercooled water provides an important testing ground for theories of water structure, since the supercooled domain is expected to be a smooth extension to $T < T_M$ of the stable region.

In this Letter we propose a correlated-site percolation model that is possibly of relevance in providing some insight into the behaviour of supercooled water. Correlated-site percolation refers to the study of the connectivity of objects ('sites') whose state is not randomly determined as in ordinary random-site percolation. Previous studies of correlated-site percolation have concerned the connectivity of spins which are partitioned into two classes on the basis of an Ising or lattice-gas interaction (Müller-Krumbhaar 1974, Coniglio 1975, Sykes and Gaunt 1976, Domb and Stoll 1977, Klein *et al* 1978). This system has been found to be particularly useful (Coniglio *et al* 1979) in interpreting experimental data on polymer gelation (Tanaka *et al* 1979), where the connectivity of the constituent polymer molecules is an essential physical feature. In contrast to these previous studies, the present model of correlated-site percolation has the novel feature that the partitioning of sites into classes arises from a purely random process, that of random bond occupancy.

2. Definition of the model

Percolation problems do not require for their definition a regular lattice, a fact that will prove to be of relevance if one uses percolation concepts for describing a fluid system. However, since the method whereby one extends lattice percolation to 'continuum percolation' has been studied elsewhere (e.g. Webman *et al* 1975), we shall define the model directly for a lattice.

Consider, then, a lattice consisting of N sites, each of which has z nearest-neighbours. Ignoring surface effects, there are $Nz/2$ pairs of nearest-neighbour sites. In the random bond percolation problem (see Stauffer 1979 and references therein), one randomly places bonds between a fraction p_B of these $Nz/2$ pairs, and then studies the properties of the resulting clusters of connected sites.

Our work begins with the simple observation that each site can be considered to be a member of one of $z + 1$ different species, depending on whether $0, 1, 2, \ldots, z$ bonds emanate from that site. Since the bond distribution is random, it follows from the binomial theorem that the mole fraction of species j is simply

$$f_j = \binom{z}{j} p_B^j (1 - p_B)^{z-j}. \tag{1}$$

Although the total number of sites belonging to each species is determined solely by the random variable p_B, the connectivity properties are very different from those of pure percolation. For example, it is impossible for a species-z site to appear as a nearest-neighbour of a species-0 site. Similarly, if the z nearest-neighbours of a given site belong to species z, then the site itself must be species z †.

Because of the fact that the positions of each species are correlated, the extensive results now available for random percolation are not applicable to this problem. Also not applicable are the results for the previously studied correlated-site model in which the correlation is introduced through an Ising or lattice-gas interaction. Indeed, in Ising-correlated percolation, none of the 2^N states of an N-site system has zero statistical weight, while in the problem introduced here, many states have zero weight as illustrated by the examples cited in the preceding paragraph.

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† Equally, one could state that if all the nearest-neighbours of a given site are species-0, then the site itself must be species-0; indeed, there is symmetry under the transformation $p_B \to 1 - p_B$ between the properties of species j and species $z - j$.

3. Bichromatic percolation

It is useful to discuss first the connectivity properties of a simple bichromatic percolation model in which we partition the sites into only two classes (i.e. we colour each site one of two possible colours). For example, suppose the members of class 1 (black sites) are the Nf_z species-z sites, so that class 2 (white sites) would then be the remaining $N(1-f_z)$ sites. We display in figure 1 the results of computer simulations for a square lattice of
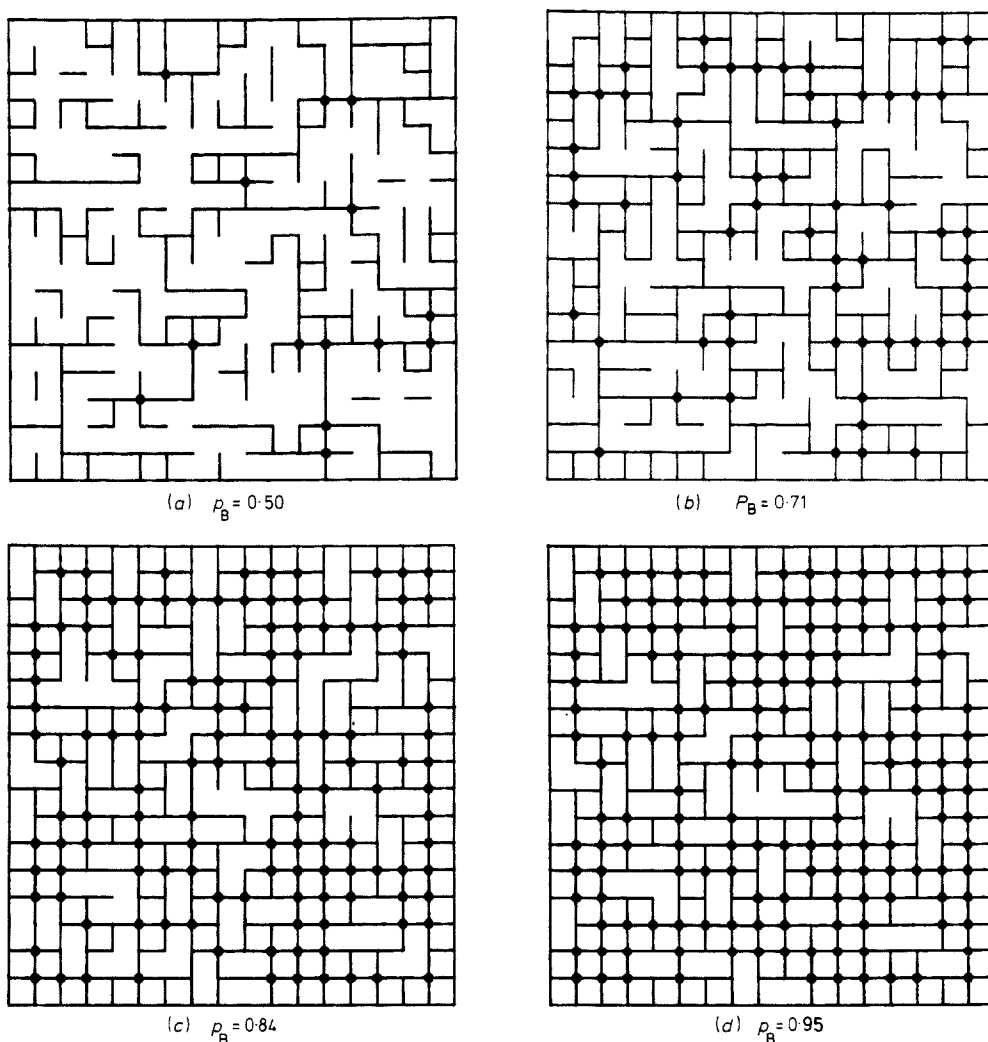

Figure 1. Computer simulations of the bichromatic correlated-site percolation problem on a square lattice ($z = 4$) with 256 sites and 512 bonds. The species-z sites ('class 1') are shown as solid circles, while the remaining sites ('class 2') are not shown. $(a)\,f_z = 0.0625$ ($p_B = 0.500$, the critical threshold of the random bond percolation problem), $(b)\,f_z = 0.25$ ($p_B = 0.707$), $(c)\,f_z = 0.50$ ($p_B = 0.841$), and $(d)\,f_z = 0.60$ ($p_B = 0.880$). One striking feature of the site clusters formed by the members of class 1 is their far lower degree of ramification in comparison with the remarkably high degree of ramification (Domb 1976) and low fractal dimensionality (Stanley 1980) exhibited by clusters in random-site percolation.
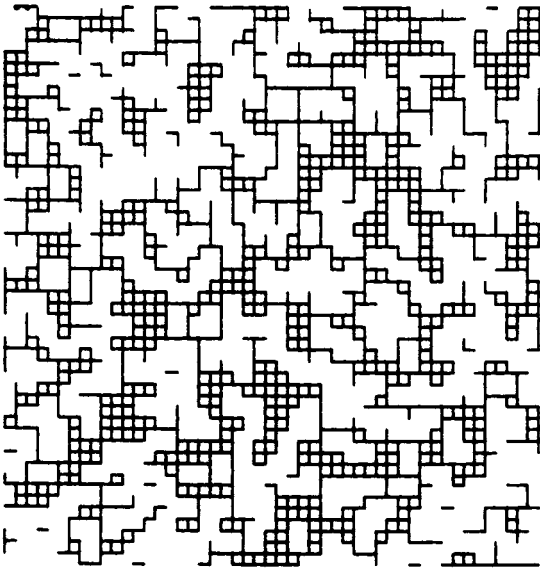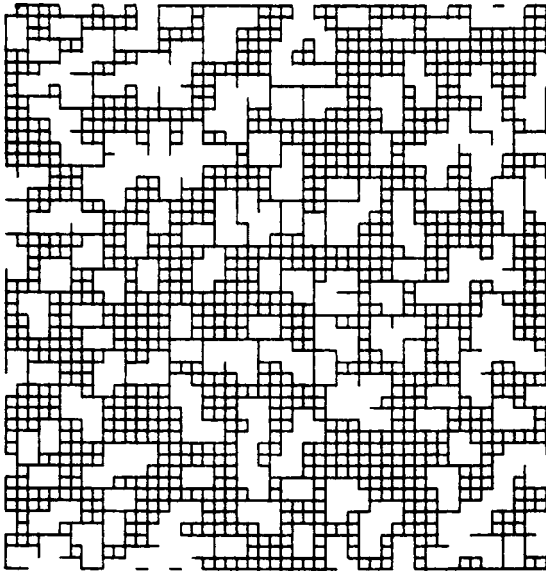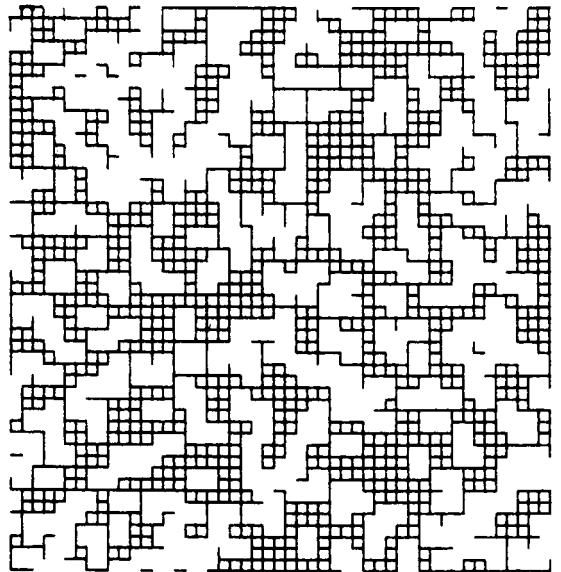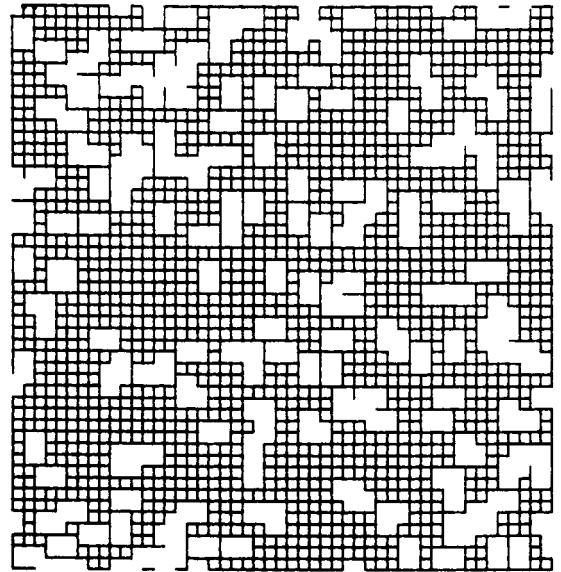
Figure 2. Computer simulations as in figure 1, except that now we have omitted all the bonds except those between species-z sites. This permits one to visualise better the 'patches' of four-bonded oxygens. Shown are $N = 2500$ sites and $2N = 5000$ bonds. (a) $p_B = 0.875$ ($f_z = 0.586$), (b) $p_B = 0.90$ ($f_z = 0.656$), (c) $p_B = 0.925$ ($f_z = 0.732$), (d) $p_B = 0.95$ ($f_z = 0.815$). Pictures such as these suggest that one might find relevant the consideration of the 'hard core' of a cluster—i.e. one might define a new class of sites to be those for which all four neighbours are species-z, and then consider the connectivity properties of this new class (e.g. Cohen and Grest 1979, Reich and Leath 1978)).

$N = 256$ sites. For this lattice, $f_z = p_B^4$ from equation (1). The bond percolation threshold is exactly 0.5, and hence the members of class 1 are largely isolated single sites unless one is well above the bond percolation threshold. Indeed, at $p_B^c = 0.5$, only 6% of the sites are members of class 1 (figure 1a), while at $p_B = 0.7$—where 99% of the sites belong to the 'gel molecule' or infinite cluster—only 25% of the sites belong to class 1 (figure 1b). It appears from preliminary Monte Carlo data (Blumberg, Shlifer and Stanley unpublished), that the critical-point exponents are the same for the correlated and the random site problem, though the threshold is somewhat lower for the correlated problem ($f_z^c \cong 0.56$, $p_B^c \cong 0.87$), than for the random problem ($p_s^c = 0.593$).

It is straightforward to obtain the exact solution of this bichromatic percolation problem for the special case of a one-dimensional ($d = 1$) lattice, using the same methods previously applied to the $d = 1$ random-site problem (e.g. Reynolds *et al* 1977 and references therein). One finds, for example, that the total number of site clusters (normalised per site)— the analogue of the Gibbs potential in thermodynamics—is

$$G(f_z) = f_z (1 - f_z^{1/2}). \tag{2a}$$

If one selects a species-z site at random, and asks how many other sites belong to this particular cluster, one obtains the 'mean cluster size'

$$S(f_z) = (1 + f_z^{1/2})/(1 - f_z^{1/2}). \tag{2b}$$

Thus the black (species-z) sites percolate at $f_z^c = 1$, and the critical exponents are the same as for random percolation.

For $d = 2$ and 3, we can compute the initial terms in low-density and high-density series expansions, though this is rather more difficult than in the random case. Also, the solution for the Cayley tree ('$d = \infty$') is readily obtained.

4. Polychromatic percolation

The division of the $z + 1$ species into only two classes is somewhat arbitrary unless justified by the particular physical system at hand. The full connectivity problem involving all $z + 1$ species is an example of polychromatic percolation (Zallen 1977, Halley and Holcomb 1978).

It is useful to consider the following line of reasoning. Suppose the sites correspond in some sense to oxygen atoms of a three-dimensional network with coordination number $z = 4$, and the bonds to hydrogen bonds between neighbouring pairs of oxygen atoms. Imagine also that the volume per oxygen atom, $\bar{V}_j$, depends on the number of bonds j emanating from the atom, with $\bar{V}_0 < \bar{V}_1 < \bar{V}_2 < \bar{V}_3 < \bar{V}_4$. Suppose we now partition the system into cells of characteristic dimension L, where L is, say, ten lattice spacings. With each cell we associate a 'local' density ρ_L, and we study the fluctuations of this local density from cell to cell. Since the positions of each species are correlated, and since the density is related to the site species, the density *fluctuations* are correlated. That is, they are quite different in character from the density fluctuations in the corresponding random-site model consisting of the same five species, present in the same mole fractions. The 'isothermal compressibility' in this correlated-site model is enhanced, just as the isothermal compressibility in a van der Waals gas is enhanced relative to its value in an ideal gas.

5. Discussion: possible relevance to supercooled H₂O and D₂O

The preceding models of correlated-site percolation are of theoretical interest, for the reasons discussed above. However, since they were conceived in an attempt to seek a physical mechanism for the unusual properties of liquid H_2O and D_2O, it is appropriate to conclude with some discussion of the way in which these models may be of relevance.

A striking feature of liquid H_2O and D_2O is that they are characterised by extensive hydrogen bonding. In fact, Geiger *et al* (1979) have very recently demonstrated, from analysis of molecular dynamics results, that for any reasonable definition of a hydrogen bond†, H_2O at 10°C is well above the bond percolation threshold. Hence the liquid consists of a single connected (hydrogen-bonded) network that is infinite in extent, as well as numerous finite networks. We shall refer to this infinite network as the 'gel molecule', recognising that this particular 'gel' differs in many respects from the more familiar and commonly occurring chemical gels (Gibbs *et al* 1973).

Let us next partition the oxygen atoms into five species, depending whether they are bonded to $0, 1, 2, \ldots, 4$ other oxygens, and let us focus on the 'patches' of the gel defined by connected regions of the four-bonded species. As T decreases. $p_B(T)$ increases and so does the fraction $f_4(T)$ of species-4 molecules; in fact, a 1% increase in $p_B(T)$ leads to a 4% increase in $f_4(T)$. The 'mean size of a patch', S, is only of order $10-10^2$ water molecules per patch in the supercooled region.

X-ray scattering studies suggest that a rather considerable degree of short-range order is present in liquid water (Eisenberg and Kauzmann 1969). Moreover, there are unusually strong and narrow peaks in the oxygen–oxygen pair correlation function at the distances appropriate to the positions of the nearest-neighbour, second-neighbour, and even third-neighbour positions of crystalline ice I_h. Accordingly, when the temperature is sufficiently low that $S \sim 10-10^2$, we might reasonably expect that the local density of the patches is less than that of the surrounding gel molecule. Thus the patches give rise to spatial density fluctuations, whose magnitude also increases as T decreases. Since the positions of the species-4 molecules are correlated, the density fluctuations associated with the patches are also spatially correlated.

To summarise thus far: as T decreases, the correlated patches increase in size, the overall mean density ρ_T decreases, and the density fluctuations associated with the patches,

$$\langle (\rho - \langle \rho \rangle)^2 \rangle / \langle \rho \rangle \propto K_T, \tag{3}$$

increase.

One immediate effect of the low-density patches of the gel is to give rise (i) to an anomalous negative contribution to the normally positive thermal expansivity and (ii) to an anomalous positive contribution to the isothermal compressibility K_T. The following intuitive arguments may be useful in this regard:

(i) Since

$$-\rho\alpha \equiv (\partial\rho / \partial T)_P, \tag{4a}$$

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† It is conventional to introduce some 'cut-off' energy V_{HB} and to state that two molecules are *bonded* if their interaction potential $V(r)$ is such that $V(r) < V_{HB}$ and *unbonded* otherwise (see, e.g., Stillinger 1975 and references therein). Though this may seem to be imposing a 'discrete' symmetry upon a physical function, $V(r)$, that is not discrete, Hill (1956) and others have sought to justify this approximation by reasoning that two particles are unbonded when $V(r)$ is less than their mutual kinetic energy (see, e.g., Coniglio *et al* 1979 and Joanny 1979).

we can write, schematically,

$$(-\rho\alpha)^A \equiv \left(\frac{\partial\rho}{\partial p_B}\right)_P \left(\frac{\partial p_B}{\partial T}\right)_P. \tag{4b}$$

Now the density decreases as the fraction of hydrogen bonds increases, while p_B itself decreases with increasing temperature. Thus $-(\rho\alpha)^A$ is the product of two negative factors and hence is positive, as observed experimentally. Moreover, it is clear that $-(\rho\alpha)^A$ increases as T decreases.

(ii) A similar schematic analysis applies to K_T, for since

$$\rho K_T \equiv (\partial\rho/\partial P)_T, \tag{5a}$$

we can write

$$\rho K_T^A = \left(\frac{\partial\rho}{\partial p_B}\right)_T \cdot \left(\frac{\partial p_B}{\partial P}\right)_T. \tag{5b}$$

Now $p_B(T, P)$ is a decreasing function of P and hence we conclude that K_T^A is positive and increases as T decreases. We can equally argue from (3) that K_T is a positive and strongly increasing function, since the density fluctuations due to the patches are correlated.

An analogous heuristic argument can be developed concerning the anomalous part, due to hydrogen bonding, of the constant-pressure specific heat, given by $T^{-1}C_P = (\partial S/\partial T) \propto \langle (H - \langle H \rangle)^2 \rangle$, where S is the entropy and H is the enthalpy.

Some of the more unusual properties of liquid H_2O occur when it is subjected to modest pressure (up to 2 kbar). Since $f_4(T, P) = (p_B(T, P))^4$, the correlated patches of lower mass density decrease in size. Thus one would expect that the pressurised system would have to be at a lower temperature in order to display the same hydrogen-bonding-caused anomalies, so that T_s, $K_T(T, P)$, and the TMD (temperature of maximum density) would all be expected to decrease with pressure. Indeed, all three phenomena are observed experimentally (Angell 1979).

A second way of reducing the connectivity of the patches is through the introduction of 'network-breaking impurities' (e.g. H_2O_2) that do not form four strongly directional hydrogen bonds. One's expectations are borne out by experimental data, which show marked decreases in both T_s and K_T. (To the best of our knowledge, extensive measurements of the TMD have not been carried out for water containing network-breaking impurities.)

There is one 'network-enhancing' impurity, D_2O, which might be expected to increase T_s, K_T, and the TMD—and all three phenomena are indeed observed.

It is tempting to speculate on the possibility that T_s is associated with the percolation of four-bonded molecules or the percolation of some subset of species-4 molecules (e.g. the percolation of those species-4 molecules all of whose neighbours are also species-4). Indeed, the fact that both pressure and network-breaking impurities decrease T_s, while D_2O increases T_s, is consistent with this possibility. Moreover, extrapolation to $T = T_s$ of experimental data on $\rho_T(T)$ strongly suggests that $\rho_T(T = T_s) < \rho_{ice}(T = T_s)$, as would be predicted if $f_4(T = T_s) \neq 1$.

The dynamic properties of water are characterised by the fact that hydrogen bonds are breaking and re-forming with a characteristic time τ that is of the order of picoseconds at room temperature[†]. If the fraction $f_0(T, P) = (1 - p_B(T, P))^4$ of

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† Thus water does not support a static or low-frequency shear stress, unlike more commonplace gels.

unbonded water molecules makes a significant contribution to transport properties such as self-diffusion $D_S(T, P)$ (Pruppacher 1972, Gillen *et al* 1972), then one would predict that $f_0(T, P)$ and hence $D_S(T, P)$ (a) decrease as T is reduced, (b) increase with pressure and (c) decrease with D_2O dilution. All three phenomena are observed in water at low temperatures (Angell 1979). Conversely, to the extent that the highly structured local patches of the infinite connected network are responsible for the dramatic decrease in transport at low temperatures, then one predicts the same observed effects of (a) T, (b) P and (c) isotope substitution.

In conclusion, we emphasise that this picture of water structure is highly oversimplified, even if regarded as a zeroth-order approximation. However, there are numerous examples from recent work in phase transitions (e.g. the lattice-gas model) where a highly simplified model has in fact been sufficient to capture the essential physical mechanisms operative in a given phenomenon—and it is quite possible that the formation of correlated low-density connected patches of the hydrogen-bonded water network is a relevant mechanism in supercooled water.

Note added in proof. Recently Stanley and Texeira (1979) have prepared a detailed comparison between the predictions of the model proposed here and the wealth of experimental data available on H_2O and D_2O at low temperatures. They find general agreement with all existing data, and propose new experiments that would serve to test further the structural assumptions on which the present model is based.

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