Dynamics of Bonded Networks with Two Energy Scales

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We model the dynamics of a molecular network with two distinct energy scales $E_1 \ll E_2$. A novel critical bond dynamics is shown to arise due to screening. We identify an order parameter and determine the related exponent at the critical temperature T_c. Above T_c, the dynamics is characterized by a power-law distribution of bond lifetimes with an exponential cutoff at a time that diverges at T_c. Our picture is applied to liquid water.

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A variety of molecular networks are found in nature. Usually, the bonds have a single characteristic energy scale. However, in liquid water[1] the hydrogen binding energy (20 kJ/mol) is much larger than kT. Still, the network of hydrogen bonds is changing on a time scale of picoseconds. Recent studies[2] suggest that this reorganization locally is mediated by a fifth molecule inside the first coordination shell—in the presence of this "excess" molecule the local strain weakens the nearby hydrogen bonds slightly. Motivated by this work we consider here a simple model of a network characterized by two *distinct* energy scales E_1 and E_2, where $E_1 \ll E_2$. We shall think of E_2 as a "pure" molecular binding energy, while E_1 is a slight change in energy (per molecular bond) in the presence of a "defect." Remarkable features are found for the model, particularly a critical behavior in space and time in the limit of infinite E_2/E_1.

To describe the dynamics we carefully distinguish between regions where at least one defect is present, and pure regions where there are no defects. In the former case, the creation of a new defect only involves energies of order E_1, while in the pure regions a defect only originates from removing a bond of energy E_2. Regarding a defect as a missing bond, these considerations lead us to study the following dynamics on a lattice with coordination number z.

(i) Let, at time t, $n=n(b)$ be the total number of bonds coming out of the two sites connected by a bond b. At time $t+1$ the bond b is removed with a probability p_r given by

$$p_r = \begin{cases} \exp(-nE_1/kT), & \text{if } n < 2z, \\ 0, & \text{if } n = 2z. \end{cases} \quad (1)$$

(ii) Bonds missing at time t are added at time $t+1$ with a fixed probability A.

In the presence of a defect, the total energy change is assumed to be nE_1 when a bond is removed. The zero probability for removing a bond when $n=2z$ represents the screening; here we assume E_2 to be infinite—a bond inside a pure region cannot be removed. Furthermore, we assume for simplicity that A is independent of the local connectivity. Any temperature dependence of the bonding rate A will define a different path in the phase diagram (T,A).

We have simulated the model in two dimensions on hexagonal ($z=3$), square ($z=4$), and triangular ($z=6$) lattices with 128×128 unit cells, and in three dimensions on cubic ice ($z=4$) and cubic ($z=6$) lattices with $32\times32\times32$ unit cells (periodic boundary conditions). Very long runs (up to 10^5 updatings per bond) have been performed near the critical line as discussed below. We shall refer to the cubic ice lattice unless otherwise stated.

From an initial random distribution of bonds, the system reaches (after a transient period) a stationary state characterized by the fraction p of bonds per lattice bond.[3] Let $\tilde{T} \equiv kT/E_1$. If $\tilde{T} \gg 1$, then $p_r \simeq 1$. At equilibrium, the fraction of bonds that are removed [$pp_r \simeq p$] equals the fraction of bonds that are added [$(1-p)A$]; i.e., $p=(1-p)A$, or

$$p(T \to \infty) = A/(1+A). \quad (2)$$

In general, the system seeks a stationary state where the competing terms (the bond removal and the bond add-

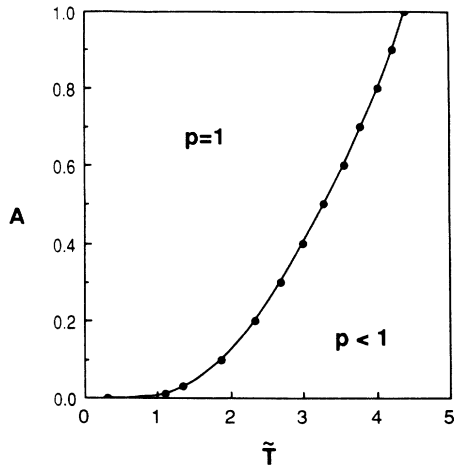

FIG. 1. $(\tilde{T},A)$ phase diagram for the dynamics given by (i) and (ii). $\tilde{T}=kT/E_1$. The critical line separates the fully connected configuration with $p=1$ (top left) and a stationary behavior with $p<1$.

ing) are equal. However, when the temperature is lowered below a certain critical temperature T_c, we find that the adding of bonds dominates, and the system is driven to the fully connected configuration with $p=1$. The critical temperature T_c at which p becomes 1 depends on A.

Figure 1 shows the $(\tilde{T},A)$ phase diagram—the line separates the fully connected regime (top left) from the regime of incomplete bonding. At the critical line we find a "second-order" transition from $p<1$ to $p=1$, and $1-p$ can be considered as an order parameter. In particular, the transition is *not* a percolation transition (in the usual sense).[4] The critical exponent β for the order parameter,

$$1-p\sim(T-T_c)^{\beta}, \tag{3a}$$

is calculated to be $\beta=0.67\pm0.02$ independent of A (Fig. 2). We also considered the first correction to the order-parameter dependence by changing A for fixed T. We find

$$1-p\sim(A_c-A)^{\beta'}, \tag{3b}$$

with $\beta'=0.83\pm0.02$ independent of the choice of T.[5] Thus, for a path $A(T)$ we have close to the critical line $[(A_c-A)\simeq|A'(T_c)|(T-T_c)]$

$$1-p\simeq a(T-T_c)^{\beta}+b(T-T_c)^{\beta'}. \tag{3c}$$

For paths $A(T)$ crossing the critical line (at T_c) we find that the prefactor ratio b/a is larger for lower values of T_c and for larger values of $|A'(T_c)|$.

To describe the bond *dynamics* further, we have also calculated the distribution $P(\tau)$ of bond lifetimes. The lifetime of a bond is defined as the number of time steps from when the bond is added to when the bond is removed. Figure 3(a) shows $P(\tau)$ for various temperatures at $A=0.5$. The data suggest a scaling form for the distribution

$$P(\tau)=\tau^{-\phi}f(\tau/\tau^*), \tag{4a}$$

with $\phi=1.0\pm0.1$, and

$$\tau^*\sim(T-T_c)^{-\gamma}. \tag{4b}$$

Figure 3(b) shows that to a good approximation $f(\tau/\tau^*)$ is given by a simple exponential function $f(x)\sim e^{-x}$ (τ^* is defined by the inverse slope). The inset shows that $\tau^*(T)$ obeys the scaling form (4b) with $\gamma=1.0\pm0.1$.[6]

If we consider the time evolution of a cluster of miss-

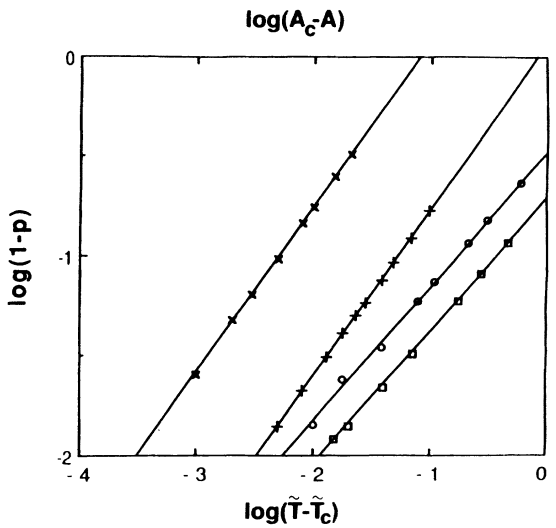

FIG. 2. Order parameter $1-p$ vs $\tilde{T}-\tilde{T}_c$ (lower scale) for fixed A: □, $A=0.9$, $\tilde{T}_c=4.230$; ○, $A=0.5$, $\tilde{T}_c=3.288$; and $1-p$ vs A_c-A (upper scale) for fixed $\tilde{T}$: +, $\tilde{T}=3.288$, $A_c=0.5$; ×, $\tilde{T}=1.876$, $A_c=0.1$.

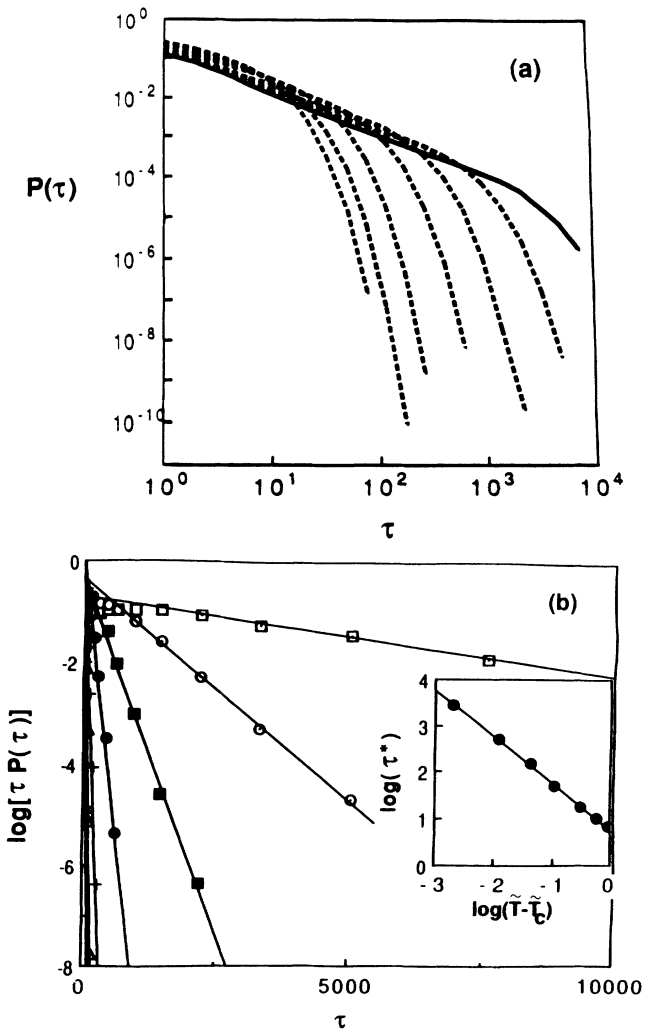

FIG. 3. (a) Distribution $P(\tau)$ of bond lifetimes for $A=0.5$ and various values of $\tilde{T}$ close to $\tilde{T}_c=3.288$. From right to left: $\tilde{T}=3.29$, 3.3, 3.33, 3.4, 3.6, 3.9, and 4.2. (b) $\tau P(\tau)$ vs τ (semi-logarithmic) for the same temperatures as in (a). The corresponding times τ^* are defined by the inverse slopes. Inset: τ^* vs $\tilde{T}-\tilde{T}_c$.

ing bonds (defects), the dynamics close to the critical point is burstlike. Some of the clusters "die," and some of them grow and burst into a number of clusters, some of which die, some of which again grow. The critical point can be viewed as the point where a burst *barely* reaches infinity. To analyze this picture, we have studied the evolution below the critical point of a fully connected configuration, except for one bond. Since the process defined by (i) and (ii) is stochastic, the time τ needed to reach the stable, fully connected configuration varies from run to run. Correspondingly, the cluster of bonds affected before the final state is reached varies in size s. We find that both the distribution $D(\tau)$ of times τ and the distribution $D(s)$ of cluster sizes s follow a power law at the critical point. Moreover, $D(\tau) \sim P(\tau)$ (same exponent ϕ).

The critical dynamics described in the simple model given by (i) and (ii) relies on the screening effect defined by (1).[7] In the mean-field (or infinite-dimensional) limit where all sites are interconnected there is no screening. Using $\epsilon = zE_1$ as the energy scale in the large-z limit we have

$$(1-p)A = p\exp(-2p\epsilon/kT)\,; \tag{5}$$

the rate at which bonds are added [left-hand side of (5)] balances the rate at which bonds are removed [right-hand side of (5)]. We immediately observe that $p < 1$ for any positive T ($T_c = 0$). Nevertheless, a closer inspection of (5) shows that some remnant of the lower-dimensional behavior persists. For instance, the p value (2) at high temperatures is valid in all dimensions. Also, $p(T)$ given implicitly by (5) has an inflection point at T_I defined by

$$p(T_I) = kT_I\epsilon\,, \tag{6a}$$

or

$$T_I = e^2 A\epsilon/(1+e^2 A)k\,. \tag{6b}$$

The behavior of $p(T)$ at this temperature is particularly noticeable when $e^2 A \lesssim 1$. In this case, $p(T)$ increases rapidly at T_I from the value (6a) to the low-temperature behavior[8]

$$p(T) = 1 - A^{-1}\exp(-2\epsilon/kT)\,. \tag{7}$$

A rapid increase of p is indeed seen for lower-dimensional systems at T_c, and (6b) (replacing T_I with T_c) gives a good approximation to the critical line below $kT_c = zE_1/2$.

More realistically, the zero probability in (1) for removing a bond when $n = 2z$ should be replaced by $p_r = \exp(-2zE_2/kT)$. However, when $E_2 \gg E_1$ the effect of E_2 on the dynamics is negligible. For $T < T_c$, $p(T)$ will behave according to (7) with ϵ replaced by zE_2, but this has no physical significance since $E_2 \gg kT_c$.

For liquid water, the defects (or missing bonds) correspond to so-called *bifurcated bonds*[2] that are associated with the presence of excess molecules inside the first coordination shell, and the probability A may be viewed as a local expansion rate. The presence of a critical dynamics at a nonzero temperature, here shown to arise from the underlying mechanism of screening, is in accord with the experimentally observed power-law increase of characteristic times, suggesting an unattainable critical temperature at $T = T_c \simeq -46\,^\circ$C.[1] In addition, recent molecular-dynamics (MD) simulations[9] yield a distribution of hydrogen-bond lifetimes that is described by a wide power-law region, followed by a fast decay above a characteristic time τ^*. The value of τ^* increases with decreasing temperature, and appears to diverge at a temperature T_c consistent with that suggested by experimental studies.

When bonds and bond defects are associated with different energies, densities, and local compressibilities, the critical behavior of the order parameter $1-p$ at T_c gives rise to a critical behavior of the thermodynamical properties (specific heat, expansion coefficient, compressibility, etc.). For example, the correspondence between a missing bond and the presence of an "extra" molecule in the first coordination shell relates the order parameter $1-p$ to the density ρ.[10] In particular, the decrease in the density of liquid water with decreasing temperature ($T < 4\,^\circ$C) is caused by the rapid decrease of the order parameter $1-p$. We emphasize that we have only considered the liquid phase of water; the model does not separate a "glassy" fully connected liquid phase from a crystalline ice structure.[11]

We notice that from an experimental point of view the presence of a genuine phase transition in supercooled liquid water is somewhat unclear due to the onset of homogeneous nucleation of ice at about $-40\,^\circ$C; also it seems impossible at the present time to extend MD simulations closer to T_c due to diverging relaxation times in the system. From the model we find $E_1 \simeq kT_c/4 \simeq 500$ J/mol, 40 times smaller than the hydrogen bonding energy E_2. Based on this result the effect of a finite E_2 on the critical behavior near T_c can be estimated from (7) (with ϵ replaced by zE_2). At $T = T_c$ we find $1-p \simeq 10^{-35}$; hence the changes due to a finite value of E_2 are physically irrelevant.

The realization of a critical dynamics and thermodynamics from an underlying and basically simple screening mechanism raises the interesting possibility of seeing an anomalous behavior similar to that of water in other materials, and we urge studies in that direction. One might consider materials like Ge, Si, GaSb, and InSb, where the coordination number *increases* by melting.[12] Other candidates are materials like S, Se, and Te, where molecular chains are present in the liquid state.[13]

In conclusion, we have shown that a critical bond dynamics arises due to screening in molecular networks with two energy scales, $E_1 \ll E_2$. We have identified an order parameter as the fraction $1-p$ of missing bonds.

At the critical temperature T_c this fraction approaches zero [cf. (3)]. The transition at T_c is characterized by a power-law distribution of bond lifetimes. As an example, we have considered liquid water where experiments[1] as well as MD simulations have suggested the presence of an (unattainable) critical temperature.

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[2]P. A. Giguère, J. Chem. Phys. **87**, 4835 (1987); A. Geiger, in *Hydrogen Bonded Liquids,* edited by J. Dore and J. Teixeira (Kluwer, Dordrecht, 1990); F. Sciortino, A. Geiger, and H. E. Stanley (to be published).

[3]Finite-size fluctuations in p were observed but will not be discussed here.

[4]H. E. Stanley and J. Teixeira, J. Chem. Phys. **73**, 3404 (1980); R. L. Blumberg, H. E. Stanley, A. Geiger, and P. Mausbach, J. Chem. Phys. **80**, 5230 (1984).

[5]The exponents β and β' are found to be independent of the lattice up to a change in dimension. For two dimensions we find $\beta=0.57$ and $\beta'=0.67$.

[6]Also the exponents ϕ and γ are found to depend only on the dimension d. For $d=2$, $\phi\simeq 1.35$ and $\gamma\simeq 1.3$.

[7]A similar critical site dynamics has been observed in the so-called A model in one dimension [R. Dickman and M. A. Burschka, Phys. Lett. A **127**, 132 (1988)].

[8]For example, for $A=e^{-2}$, $p(T)$ "jumps" at T_l from $p=0.5$ to $p=1-e^{-2}\simeq 0.9$.

[9]F. Sciortino, P. H. Poole, H. E. Stanley, and S. Havlin, Phys. Rev. Lett. **64**, 1686 (1990).

[10]A simple relation between p and ρ could be

$$\rho(T)=[x-(x-1)p(T)]\rho_{\rm ice}/[1+\alpha(T-T_c)]\,,$$

where the factor $x-(x-1)p=p+x(1-p)$ comes from assuming x molecules per bond defect ($1<x<2$), and the denominator is the usual linear volume-expansion term. At $T=T_c$, $\rho(T)$ is normalized to the density $\rho_{\rm ice}$ for ice. The temperature scale for $p(T)$ is set by $T_c=-46\,^\circ$C. For $A=0.5$, this temperature corresponds to an energy $E_1=kT_c/3.288=452$ J/mol. Also, we find $p=0.75$ at $T_0=4\,^\circ$C, and $p=0.62$ at $T_b=100\,^\circ$C, in agreement with recent experiments [O.E. Hare and C. M. Sorensen, J. Chem. Phys. (to be published)]. To find x and α we use the values $\rho(T_0)=1.09\rho_{\rm ice}$ and $\rho(T_b)=1.04\rho_{\rm ice}$. We obtain $x=1.74$ and $\alpha=1.76\times10^{-3}\ {\rm K}^{-1}$. Based on these values, $\rho(T)$ is found within the 0.3% variation of experimental values in the range $-15\,^\circ{\rm C}<T<100\,^\circ$C [R. J. Speedy, J. Phys. Chem. **91**, 3354 (1987), and references therein]. For $-35\,^\circ{\rm C}<T<-15\,^\circ$C, the error in ρ increases to 1%. Below $-35\,^\circ$C, ρ has not been measured.

[11]For instance, an enhanced (transient) local density due to excess molecules trapped inside the solid phase can only change by "melting" an expanding path, thereby removing strong (E_2) bonds. This is in contrast to the model for the liquid phase which can move as a whole. Also there is a large entropy release connected with melting from the solid to the liquid phase. The differences between the solid and the liquid phase can be naturally modeled, differentiating between bonds in the liquid phase ("liquid" bonds) and bonds in the solid phase ("solid" bonds): Solid bonds are defined as bonds with lifetime larger than a certain (crystal) restructuring time $\bar\tau$. Bonds added are by definition liquid bonds. The removal of solid bonds are associated with a change in free energy $\Delta F=E_2-T\Delta S$ (per bond), where ΔS is the entropy change. At the melting temperature T_m, $\Delta F=0$, i.e., $\Delta S=E_2/T_m$. Hence at $T\simeq T_m$, ΔF is well approximated by $\Delta F=E_2(T_m-T)/T_m$. Now, the evolution is determined by replacing (1) by $p_r=\exp[-(n_s\Delta F+n_lE_1)/kT]$ when $n<2z$, and $p_r=\exp[-(n_s\Delta F+n_lE_2)/kT]$ when $n=2z$, where $n=n_s+n_l$ is divided into a number of solid (n_s) and liquid (n_l) bonds. For $A=0.5$, $T_c=-46\,^\circ$C, and $T_m=0\,^\circ$C, $\Delta F\simeq 4$ kJ/mol$\gg E_1$ at T_c. Besides the melting, the modified dynamics accounts for homogeneous nucleation at a temperature at which $P(\bar\tau)\sim 1/N$ (N is the number of molecules). For a volume of $(10\ \mu{\rm m})^3$, $\bar\tau\simeq 10^3$ time steps correspond to homogeneous nucleation at $T=T_{\rm HM}=-39\,^\circ$C (each time step can be estimated to about 0.2 ps).

[12]In practice, the semiconductors mentioned are not the best candidates. The substantial change in coordination number from 4 in the crystal to 8 in the (metallic) liquid indicates that the expansion rate A is small, implying a rapid decrease of p at T_c (p equal to the fraction of semiconducting bonds). In agreement with this, the liquids are bound to be purely metallic at the melting point.

[13]Based on the anomalous behavior of sulfur at 160 °C, sulfur seems to be a candidate that "almost made it." In our picture the dissolution of the S_8 chains at 160 °C means that A drops to zero at this temperature (40° above the melting point). More promising are Se and Te. In particular, a conductivity maximum is found for liquid tellurium [A. S. Epstein, H. Fritzsche, and K. Lark-Horovitz, Phys. Rev. **107**, 412 (1957)]. This maximum has been attributed to the presence of two conductivity terms; one semiconducting $\sigma_{\rm sc}$ associated with the chains, and one metallic $\sigma_{\rm m}$ associated with the "free" Te atoms. The fraction $1-p$ of Te ions increases with temperature. Our model suggests a critical behavior of $p(T)$ and consequently of the conductivity.