Dimer Model for Electronic and Molecular Systems and the Intermediate Phase

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Abstract

We introduce a lattice model of dimers with directional interactions as a paradigm of molecular fluids or strongly correlated Cooper pairs in electronic systems. The model supports an intermediate phase that is common to both systems. There are two different ideal glasses having no mobility since they possess zero entropy. A pairing parameter is introduced to study the geometrical distribution of holes in various phases.

Phillips [1] has provided strong arguments to suggest topological similarities between the phase diagrams of electronic and molecular systems, and the presence of generic intermediate phases with novel properties by considering numerous classical molecular systems and quantum electronic systems. If true, this will be a major progress in our conceptual understanding of glasses [2]. Unfortunately, these topological similarities cannot be demonstrated because of a lack of reliable analytical solutions. To overcome this, we propose a phenomenological lattice dimer model (on a regular lattice) that describes both a molecular and an electronic system. We investigate its phase diagram by solving it exactly on a Husimi cactus as an approximation of the original lattice. The solution on the cactus goes beyond the conventional mean-field approximation [3]. Dimers represent the smallest molecules that, in the absence of any hole (collectively representing hole, solvent, free volume, dopant, impurity or dissociated dimers), can get into a unique ordered state not because of the regular lattice structure, but because of physical interactions. On the other hand, monomeric molecules form an ordered state merely because of the lattice structure. Thus, dimers can be regarded as the simplest model molecules whose physics is primarily controlled by interactions and not by the underlying lattice, although the latter certainly affects it. The extrapolation of the disordered liquid below the melting temperature $T_M$ gives rise to the supercooled liquid (SCL), which remains disordered at temperatures where the crystal (CR) is more stable, and represents the stationary limit of metastable states (SMS) which can be studied by the use of the partition function formalism [4]. It is found that the mathematical continuation of the SCL entropy $S$ becomes negative (entropy crisis) [5] below a positive Kauzmann temperature $T_K$. A continuous ideal glass transition has to be invoked at $T_K$ to avoid the genuine entropy crisis, since states with negative entropy cannot be observed in Nature [6]. The SCL freezes at $T_K$ and turns into an ideal glass (IG) for $T \leq T_K$. The glass is inert, independent of the temperature, and has zero entropy so that there can be no mobility in it, since mobility requires thermodynamically many configurations (positive entropy) to change into each other.

Dimers can also be thought of as representing strongly correlated Cooper pairs of electrons in high-$T_c$ superconductors [9], and have been investigated by various workers [10, 11]. Since the antiferromagnetic Mott insulator does not support the motion of holes created on doping, it is thought that there must exist another insulating but disordered state, the spin-liquid [9], which becomes superconducting under doping. At higher doping, superconductivity disappears, which makes the superconductor an intermediate phase [1]. Similarly, it has become gradually apparent in molecular systems (such as SiO$_2$, GeO$_2$ that are tetrahedrally bonded) that the short-ranged orientational bonding plays an important role in giving rise to a liquid-liquid (L-L) phase transition [1, 2] to an intermediate disordered phase. In ordinary electrolytes, the attractive dipolar interactions give rise to a similar intermediate phase in the form of head-to-tail chains [3]. Orientation interactions in the dimer model endow the model with enough richness to predict a transition that can be identified as a L-L transition to an intermediate phase with orientational order that is different from the crystalline order. The model, when applied to Cooper pairs, also gives rise to the columnar, staggered, and plaquette phases that have been seen in the short-ranged resonance-valence bond model (RVB) of Anderson [10, 11]. The classical dimer model that we consider gives rise to both an ordered crystal and two disordered ideal glasses at low temperatures; the latter have higher energies than the $T = 0$ crystal.

Model. We start with a lattice containing $N$ sites, which we will take as a square lattice, a bipartite lattice [7]. A hole occupies a lattice site, while a dimer occupies two consecutive sites and the intervening lattice bond. Let $E$ denote the energy or the energy eigenvalue, $\mu$ the hole chemical potential, $N_0$ the number of the holes, and $\Omega(N_0, E)$ the multiplicity of the state. The rigorous thermodynamic treatment of the model is carried out by using the partition function $Z_N$ given by

$$Z_N = \sum \Omega(N_0, E) \eta^{N_0} \exp(-\beta E), \quad (1)$$

where $\eta = \exp(\beta \mu)$ is the hole activity, and $\beta = 1/T$ ($k_B = 1$), $T$ being the temperature. The limit $\eta \to 0$ represents the absence of holes. In the classical treatment, the kinetic term is absent; the remaining energy $E$ is taken as a.
with a fixed state at absolute zero. The adimensional free energy \( w \) mann weights \( w \) point in the vertical directions. (C),(D) show the resonance due to capture the ground states; see description in the text. We show FIG. 1: Columnar (A) and staggered (B) states on Husimi cactus; the labels 1,2,... in (A) and 1-4 in (B), respectively, are introduced to capture the ground states; see description in the text. We show dimers (thick bonds) in the horizontal directions; they can also point in the vertical directions. (C),(D) show the resonance due to attractive interaction (dotted line) \( \varepsilon_p \); (E) shows the axial interaction (dotted line) between collinear dimers. 

sum of various interaction energies. Excess interaction (energy \( \varepsilon \)) between a hole and a dimer endpoint is sufficient to describe orientation-independent mutual interactions [15], which we restrict to nearest-neighbor hole-endpoint pairs for simplicity. There is an orientational interaction (energy \( \varepsilon_p \)) between a nearest-neighbor pair of two unbonded dimer endpoints provided the corresponding dimers are parallel (resonance energy, see Figs. 1C,D). If this interaction is attractive (\( \varepsilon_p < 0 \)), the ground state at \( T = 0 \) is columnar. If the interaction is repulsive (\( \varepsilon_p > 0 \)), we introduce an additional attractive axial interaction \( \varepsilon_c(< 0) \) between the endpoints of two collinear dimers (see Fig. 1E) so that the ground state at \( T = 0 \) is staggered. Such ground states also play a central role in the short-ranged RVB model of high-temperature superconductivity [16], where the pair of parallel dimers within a square are said to resonate. Let \( N_p \) denote the number of resonating dimer pairs, \( N_a \) the number of nearest-neighbor axial contacts (endpoint-contacts between colinear dimers), and \( N_c \) the number of nearest-neighbor hole-endpoint contacts, so that 

\[ E = 2N_p\varepsilon_p + N_a\varepsilon_a + N_c\varepsilon. \]

We introduce the Boltzmann weights 

\[ w = \exp(-\beta\varepsilon), \quad w_p = \exp(-\beta\varepsilon_p) \quad \text{and} \quad w_a = \exp(-\beta\varepsilon_a) \]

for later convenience.

The sum in (1) is over \( N_0, N_p, N_a \) and \( N_c \), consistent with a fixed \( N \). The densities \( \phi_i \) are the limiting ratios \( N_i/N \) as \( N \to \infty \); here \( k = 0, p, a, \) and \( c \). We always take negative \( \mu(< 0) \) to insure a fully dimer-packed ground state at absolute zero. The adimensional free energy \( \omega = (1/N) \ln Z \) in the limit \( N \to \infty \) represents the osmotic pressure across a membrane permeable to the dimers, but not holes [16]. The reduced pressure \( \pi_0 \equiv P\nu_0 \), where \( \nu_0 \) is the volume of a lattice site, is given by \( \pi_0 = T\omega - \mu \). For \( \eta = 0 \), \( \pi_0 \) is not a useful quantity. Therefore, it is convenient to introduce the shifted free energy \( \bar{F}(T) = F(T) - F(0) \), which remains meaningful for all \( \eta \geq 0 \); here \( F(T) = -T\omega \). The equilibrium state must have the lowest \( \bar{F}(T) \) among all possible states obtained at given \( T, w_p, w_a \) and \( \mu \) [16]. The entropy per site \( s \) is given by 

\[ s = \omega - \beta\varepsilon - \phi_0 \ln \eta. \]

At \( T = 0 \), \( \phi_c = 0 \) since there are no holes (\( \eta = 0 \)). The maximum value of \( \phi_p \), and \( \phi_a \) is 1/2.

The ratio 

\[ D_0 \equiv \frac{\phi_{00}}{\phi_0} \]  

(2)

denotes the number of hole pairs per hole; here, \( \phi_{00} \) is the density of nearest-neighbor contacts between holes. In the RVB model, it is a measure of how effective is the pairing mechanism for mobile dopants. If all holes were paired as isolated pairs, we have \( D_0 = 1/2 \). It is commonly believed that holes are always paired in the crystal on a square lattice, but may not be on other lattices [17]. If holes are separately clustered as four sites of a square cell, then \( D_0 = 1 \). For randomly distributed holes, \( \phi_{00} = 2\phi_0^2 \) on the current lattice, and \( D_0 \equiv 2\phi_0 \) However, the dimer connectivity will create correlations even at infinite temperatures, and we expect a higher tendency to pair so that \( D_0 > 2\phi_0 \).

Our results below confirm the additional correlations in the disordered phase. It is clear that the values of \( \phi_0 \), and \( D_0 \) allow us to draw important conclusions about the way holes are distributed in the system.

**Husimi Cactus Solution.** In order to solve the model exactly, we replace the square lattice by a site-sharing Husimi cactus, a recursive lattice, obtained by connecting two squares at each sites. This is the only approximation we make. The cactus can be thought of as a checkerboard version of the square lattice, representing squares of a given color [7]; the squares of the other color are missing. However, a pair of dimers on the cactus that would have belonged to a missing square on the original square lattice is counted as a parallel pair on the cactus [4].

The model is solved exactly using by now the standard recursive technique, as discussed elsewhere [5,7,8]. Because of its exactness, the calculation (i) respects all local (such as gauge) and global symmetries, in contrast to the conventional mean-field solution which is known to violate local symmetries, and (ii) thermodynamics is never violated [3]. The fix-point (FP) solutions of the recursion relations represent possible states in the system. The free energy is calculated using the method originally proposed by Gujrati [5]. The FP solution that maximizes the osmotic pressure represents the three stable states that are found: the ordered phase, i.e. the crystal (CR) at low temperatures, the disordered phase, i.e. the equilibrium liquid (EL) at high temperatures, and an intermediate phase (IP) with intermediate orientational order involved in a liquid-liquid (L-L) transition; see below for a complete description. **Abandoning** this maximization principle and continuing the FP solutions allows us to obtain the stationary metastable states,
be stressed that the existence of IP depends on the choice of the energy parameters and the hole chemical potential. We note that in Fig. 2, the stable states (EL, IP, and CR) are shown by filled symbols (circles, triangles, and diamonds, respectively), the realizable metastable states ($S \geq 0$) resulting from EL and IP by the same respective empty symbols, and unrealizable metastable states ($S < 0$) by the smaller empty symbols. The point $S = 0$ denotes the Kauzmann point. The extensions corresponding to the unrealizable states must be replaced by horizontal lines passing through the Kauzmann point (not shown), which represent ideal glass states that are frozen in their respective metastable state at Kauzmann point.

**Disordered Phase.** The disordered phase is characterized by random orientations of individual dimers, and represents EL at high temperatures ($T > T_K$) and its analytical continuation SCL at low temperatures ($T > T_K$). The disordered phase free energy, hole density $\phi_0$, and $D_0$ are shown in Figs. 2A and 2B when the ground state is columnar and staggered, respectively. We immediately note the existence of the entropy crisis in SCL in both cases below their respective $T_K$. The states that represent the continuation of SCL over the temperature range $T < T_K$, where it is unphysical due to negative entropy must be replaced by an IG at $T_K$ as discussed above. In terms of $r \equiv [\lambda/w_p^2]^{1/4}$, $\lambda = 1 + 6w_a w_p + (w_a w_p)^2$, and $u'' = 2 + w_p + w_a + r^2 w_p^2$, the analytical expressions for thermodynamic quantities for $\eta = 0$ are $\phi_{\text{dis}}^a = (w_a r^2 + 3 w_a w_p + w_p^2)/4 r^2 u''$, $\phi_{\text{dis}}^d = (w_p r^2 + 3 w_a w_p + (r^4 + w_p^2) w_p^2)/4 r^2 u''$, and $\omega_{\text{dis}} = (1/2) \ln u'' - \ln 2$. We note that the high-temperature limit ($w_a \to 1$, $w_p \to 1$) of $s_{\text{dis}}$ gives $\varphi_{\text{Husimi}} = 1.7071$, where $\varphi = \exp(2s)$ is the average number of configurations per dimer in the absence of interactions. This is closer to the exact value on the square lattice, $\varphi_{\text{exact}} = 1.7916$, than that of for Bethe lattice $\varphi_{\text{Bethe}} = 1.6875$.

**Ordered & Intermediate Phases.** The calculation for the ordered phase requires separate consideration for the two cases. For the attractive case ($\epsilon_p < 0$, $\epsilon_a = 0$), shown in Fig. 2A, the ordered state at $T = 0$ is the perfect columnar CR. For this phase, $T \omega_{\text{ord}} = -\epsilon_p$, $s_{\text{ord}} = 0$, $\phi_{\text{p}}^d$, $\phi_{\text{a}}^d = 1/2$. We take dimers in the perfect CR to be oriented in the horizontal direction. As $T$ is raised, CR begins to distort so that $s_{\text{ord}}$ increases, but $\phi_{\text{p}}^d$ and $\phi_{\text{a}}^d$ decrease. As a result, some dimers begin to resonate in the vertical directions until resonating dimers in both directions have equal density at $T_{\text{IP}} \cong 1.37$, at which point CR undergoes a continuous transition into a new state IP which is analogous to the plaquette RVB state [21]. This phase melts into EL at $T_M \cong 1.58$. The continuation of EL below $T_M$ gives rise to SCL, whose entropy vanishes at $T_K \cong 0.54$. Similarly, the continuation of IP below $T_{\text{IP}}$ describes its metastable state whose entropy also vanishes but at $T_K \cong 0.44$, thus giving rise to another IG. Both IG’s have zero entropy, but have different energies and contact

**Results.** We briefly discuss some important results, with details found in [4]. For $\eta = 0$ ($\mu \to -\infty$), we have analytical results, which clearly establish three distinct phases. For finite $\mu$, the results are obtained numerically. It should
creases. Adding too many holes moves melting to as a function of hole composition can be studied on a square lattice for molecular and RVB systems. The solution \[4\]. Thus, excess holes destroy not only the IG’s but also IP; the former was also seen in a polymer model recently \[8\]. We note that the IG_{ds} and IG_{IP} have almost the same hole density as CR. Despite this, \(D_0\) for IG_{ds} has a much lower value than for IG_{IP} or CR. It is clear from \(D_0 \approx 0.5\) that most holes in the latter are dimerized. In the disordered phase, even at high temperatures, \(D_0 > 2\phi_0\), indicating that there are correlations induced in the hole distribution due to dimer connectivity. Loosely speaking, holes in the disordered phase are mostly isolated, with a tendency to dimerize at lower temperatures, which is evident from the values of \(D_0\) near the Kauzmann temperature where \(\phi_0 \approx 0\); see Fig. 2A.

The staggered ground state for the repulsive case \((\varepsilon_a = -1, \varepsilon_p = 1)\) is completely frozen for \(\eta = 0\) \((\mu = -\infty)\), and has \(\phi_{0,ord} = 1/2, \phi_p = 0, s_{ord} = 0\). It melts at \(T_M\) via a first-order transition into EL. There is a continuous L-L transition at \(T_{IP}\) in the SCL region where a new IP phase emerges. The latter corresponds to configurations of dimers preferentially aligned in one direction (vertical or horizontal). Its SCL continuation below \(T_{IP}\) gives rise to the entropy crisis at \(T_K\). The IP also exhibits its own entropy crisis at \(T_{IP,K}\). The CR state is no longer frozen for a finite \(\mu\) as shown in Fig. 2B; here, \(T_{IP} \approx 1.05, T_{IP} \approx 0.65, T_{K} \approx 0.41, \) and \(T_{K} \approx 0.56\). For a given \(\varepsilon_p\), \(T_{IP}\) moves towards zero, but \(T_{IP}\) decreases to a non-zero value \(T_{IP} \approx 1.3, \) as \(\varepsilon_a \rightarrow 0\) \([4]\). On the other hand, raising \(\varepsilon_a\) eventually makes \(T_{IP} > T_M\), hence causing the L-L transition to appear in the stable region of the phase diagram \([4]\). We note that at high temperatures, \(D_0 > 2\phi_0\) in EL, indicating the presence of correlations in the hole distribution due to dimer connectivity. At low temperatures, the holes appear dimerized in CR and the two IG’s. While the SCL hole density is larger then that of IP, \(D_{0,IP} < D_{0,CR}\) indicating higher hole pairing tendency in IP. We find that \(T_K\) as well as \(D_0\) decrease and move to zero as \(\mu \rightarrow -\infty\). Adding too many holes moves melting to \(T = 0\), thus destroying the CR state and, therefore, the IG transition \([4]\).

In conclusion, we have introduced an empirical classical model of dimers, and presented its exact calculation on a Husimi cactus which serves as an approximate theory on a square lattice for molecular and RVB systems. The behavior as a function of hole composition can be studied by varying the temperature. The calculation provides a strong support for the parallel between the two systems as observed recently, in particular about the presence of intermediate phases \([1]\). The empirical model reproduces all the known or observed phases in the two systems, which justifies its choice. The calculation establishes the existence of ideal glasses in the metastable states, and provides a qualitative comparison of various stable and metastable states. In particular, attention has been paid to study how holes are distributed by calculating a pairing parameter \(D_0\) in various stable and metastable states, which is another novel feature of this work. Our work also suggests that the ideal glass related to IP may be a strong candidate for the spin liquid in the electronic system. We also believe that there is a quantum analog of IP that could be relevant in high-Tc superconductors.

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[1] J.C. Phillips, Phys. Rev. Lett. 88, 216401 (2002).
[2] P.W. Anderson, Proc. Natl. Acad. Sci. U.S.A. 92, 6653 (1995).
[3] P. D. Gujrati, Phys. Rev. Lett. 74, 809, (1995).
[4] F. Semerianov and P. D. Gujrati, cond-mat/0401047
[5] W. Kauzmann, Chem. Rev. 43, 219 (1948).
[6] P.D. Gujrati, cond-mat/0309143 cond-mat/0401478
[7] P.D. Gujrati and A. Corsi, Phys. Rev. Lett. 87, 025701 (2001), A. Corsi and P.D. Gujrati, Phys. Rev. E 68, 031502 (2003), cond-matt/0308555
[8] P.D. Gujrati, S.S. Rane, and A. Corsi, Phys. Rev. E 67, 052501 (2003).
[9] P.W. Anderson, Science 235, 278 (1987).
[10] D.S. Rokhsar and S.A. Kivelson, Phys. Rev. Lett. 61, 2376 (1988).
[11] E. Fradkin, D.A. Huse, R. Moessner, V. Oganeesyan, and S.L. Sondhi, cond-mat/0311353 v3, and references therein.
[12] D.R. Nelson, Phys. Rev. B 28, 5515 (1983); E.W. Fischer, Physica A 210, 183 (1993); H. Tanaka, Phys. Rev. E 62, 6968 (2000).
[13] C.J. Roberts, A.Z. Panagiotopoulos, and P.G. Debenedetti, Phys. Rev. Lett. 77, 4386 (1996). S. Harrington, R. Zhang, PH. Poole, F. Sciortino, and H.E. Stanley, Phys. Rev. Lett. 78, 2409 (1997). PH. Poole, M. Hemmati, and C.A. Angell, Phys. Rev. Lett. 79, 2297 (1997).
[14] D. Levesque and J.J. Weis, Phys. Rev. E 59, 5131 (1994). T. Tlusty and S.A. Safran, Science 290, 1328 (2000).
[15] P.D. Gujrati, J. Chem. Phys. 112, 4806 (1994).
[16] P.D. Gujrati, J. Chem. Phys. 108, 6952 (1994).
[17] N. Bulut, D. Hone, D.J. Scalapino, and E.Y. Loh, Phys. Rev. Lett. 62, 2192 (1989), S. Dommange, M. Mambrini, B. Normand, and F. Mila, Phys. Rev. B68, 224416 (2003).
[18] P. W. Kasteleyn, Physica 27, 1209, (1961); M. E. Fisher, Phys. Rev. 124, 1664, (1961).
[19] T. S. Chang, Proc. Roy. Soc., London, A 169, 512, (1939).
[20] N. Read and S. Sachdev, Nucl. Phys. B316, 609 (1989); T. Dombre and G Kottiar, Phys. Rev. B 39, 855 (1989).