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# Structure of an amphiphilic lattice gas, and its relationship to microclustering of methanol in water

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We present a lattice gas model to show that a system of amphiphilic molecules in solution forms clusters without phase separating. This is designed to be the simplest possible model that captures the essence of the so-called microclustering observed both experimentally and by molecular-dynamics computer simulation of methanol in water. The Hamiltonian contains no adjustable parameters, yet exhibits surprisingly complex behavior as a function of temperature and concentration. By studying the specific heat, we reveal three phase boundaries—between a low-temperature phase comprising straight bilayers, intermediate phases exhibiting twisted bilayer and clustering, and a high-temperature phase, which is essentially gaslike. None of the observed phases correspond to the crystalization or phase separation expected of a simple mixture; instead, they correspond to loss of different types of entropy.

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## I. INTRODUCTION

Amphiphilic molecules are composed of a hydrophobic and hydrophilic part. The hydrophilic end forms ionic or hydrogen bonds with water, whereas the hydrophobic end does not bind. Since water hydrogen bonds to itself, the energy of an arrangement of amphiphilic molecules is minimized when the hydrophobic ends are in contact with one another. This is often referred to as the nonbonding interaction; in fact, increased contacts between hydrophobic groups reduce the system energy because they allow additional hydrogen bonding elsewhere.

Although familiar amphiphilic molecule physics arises from self-assembling complex structures formed by macromolecules, there has been a lot of recent interest in microsegregation in small molecules, in particular in the smallest amphiphilic molecule, methanol. Despite the lack of bonding between the methyl group and water, this system shows no tendency to phase separate, although the entropy of mixing is notably lower than would be expected for an ideal solution. In addition to this, numerous thermodynamic anomalies implying sharp changes in entropy have been reported in water-alcohol mixtures. The traditional view [1] of this postulated "icebergs:" an enhancement of water structure around the hydrophobic group as the source of reduced entropy, but recent experimental [2] and computational [3] studies have failed to find evidence of this, suggesting a picture of imperfect mixing or "microsegregation."

Defining phase diagrams for molecular amphiphilic mixtures is nontrivial at the most fundamental level of defining the basic components to which the Gibbs phase rule for miscibility can be applied. For the water-methanol system, it may seem clear that the two molecules comprise the basic components. This already contains a hidden assumption that the covalent bonds in the molecules are inviolable. This is jusified at normal temperatures because covalent bonds are much stronger than hydrogen bonds. However, methanol itself has a hierarchy of bond strengths—this is best seen in the solid phase where the hydrogen bonding forms strongly bound one-dimensional (1D) chains, one hydrogen bond per molecule, with weaker dispersion forces binding one chain to another. In the liquid phase, the chainlike structure remains, with interchain forces being overcome by temperature. At high pressure and low temperature, the solid also retains the hydrogen-bonded chains, which are twisted to allow more efficient packing [4,5]. There is evidence that similar chainlike structures exist in solution [6].

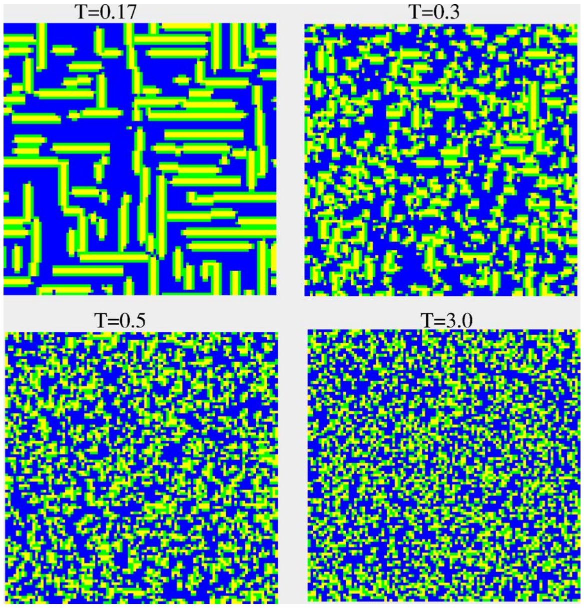

FIG. 1. (Color online) Snapshots visualizing the system at various temperatures at an M concentration of 0.5. W sites are show in dark blue (black), M molecules occupy two adjacent sites and are show as midgreen (light green) (OH) and light yellow (white) ($CH_3$), respectively. The methanol bilayer with the OH -$CH_3$..$CH_3$-OH motif maximizes $CH_3$-$CH_3$ contacts. The four phases can be categorized as disordered (I, $T$=3.0), clustering (II, $T$=0.5), bilayers (III, $T$=0.3), bilayer liquid crystal (IV, $T$=0.17). The underlying square lattice manifests itself in the two orientations of the liquid-crystal phase IV.

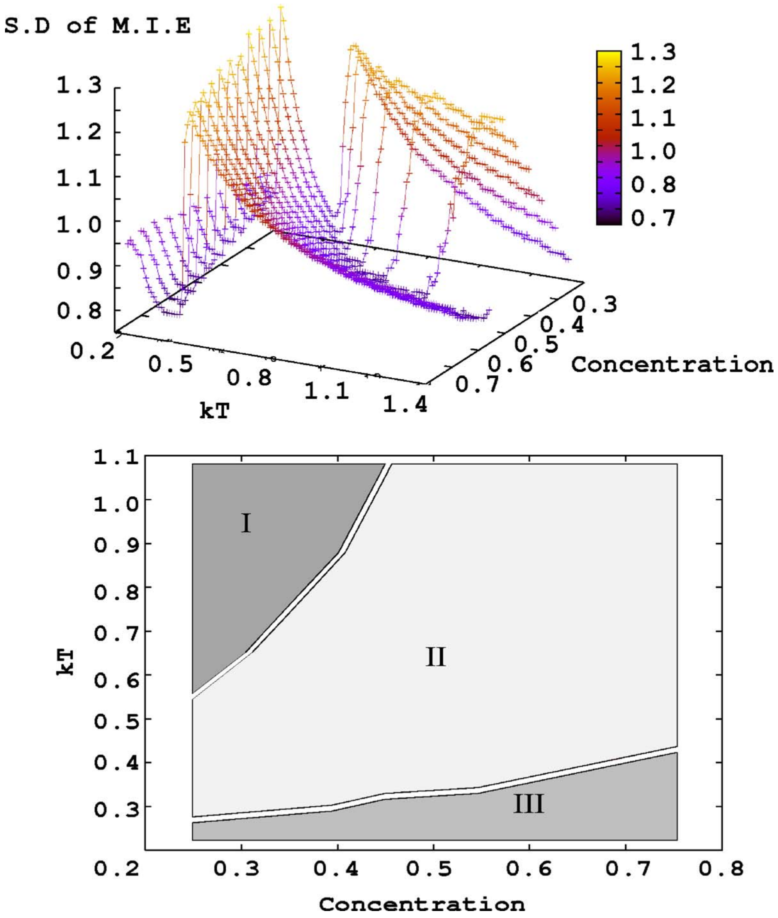

FIG. 2. (Color online) (a) Measured standard deviation of the mean interaction energy [standard deviation (SD) of MIE], shown by color and height, as a function of concentration and temperature. Crosses show data from state point calculations; lines join datapoints for constant concentration; (b) Phase diagram deduced from (a), with phase boundaries taken from the peaks in the specific heat. The nature of the phases is described in the text.

Recently, the water-methanol system has been studied by microwave [6], Raman [7], x-ray [9] and neutron scattering [2,8], thermodynamics [9], and molecular dynamics [3,10,11], and the picture that emerges from study of clusters of water molecules is one of increasing microsegregation at low temperatures. It has been suggested [10] that this is a precursor to full-phase separation, which is not observed in practice because of the freezing transition.

Here, we introduce and study a simple lattice model of an amphiphilic system. The model shows a picture of microsegregation consistent with the observations in the water-methanol system, but at variance with their interpretation. Specifically, the amphiphilic molecules form low-dimensional structures, reducing both energy and entropy by excluding the water molecules. Despite this microsegregation, the amphiphilic molecules never form a macroscopic phase, as implied by the Gibbs rule. This is essentially because chains are formed that have zero interface energy with surrounding water; thus, there is no driving force toward macroscopic phase separation.

There have already been many molecular-dynamics simulations of water-methanol using interatomic potentials to describe the geometry of the two molecules [3,10,11]. These simulations are limited in size to a few hundred molecules, such that finite size effects make it difficult to determine phase separation or calculate entropy. At another extreme, mesoscale lattice gas models [12,13] can describe the dynamics of oil-water interfaces with particle-level detail integrated out. Large amphiphiles have been modeled with an Ising model biased toward intermediate numbers of like neighbors representing a coarse-grained lattice gas model [14,15]. Here, our intention is not to reproduce this level of detail or the exact geometry of liquid methanol water; rather we will have to investigate the type of structures that cause entropic anomalies, without necessarily being precursors to macroscopic phase separation, and to do so in a sufficiently large system that the microsegregated clusters do not percolate due to finite-size effects.

## II. MODEL

For clarity, we describe the model in terms of its relation to the water-methanol system, showing how this reduces to a dimer gas.

Consider methanol (M) and water (W) molecules moving on a lattice. The W particles occupy one site, the M particles occupy two adjacent sites, one with the -OH group (OH) and one with the $CH_3$.

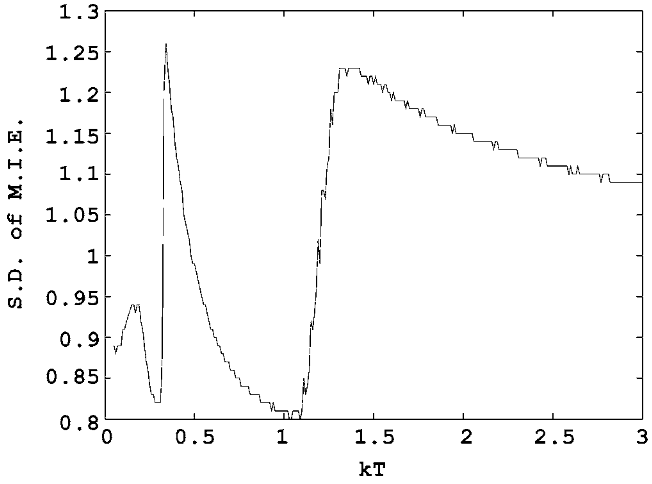

FIG. 3. Standard deviation of mean interaction energy as a function of temperature at a concentration of 0.5 for $0.05 < kT < 3.0$, with $kT$ datapoints collected every 0.01. Peaks showing the three phase-transition boundaries can be clearly seen.

The system is hydrogen bonded. W and OH bonds to themselves and each other while $CH_3$ does not bond to anything. The hydrogen bonds are all of similar strength, consistent with recent ab initio calculations [16,17]. The energy of the system can be written as a sum of pairwise interactions

$$U = \sum_{i=1,N} \sum_{k=1,4} - \sigma_i \sigma_k, \qquad (1)$$

where $\sigma_i$ depends on the object occupying the site, and there are $N$ sites. Assuming all hydrogen bonds are of equal strength, for W and OH, $\sigma = 1$. For $CH_3$, $\sigma = 0$.

This formulation requires a sum over all molecules. An equivalent expression, which is more efficient computationally, is

$$U = -4N + 4N_{\mathrm{M}} - \sum_{i=1,N} \sum_{k=1,4} S_i S_k \qquad (2)$$

with $N_{\mathrm{M}}$ being the number of methanols in the system, $S = 0$ for W and OH and $S = 1$ for $CH_3$. Now we need only keep track of the positions of the M molecules: the Ws form an inert background. We have gone from counting hydrogen bonds to counting the "nonbonding" interactions.

We use periodic boundary conditions and find thermal equilibrium using the Metropolis Monte Carlo method in the canonical ensemble. To do this we postulate moves of the M molecules and accept them according to the Metropolis algorithm.

We use a single-particle, long-range update method, which picks an M and removes it. It then picks two adjacent W sites anywhere in the lattice and attempts to move the M there, the move being accepted with the Metropolis probability $\min(1, \exp(U_0 - U_t)/T)$ where $U_0$ is the energy of the current state [Eq. (2)], $U_t$ the energy of the trial state, and $T$ is the temperature in reduced units. If the move is rejected, then the M is returned to its original location. It is important to implement this so as to allow the moving particle to flip or rotate (i.e., for its destination to overlap its original position).

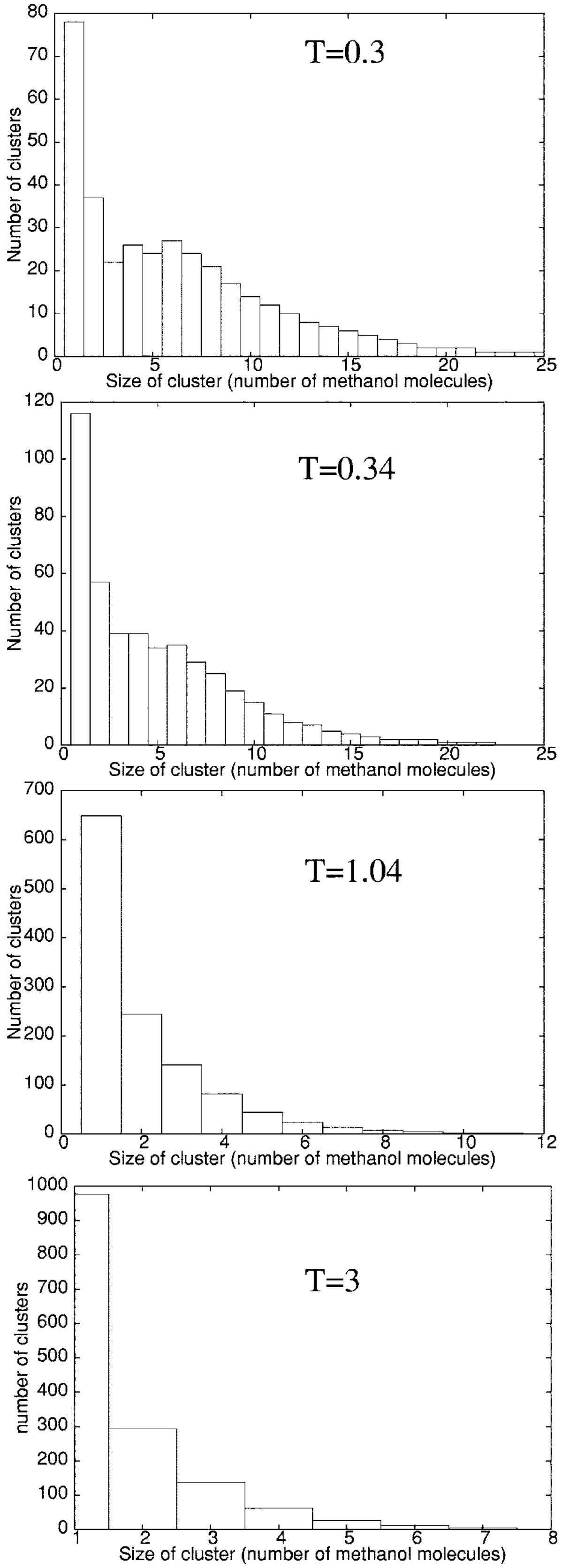

FIG. 4. Cluster size distribution at various temperatures for concentration 0.5. The preference for even-sized clusters due to the end effects becomes pronounced between $T = 0.34$ and $T = 0.3$ (phases II and III).

We were unable to construct a collective Monte Carlo move of an entire cluster that obeyed detailed balance, except for the trivial one, which is accepted only if the energy is unchanged (i.e., the cluster does not develop new $CH_3$-$CH_3$ contacts with another cluster). Despite violating detailed balance, simulations in which clusters were allowed to move en masse did not seem to give significantly different structures from those found in Fig. 1.

We monitored the total energy ($U$) for the system as a function of temperature and concentration, assuming equilibrium had been reached when this stabilized, and plotted the mean interaction energy (MIE) per molecule $\langle U/N_{\mathrm{M}}\rangle$. Values of $\langle U/N_{\mathrm{M}}\rangle$ vary smoothly with concentration and temperature. We also monitored the standard deviation of this quantity, which follows the specific heat of the system and peaks at structural transitions (Fig. 2).

## III. CALCULATIONS AND RESULTS

The phase behavior of the system was examined by investigating the standard deviation of energy over time at different values of M concentration and temperature (Fig. 2) The calculations were done on a $100\times 100$ lattice, with temperature varying from $kT=0.2$ to $kT=1.39$ in increments of 0.01, and with concentration varying from 0.25 ($N_{\mathrm{M}}=1250$) to 0.75 ($N_{\mathrm{M}}=3750$). Peaks in the standard deviation correspond to peaks in the specific heat: since we are working with fixed-size systems, we cannot be certain of whether these are the $\delta$ functions, which characterize true thermodynamic phase transitions [18]. Similarly, the anomalies observed in the experimental studies are not reported as "true" phase transitions. We use the terms "phase" and "phase boundary" loosely; nevertheless, all peaks are well pronounced and the structures in each phase are readily distinguishable. The system shows two pronounced phase boundaries, one of which is strongly concentration dependent.

There is evidence of a third phase boundary at even lower temperatures; however, the equilibration times are very long here and our statistics were too poor to map the full line in concentration-temperature space. Therefore, we extend our sampling to low temperatures at the single concentration of 0.5 to characterize this transition (Fig. 3). Despite its extreme simplicity of the amphiphilic molecule model, it exhibits four phases, which we label I–IV. Snapshots of the systems (Fig. 1) and the size of clusters of M molecules, defined by sharing $CH_3$-$CH_3$ contacts, were examined to determine what the phases are. The cluster distributions are shown in Fig. 4. These show a more or less exponential decay of cluster frequency with size at high temperature, then the development of a strongly preferred cluster size in phase II. By the transition to phase III, the end effects (which favor even numbers of particles in a cluster) begin to appear, and at the lowest temperature shown they become pronounced. For the very low temperatures in phase IV, essentially all molecules are assimilated into clusters. Because of the extremely slow kinetics in this regime, we were unable to verify whether the cluster size distribution had fully equilibrated, and what its dependence on the finite simulation cell was.

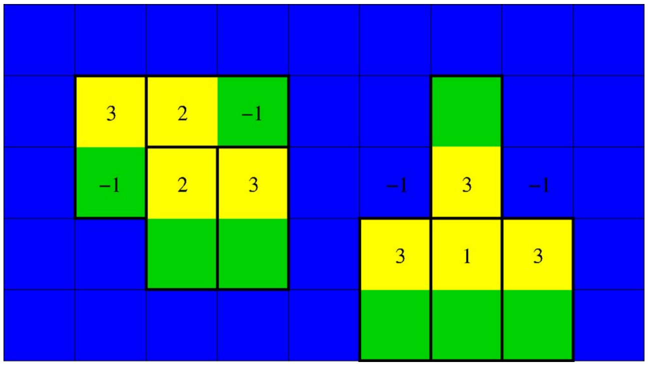

FIG. 5. (Color online) Two of the 380 degenerate four-molecule three $CH_3CH_3$-contact clusters [OH green (light gray), $CH_3$ yellow (white)]. Numbers on the $CH_3$ sites show the number of possible OH positions; negative numbers show impossible combinations. The number of equivalent clusters is given by multiplying the number in $CH_3$ sites, subtracting the off-$CH_3$ sites, then multiplying by 4 and dividing by the rotational degeneracy. Hence the left-hand cluster has $(3\times 2\times 2\times 3-2)4/2=68$ equivalent configurations, and the right hand has $(3\times 3\times 3\times 1-2)4/1=100$. Two further degenerate configurations are not shown: the L shape has $(3\times 2\times 2\times 3-1)4=140$, and the I shape $(3\times 2\times 2\times 3)4/2=72$. The lowest energy four-molecule cluster is the square, which is only $(2\times 2\times 2\times 2)4/4=16$-fold degenerate. Similarly, the five-bonded five molecule cluster is 92-fold degenerate, whereas the four-bonded five-molecule one is over 1600-fold degenerate. For phase IV, the long even bilayer has OH positions and is fixed except at the ends, giving 16-fold degeneracy.

The high-temperature, low-density phase I is dominated by single molecules and is clearly a simple lattice gas.

Phase II has a majority of molecules in small clusters.

Phase III, appears to have a favored cluster size, which increases as $kT$ is reduced. Larger clusters favor a bilayer structure and odd-even effects pronounced in the cluster distribution (bilayers with even numbers of molecules have lower energies associated with their ends than those with odd numbers).

Phase IV is dominated by long, straight bilayer rods. The rods show a tendency to align in a liquid crystallike phase.

The thermodynamic stability of the phases can be understood qualitatively by considering minimizing free energy through a subtle interplay between energy and entropy. The extreme phases I and IV are dominated by entropy and energy, respectively. Exact calculation of the entropy is beyond the scope of this paper; however, the transitions observed here are probably due to the loss of different "types" of entropy [19]. As shown in Figs. 1 and 5 small clusters can be constructed in many ways, so phase II is stabilized by the energy gain from clustering while retaining some entropy from this degeneracy. In phase III, the short bilayers have still lower energy, and all have similar entropy from cluster degeneracy (lower than phase II); however, phase III has excess entropy compared to IV due to liquid-crystallike ordering of parallel bilayers.

## IV. CONCLUSIONS

In conclusion, we have made the simplest possible lattice model of an amphiphilic molecular system, in an attempt to obtain some qualitative understanding of the microsegregation behavior reported for small molecule systems. Although we find a rich variety of phases, none of them correspond to either crystallisation or phase separation, nor is there a phase change driven primarily by concentration—all the phases exist at an appropriate temperature for any concentration.

Consistent with experimental results for amphiphilic systems [6–10,20], we find that there is no phase separation, but there is strong local microclustering, leading to thermodynamics anomalies. Hence although the geometry is different, our model captures the essential link between amphiphilic molecules and microclusters, leading to imperfect mixing as the cause of nonideal entropy of mixing, and low-dimensional structures as the cause of thermodynamics anomalies without full liquid-liquid phase separation.

In the model geometry, the stable M cluster structure is a bilayer with $CH_3$ near neighbors. Three higher temperature phases arise as the chains lose orientational correlation, decompose into clusters, and finally into free molecules. Note that the definition of these M clusters by nonbonding interaction is consistent with work on large amphiphilic molecules forming micelles. It contrasts with that used in previous analysis of water methanol, where M and W clusters are defined by hydrogen bonding. Each of these corresponds to the loss of different types of entropy: first, through forming clusters; second, from loss of cluster-shape degeneracy; and third, through local orientational disorder.

The classic picture of the stable structure showing either macroscopic mixing or demixing based cannot fully describe this model because the lowest energy structure for the amphiphiles has a lower dimensionality than the system as a whole. This will be a general phenomenon whenever the stable state of one component has lower dimensionality than the whole system. It will manifest itself in the existence of thermodynamic anomalies, as are observed in alcohol solutions, due to discontinuities in the entropy due to structural change as local ordering increases.

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