PHYSICAL REVIEW E **71**, 021502 (2005)

Solvent-induced symmetry breaking: Varying solvent strength

F. S. Zhang[1,2,3] and R. M. Lynden-Bell[3,*]
[1]*Institute of Low Energy Nuclear Physics, Beijing Normal University, Beijing 100875, China*
[2]*Institute of Modern Physics, Chinese Academy of Sciences, P. O. Box 31, Lanzhou 730000, China*
[3]*Atomistic Simulation Group, School of Mathematics and Physics, Queen's University, Belfast BT7 1NN, United Kingdom*

(Received 20 June 2004; revised manuscript received 11 November 2004; published 23 February 2005)

The triiodide ion is an example of a system where symmetry breaking may be induced by a solvent. The Landau free energy is expected to have a similar form to that for the mean field Ising model, but with solvent strength rather than temperature as the control parameter determining whether there is symmetry breaking. In order to examine the extent of anomalous behavior near the critical point we have studied the properties of the ion in a solvent based on a model for water with charges scaled by a factor λ. As λ is increased from zero the solvent strength increases and the system changes from one with no symmetry breaking to one with strong symmetry breaking. The Shannon entropy as a function of λ shows only a weak maximum near the critical value of $\lambda = \lambda_c$, while the susceptibility has no anomalous behavior. We examine a simple model and show that anomalies near the critical point would increase as the temperature decreases, but divergences associated with a second order phase transition would only be seen in the limit of zero temperature.

DOI: 10.1103/PhysRevE.71.021502 PACS number(s): 61.25.Em, 31.70.Dk

I. INTRODUCTION

In an earlier paper we showed that symmetry breaking could be induced in the triiodide ion by varying the solvent [1]. Experiments and simulations [2–6] suggest that protic solvents which can form hydrogen bonds with a negative ion cause symmetry breaking of the ion, so that the charge becomes concentrated at one end of the ion and the corresponding bond elongates. We suggested that one could draw an analogy between the mean field Ising model with free energy

$$F = a(T - T_0)\eta^2 + C\eta^4 \tag{1}$$

and solvent induced symmetry breaking with

$$F = a(R_0 - R)\eta^2 + C\eta^4. \tag{2}$$

In these expressions F is the Landau free energy per molecule (or per spin), η is an order parameter, and a and C are coefficients [7]. The Ising model has a critical point when the temperature T reaches T_0; below this temperature the symmetry is broken to give domains with nonzero order parameters, while above this temperature the order parameter is equal to zero. Various critical phenomena, such as vanishing of the inverse susceptibility and diverging fluctuations in the order parameter, are observed as the critical point is approached. Although in real systems critical behavior is caused by cooperative effects which are not present in our system, the similarity of Eqs. (1) and (2) led us to investigate the behavior of our system near its critical solvent strength. In order to vary the solvent strength in a systematic way we used a series of modified waters as solvents. The models are based on the standard spc/e [8] model with a Lennard-Jones center on the oxygen atom and charges on the atomic sites. The charges are scaled by a factor λ. When $\lambda = 1$ the solvent is the standard spc/e model which causes strong symmetry breaking [9]; when $\lambda = 0$ the solvent is a Lennard-Jones solvent which does not cause symmetry breaking. Thus varying λ provides a method of tuning the solvent strength R through the critical value R_0.

II. THEORY AND COMPUTATIONAL DETAILS

A. Valence bond model for I_3^-

The model for triiodide ion is the same as used in our previous work [1,5,6,9,10]. The electronic structure of the ion is described using a semiempirical valence bond model based on the diatomics in molecules method [11] with additional terms due to the fact that the species is charged [12]. Provided the ion is constrained to be linear, its ground state is described by a 3×3 Hamiltonian matrix, whose matrix elements depend on the instantaneous values of the bond lengths and the instantaneous external electrostatic potential due to the solvent. Full details are given in the appendix to Ref. [10]. The solvent molecules are rigid three-site models based on spc/e water [8], with partial charges on all three atomic sites and Lennard-Jones interactions on the oxygen site. The total energy of the system can be written as

$$E(\{r_i\}) = \sum_{\alpha\beta} c_{0\alpha} c_{0\beta} H_{\alpha\beta} + \sum_{ij} \frac{q_j q_k}{4\pi\epsilon_0 r_{jk}} + \sum_{jk} V_{jk}^{LJ}(r_{jk}) + \sum_{jm} V_{jI}^{LJ}(r_{im}), \tag{3}$$

where the first term is the quantum mechanical energy of the ground state, with $H_{\alpha\beta}$ being the Hamiltonian matrix element between basis states α and β and $c_{0\alpha}$ the coefficient of basis state α in the ground state. The second and third terms are sums of the electrostatic and Lennard-Jones interactions over all pairs of solvent sites j and k and the last term is the sum of Lennard-Jones interactions between solvent sites and iodine atomic sites m.

---

[*] Present address: University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

TABLE I. Intermolecular Lennard-Jones site-site parameters for modified water models. Cross terms in the Lennard-Jones interactions were calculated using the Lorentz-Bertholet rules. λ varied between zero and 1.25.

Atom i	ϵ_{ii} (kJ mol^{-1})	σ_{ii} (Å)	$q(i)/e$
O	0.6502	3.169	−0.8476λ
H	0	0	0.4238λ
I	0.4184	5.167	Varies

Quantum mechanical forces on both iodine and solvent sites were calculated using the Hellmann-Feynman theorem while the forces arising from the three classical terms in Eq. (3) were calculated in the usual way within the molecular dynamics program. The ion was constrained to be linear throughout.

B. Modified water models

The solvent molecules were based on the standard spc/e model for a water molecule [8] with a Lennard-Jones center on the oxygen and charges on the atomic sites. In spc/e water hydrogen bonds and all other orientational correlations are due solely to electrostatic interactions between molecules. Thus the hydrogen-bond strength can be controlled by scaling the charges. In this study, nine solvent models were used with the charges scaled by a factor λ which varied from 1.125, giving a superstrong water, through 1, giving the standard spc/e model, to zero, giving a pure Lennard-Jones solvent.

The Lennard-Jones potential between the iodine and oxygen sites was the same as used in our previous work with water [1,3,5]. The Lennard-Jones parameters and the partial charges for sites are given in Table I.

C. Simulation details

Molecular dynamics simulations were carried out using a version of the DLPOLY program [13] which was modified to include the construction and diagonalization of the Hamiltonian matrix and the calculation of the Hellmann-Feynman forces. The simulation cell contained one triiodide ion and 509 modified water molecules in a cubic box with an edge length of 24.8 Å. In our earlier work [9,10] we verified that this cell was large enough to avoid finite size effects and that the properties of the triiodide ion in this system size were the same within the noise as those in a system size with 726 water molecules at the same density. The long-range electrostatics were treated using the Ewald method, with the net charge of the ion balanced by a uniform background charge which exerts no force on any atom. Simulations were carried out at 300 K with a time step of 1 fs. For each value of the charge scaling constant λ, the system was thoroughly equilibrated before collecting data for 1 ns.

Our earlier work has shown that two order parameters were necessary to describe the symmetry breaking. The order parameters chosen are the molecular dipole moment μ (relative to the center of mass) and the normal coordinate for the antisymmetric stretch $\zeta=(b_{12}-b_{23})/\sqrt{6}$. The former measures the extent of electronic distortion, while the latter measures the geometrical distortion. The instantaneous values of these parameters were determined at each time step, and averages, mean square fluctuations, and probability histograms were constructed.

D. Shannon's information entropy

From the two-dimensional histograms for the probability distributions of the two order parameters, the Shannon information entropy function $H(\zeta,\mu)$ was constructed for each bin,

$$H(\zeta,\mu) = -\,p(\zeta,\mu)\ln p(\zeta,\mu), \tag{4}$$

where $p(\zeta,\mu)$ is the probability of being in that bin, with $\Sigma\Sigma p(\zeta,\mu)=1$. The Shannon entropy of the system [14] is then

$$h = \sum_{\zeta}\sum_{\mu} H(\zeta,\mu). \tag{5}$$

The limit of this sum as bin sizes tend to zero is a property of the system, rather than of our information about it, and is the entropy associated with the spread of order parameter values. The bin sizes used were $\delta\mu=3$ D and $\delta\zeta=0.04$ Å. The values of the bin sizes affect the zero of entropy, but, as they were kept constant for all the simulations, entropy differences between runs are real although absolute values are arbitrary.

III. RESULTS

Figure 1 shows the distribution of the Shannon entropy function $H(\zeta,\mu)$, with the unit of information "nats" (natural digits), for selected values of λ. When λ is small there is a single maximum while when lambda is high enough two maxima are seen. Figure 2 shows cross sections through this H surface for all the runs. The direction of cross section is different for each λ and is either chosen to go through the two maxima, or, when there is only a single maximum, it is chosen to go through the direction of minimum curvature. These figures show that there is symmetry breaking in the curve marked 4 ($\lambda=0.5$) and there is no symmetry breaking in the curve marked 3 ($\lambda=0.375$) Thus the critical solvent strength is $\lambda_c=0.43\pm0.04$. These results confirm that varying the scaling parameter λ induces symmetry breaking.

There is no *a priori* reason to identify λ rather than some function of λ with the solvent strength in the free energy equation (2). However, Fig. 3 shows that the solvent-triiodide interaction energy (lowest curve) decreases smoothly with the scaling factor λ and is approximately linear in the critical region. This figure also shows (upper curve) the energetic cost of polarizing the ion.

The inverse susceptibilities for the response to an external electric field

$$\chi^{-1} = kT/\langle\mu^2\rangle \tag{6}$$

are plotted in Fig. 4 as a function of λ. It can be seen that there is a monotonic decrease in the inverse susceptibility as

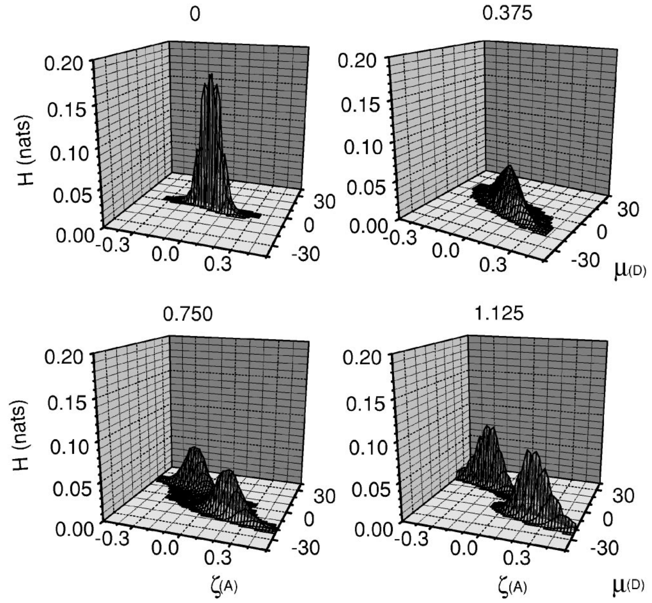

FIG. 1. Three-dimensional plots of Shannon's information entropy function $H(\zeta,\mu)$ of I_3^- at 300 K as a function of the antisymmetric vibrational normal coordinate ζ and the dipole moment μ for different modified water solvents. The distributions correspond to charge scaling factors $\lambda = 0$, 0.375, 0.75, and 1.125. Note the gradual changes from a single peak (symmetry preserving) to double peaks (symmetry breaking) and also the changes of distortions around each peak.

a function of the scaling factor λ, but χ^{-1} does not tend linearly to zero near the critical solvent strength $\lambda = \lambda_c = 0.43$. In a true second-order phase transition, however, inverse susceptibilities would tend linearly to zero at the critical solvent strength.

The Shannon entropy h might also be expected to show anomalous behavior near the critical solvent strength. Figure 5 shows that in the triiodide case this quantity has a weak maximum at a value of λ which is slightly greater than the critical value λ_c. In a true second-order phase transition, however, h diverges at the critical point.

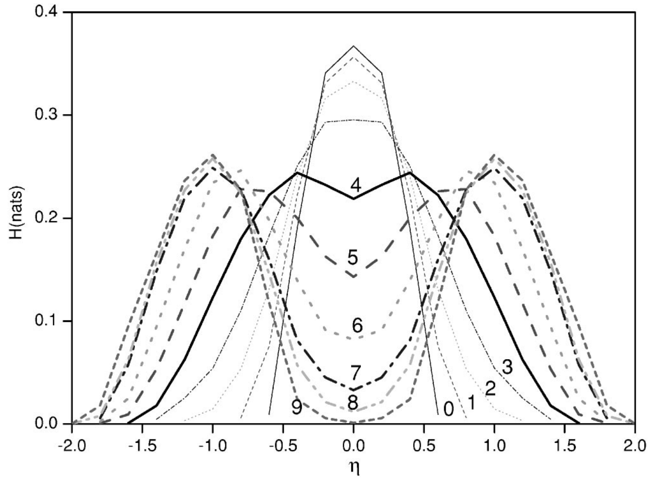

FIG. 2. Cross sections through the Shannon entropy function surfaces for different λ values. The curves are labeled with $\ell = 8\lambda$. Note that symmetry breaking first occurs between $\ell = 3$ and 4, giving $\lambda_c = 0.43 \pm 0.04$.

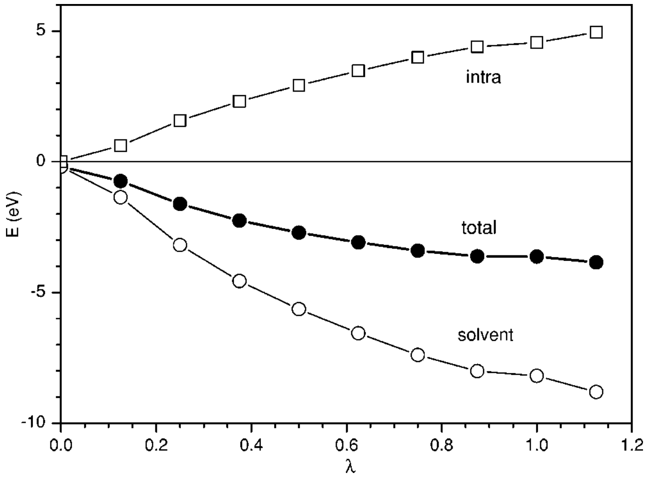

FIG. 3. Solvent-solute energetics. The top curve (squares) shows the change in the average internal energy of the molecule relative to the gas phase which is a measure of the cost of polarizing the molecule. The lowest curve (open circles) shows the average solute-solvent interaction energy and the middle curve (filled circles) shows the sum of these two energies, as a function of λ.

IV. A SIMPLE MODEL

In order to understand the difference between the behavior of the triiodide ion and the mean field Ising model, we study the properties of a simple model. The model we consider has a single order parameter η and a Landau free energy per molecule given by

$$\tilde{F} = a(R_0 - R)\tilde{\eta}^2 + C\tilde{\eta}^4. \tag{7}$$

This can be rewritten [by rescaling $F = C\tilde{F}/(aR_0)^2$ and $\eta^2 = C\tilde{\eta}^2/(2aR_0)$] as

$$F = (1-\rho)\eta^2/2 + \eta^4/4, \tag{8}$$

where $\rho = R/R_0$ is a measure of the relative strength of the solvent interaction. The critical point where symmetry break-

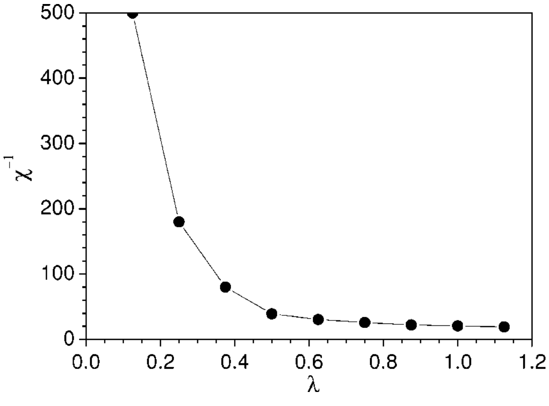

FIG. 4. Inverse susceptibility of the triiodide ion in solution as a function of λ. Note that this does not tend to zero at $\lambda_c = 0.43$.

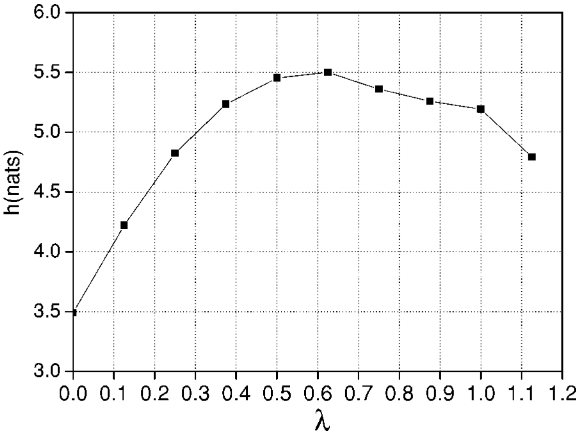

FIG. 5. Total Shannon entropy h as a function of λ for a triiodide ion in solution. Note that there is a weak maximum at about $\lambda=0.6$ although the critical value of λ for symmetry breaking is $\lambda=0.43\pm0.04$.

ing occurs is $\rho=1$. In order to find the behavior near the critical point, we examine the properties of the probability distribution of the order parameter

$$p(\eta)=\exp[-\beta F]/Z=\exp\{-\beta[(1-\rho)\eta^2/2+\eta^4/4]\}/Z \tag{9}$$

as a function of the parameter β. In this expression

$$Z=\int_{-\infty}^{\infty}\exp\{-\beta[(1-\rho)\eta^2/2+\eta^4/4]\}d\eta. \tag{10}$$

Figure 6 shows the values of the Shannon entropy of the model, $h=-\int p\ln p\,d\eta$, as a function of ρ for a number of values of β. It can be seen that h has a maximum as a function of ρ. As β increases, this maximum gets sharper and shifts downwards towards $\rho=1$. Figure 7 shows the values of the inverse of the susceptibility of the model system as a function of ρ for a range of values of the parameter β. In all cases the inverse susceptibility decreases with ρ, but it is only when β is greater than about 500 that the inverse susceptibility decreases linearly toward a value of zero at $\rho<1$.

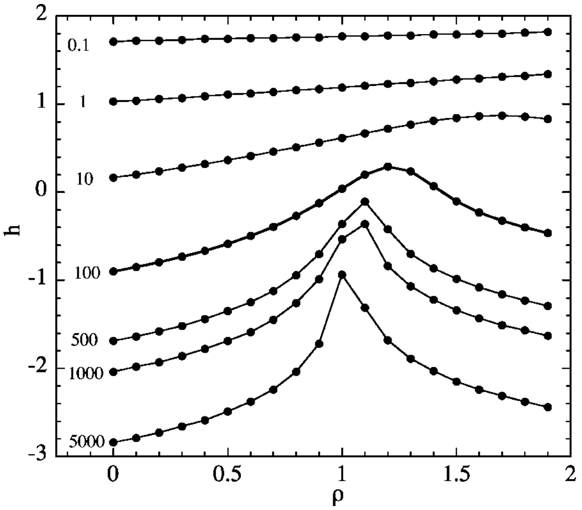

FIG. 6. Variation of the Shannon entropy of the model, h, with relative solvent strength ρ for different values of the parameter β. Note that as β increases the maximum gets sharper and moves closer to the critical value $\rho=1$.

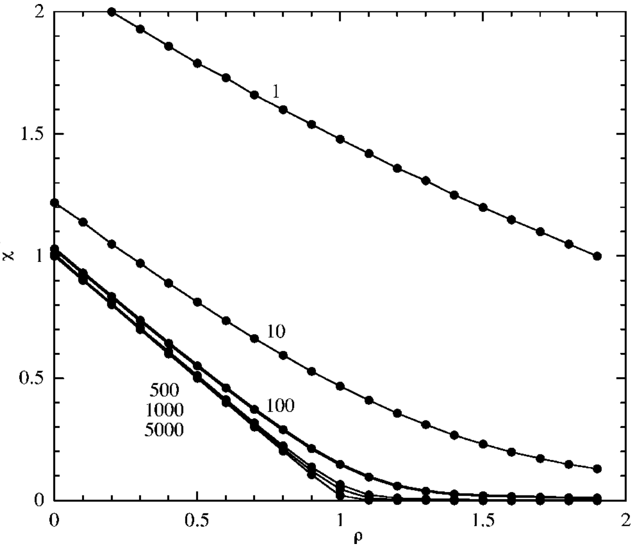

FIG. 7. Inverse susceptibility of the model as a function of the solvent strength for various values of the parameter β. The curves are labeled with the corresponding values of β. Note the linear decrease in inverse susceptibility between $\rho=0$ and near $\rho=1$ for the highest values of β.

When β is sufficiently large the results for both the Shannon entropy and the susceptibility are very similar to those obtained from a mean field model of a second-order phase transition with Landau free energy. At smaller values of β the anomalous behavior gradually becomes less marked and eventually disappears. In the standard treatment [7] of the mean field Ising model [Eq. (1)], one is only concerned with the minima of the free energy function and fluctuations in the order parameter are ignored, while the expression that we have used [Eq. (9)] gives the full range of possible values. The reason that one can ignore fluctuations in the treatment of phase transitions is that the expression for the free energy given in Eq. (1) is the free energy per unit cell or per spin. The observed η is the average over all the unit cells or all the spins and, as one observes the average over a large number N of unit cells or over N spins, the probability of observing a given value of η is given by

$$p(\eta)=\exp\{-(N/kT)[a(T_0-T)\eta^2/2+C\eta^4/4]\}/Z. \tag{11}$$

In the limit $N\rightarrow\infty$ it is indeed only the minima that are observed. In the solvent-induced symmetry breaking situation we observe individual molecules and the relevant probability is given by the similar equation (9) but with the difference that $\beta=(4aR_0)^2/(CkT)$ rather than N/kT. The fact that we only see significant maxima in the Shannon entropy near the critical value of ρ when β is large is consistent with the fact that true critical phenomena only occur in the limit of $N\rightarrow\infty$ and depend on the observation of an order parameter which is an average over many replicated systems. While solvent-induced symmetry breaking will never show true divergences, there will be maxima in the Shannon entropy if the value of the dimensionless parameter $(aR_0)^2/CkT$ is large enough. Comparing the model results with those observed for the triiodide ion, we estimate that the order of magnitude of $(aR_0)^2/CkT$ in our system of a triiodide ion in modified water is about 100. At this value there is a weak maximum in the entropy at a higher solvent strength than the critical one and the inverse susceptibility decreases smoothly but not linearly below and through the critical point.

V. CONCLUSION

In this paper we have examined the solvent-induced symmetry breaking of the triiodide ion induced by water and modified water. The use of scaled charges in the solvent models allows us to vary the solvent strength continuously through the critical point at which symmetry breaking first occurs and to determine whether there is any anomalous behavior near this point. In this particular system the transition from no symmetry breaking to symmetry breaking is weak and there is only a small maximum in the Shannon entropy and the inverse susceptibility does not decrease linearly. By comparing the results to a simple model we see that if $(aR_0)^2/CkT \approx 100$ the model system shows a rather similar behavior to our system of a triiodide ion in modified water. In order to see anomalies near the critical solvent strength this parameter needs to be larger by a factor of 10 or more. Although this could in principle occur at a lower temperature, in practice the solvent would freeze. A system that was less polarizable would have a larger value of aR_0, and so might show anomalous behavior but a strong interaction with the solvent would be needed for symmetry breaking to occur at all.

The essential difference between the solvent-induced symmetry breaking and the mean field Ising model is that in the latter the observed quantity is an average over many spins, while in the former observations are made on individual molecules.

ACKNOWLEDGMENTS

We thank EPSRC (Grant No. GR/N38459/01) and NSFC (Grant No. 10435030) for financial support.

---

[1] F. S. Zhang and R. M. Lynden-Bell, Phys. Rev. Lett. **90**, 185505 (2003).

[2] A. E. Johnson and A. B. Myers, J. Phys. Chem. **100**, 7778 (1996).

[3] R. M. Lynden-Bell, R. Kosloff, S. Ruhman, D. Danovich, and J. Vala, J. Chem. Phys. **109**, 9928 (1998).

[4] H. Sato, F. Hirata, and A. B. Myers, J. Phys. Chem. A **102**, 2065 (1998).

[5] C. J. Margulis, D. F. Coker, and R. M. Lynden-Bell, J. Chem. Phys. **114**, 367 (2001).

[6] C. J. Margulis, D. F. Coker, and R. M. Lynden-Bell, Chem. Phys. Lett. **341**, 557 (2001).

[7] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Oxford, 1969).

[8] H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, J. Phys. Chem. **91**, 6269 (1987).

[9] F. S. Zhang and R. M. Lynden-Bell, Mol. Phys. **101**, 1641 (2003).

[10] F. S. Zhang and R. M. Lynden-Bell, J. Chem. Phys. **119**, 6119 (2003).

[11] F. O. Ellison, J. Am. Chem. Soc. **85**, 3540 (1963).

[12] I. Last and T. F. George, J. Chem. Phys. **86**, 3787 (1987).

[13] W. Smith, M. Leslie, and T. R. Forester, *The DL-POLY User Manual* (Daresbury Laboratory, Daresbury, 2003).

[14] K. G. Denbigh and J. S. Denbigh, *Entropy in Relation to Incomplete Knowledge* (Cambridge University Press, Cambridge, U.K., 1995).