RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 62, NUMBER 8 15 AUGUST 2000-II

Simulation of an order-disorder transition in monolayer N_2/NaCl(001)

A. K. Sallabi and D. B. Jack*

Department of Chemistry and Biochemistry and Department of Physics, Concordia University, Montréal, Québec, Canada H3G 1M8

(Received 24 March 2000)

Monte Carlo simulations of N_2 molecules physisorbed on a NaCl(001) surface show that at low temperature a monolayer forms an ordered $p(2\times1)$ structure which, upon heating, undergoes a continuous order-disorder phase transition around 25 K. This transition is characterized by a logarithmically divergent heat capacity and the formation of pairs of counter rotating vortices.

The study of phase transitions and critical phenomena at solid surfaces has been of interest both experimentally and theoretically for some time.[1] In part this is due to the prominent role that fluctuations play in two-dimensional systems and the variety of transitions that arise. One of the more intriguing theoretical predictions made for a two-dimensional system is the existence of a symmetry class whose critical exponents are nonuniversal.[2] One of the systems obeying this kind of behavior is the *XY* model with cubic anisotropy. In the limit of infinite anisotropy the four state clock model with Ising behavior and exponents is recovered whereas in the limit of zero anisotropy the Kosterlitz-Thouless (*K*-*T*) model occurs. The few experimental systems that fall into this category[1] deal with chemisorbed systems that show small deviations from Ising behavior. In order to further test this theory, it is useful to have other experimentally relevant systems which exhibit this phenomena so that values for the critical exponents may be determined from either experiment or computer simulations. In particular, it would be advantageous to examine systems where the anisotropic surface potential was weaker than in the case of chemisorption so that stronger deviations from the Ising values and elements of *K*-*T* behavior might be observed.

Through the use of MC simulations the CO/NaCl(001) and CO/LiF(001) systems have been identified[3,4] as falling into this class. The phase transition in the former system was originally observed experimentally via polarized infrared spectroscopy[5] and helium atom scattering (HAS).[6] The low-temperature ordered phase was found to have a $p(2\times1)$ structure with two molecules per unit cell that converts to an orientationally disordered $p(1\times1)$ structure above the transition temperature. Monte Carlo (MC) simulations[3] have provided details of the ordered monolayer structure and successfully reproduced the transition to the disordered state at temperatures around 30–35 K. It was argued that these phase transitions are of interest because they fall into the universality class of the *XY* model with cubic anisotropy and hence should have nonuniversal critical exponents,[7] i.e., their values depend on the relative strengths of an anisotropic external potential (provided by the substrate) and the molecule-molecule interactions. Unfortunately, the CO monolayer systems may not computationally provide as clean a test of this theory as one might hope because of the presence of a permanent, albeit weak, dipole moment on the CO molecule. Dipolar interactions ($\sim r^{-3}$) can lead to long relaxation times for energy and order parameter equilibration thus making a quantitative analysis of their critical behavior difficult. In partial contrast to earlier theoretical work[8] on Ising-type systems, recent computational work[9] suggests that molecules cannot have an electrostatic multipole moment lower than a quadrupole for the short-range Ising results to hold. This finding suggests that the above problem may be circumvented if a homonuclear diatomic molecule such as N_2 is substituted for CO so that only quadrupole-quadrupole interactions ($\sim r^{-5}$) are present. As with CO/NaCl, the N_2/NaCl system exhibits epitaxy so that, as determined by induced IR in the monolayer case,[10] a nitrogen molecule occupies every adsorption site and a uniform film is formed. Other than differences in details such as transition temperature and molecular tilt angle, these two systems should behave similarly so that spectroscopic[11] and HAS studies of the CO/NaCl system can serve as a guideline for work on N_2/NaCl and vice versa for computational work.

In this paper we report on a set of Metropolis Monte Carlo (canonical ensemble) simulations of the N_2/NaCl(001) system intended to examine the monolayer structure and possible existence of a phase transition. These simulations predict that at low temperatures a monolayer of nitrogen molecules forms an ordered $p(2\times1)$ structure which, upon heating past 25 K, undergoes an order-disorder phase transition. In the disordered phase the long-range orientational order among molecules is destroyed although residual short-range order persists in the form of small ordered domains and pairs of counter rotating vortices. A sharp peak in the heat capacity is also observed.

The potentials and methods used are the same as those used in simulatations of the CO/NaCl and CO/MgO systems.[3,12] The molecule-molecule and molecule-surface interactions employed the two-body approximation and used the Tang-Toennies and Buckingham potentials for the atom-ion and atom-atom nonelectrostatic interactions, respectively. The values of the coefficients used in these potentials, which were obtained from empirical and semiempirical methods, are similar to those of the CO/NaCl, CO/LiF, and CO/MgO systems[3,4,12] and will be presented in a later paper. The electrostatic interactions are mediated by point dipoles of strength 1.288 D assigned to each of the two nitrogen atom sites. The atomic dipoles were aligned along the N_2 bond axis pointing towards each other so as to reproduce the experimental molecular quadrupole moment[13] of $\Theta = -1.41\,\mathrm{D\,Å}$ and yield a molecular dipole moment of zero.

0163-1829/2000/62(8)/4841(4)/$15.00

The molecules were taken as rigid bodies and allowed translations in all directions and rotations around the carbon atom. These moves were generated randomly and subjected to the usual Boltzmann weighted acceptance criterion. The amplitudes of these moves were adjusted on the fly to maintain a 50% acceptance rate. One cycle consisted of every molecule attempting a move. The coordinate system used to describe the positions of the molecules on the (001) surface is the same as that used in Refs. 3 and 12. The origin is located on an anion site in the plane of the surface with the x and y axes running along the $[1,-1,0]$ and $[1,1,0]$ crystallographic directions, respectively, and with the z axis set perpendicular to the surface. A polar angle θ (tilt with respect to the surface normal) and an azimuthal angle φ (angle between the x axis and the projection of the molecular axis onto the plane of the surface) are defined in the usual way.

Using the steepest descent method for energy minimization, it was determined that when a single N_2 molecule is adsorbed on NaCl(001) it sits perpendicular to the surface (i.e., the polar angle θ is zero) with the bottom nitrogen atom at a height of 2.65 Å above the Na^+ ion. The orientation of a single molecule for the temperature range 1–50 K was examined through MC simulations which yielded a uniform distribution in the azimuthal angle and a Gaussian-like distribution centered on $\theta = 0°$ for the polar angle. In other words, the molecule remained perpendicular to the surface with no preferred azimuthal orientation. The surface binding energy was -2.88 kcal/mol, in agreement with the experimental values corrected to 1 K.[10]

To simulate a full monolayer of N_2 an ensemble of 400 molecules was placed in the NaCl surface potential. Periodic boundary conditions in the lateral direction were imposed as well as a cutoff radius of 16.5 Å for the N_2-N_2 interactions. MC simulations were run for 0.6–2.0 Mcycles at various temperatures over the range 1–60 K. To ensure equilibration of the system the first 0.2 Mcycles were discarded at low temperatures with the number of discards increased to 0.5 Mcycles in the vicinity of the phase transition. Statistical data for the variables of interest (energy in this case) were collected for the last 0.6–1.5 Mcycles of each run with the longer runs being necessary near the transition temperature. At all of the tested temperatures the molecules were on average tilted from the surface normal by 29° and displaced off of the Na^+ site by 0.15 Å in the direction of the tilt. The constant average molecular tilt indicates the transition is of the order-disorder type in contrast to the N_2/graphite system,[14] where a change in molecular tilt leads to a first-order transition.

At temperatures below 25 K the monolayer adopts an azimuthally ordered $p(2\times1)$ antiferroelectric-type structure with two molecules per unit cell. An overview of this structure is shown in the top panel of Fig. 1. As in the case of the CO/NaCl system, this structure consists of rows of molecules that have the same azimuthal orientation but with adjacent rows oriented in the opposite direction. A snapshot of the disordered phase above T_c is shown in the bottom panel of Fig. 1. Although long-range azimuthal order has been lost, some degree of short-range order remains in the form of small ordered domains with the $p(2\times1)$ structure and pairs of counter rotating vortices. The vortices, highlighted by the solid and dashed circles denoting rotations in the clockwise and counterclockwise directions, respectively, are formed by quartets of neighboring molecules and appear in disordered regions both below and above the transition temperature. The role of these vortices and whether their presence is an indicator of *K-T* type behavior has yet to be determined.

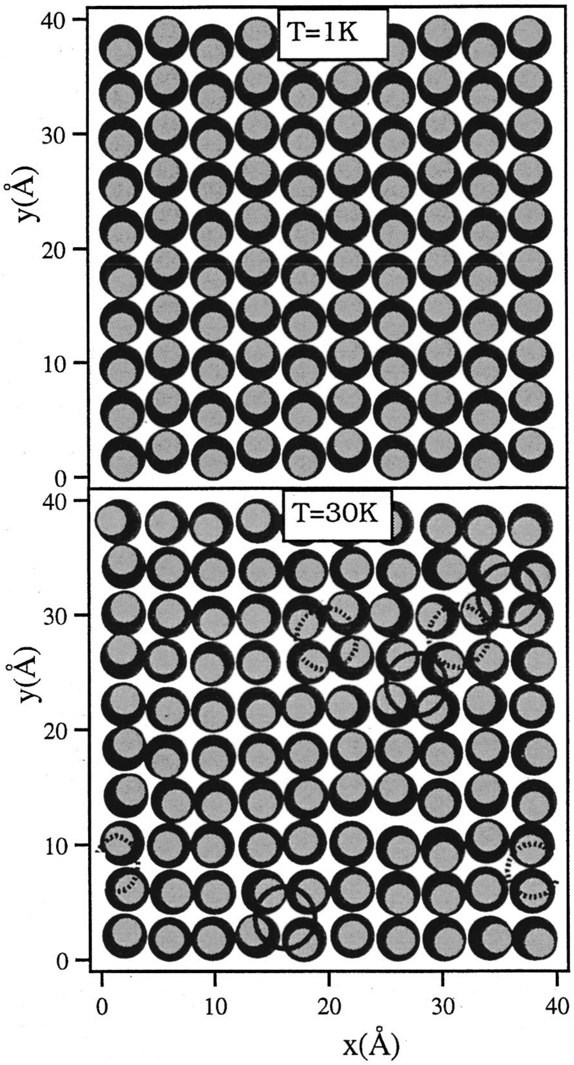

FIG. 1. An overview of a typical configuration of 100 N_2 molecules at 1 K (top panel) and 30 K (bottom panel). The nitrogen atoms closest to the surface are shown as black and the upper nitrogen atoms as gray. Clockwise (counterclockwise) vortices are denoted by the solid (dashed) circles.

The destruction of orientational order is further shown in Fig. 2, where the azimuthal angle distributions are plotted for several temperatures. The distributions are sharply peaked at $\pm90°$ at low temperatures and broaden as the temperature increases. Around 25 K the distribution becomes uniform indicating a loss of long-range azimuthal order and signaling a transition to a disordered phase. However, minor residual peaks at $\varphi \sim 0, \pm 90$, 180, are still observed at $T = 30$ K. As one might expect, this overall behavior is similar to that of the CO/NaCl system with differences occurring in the details, such as the values of the transition temperature and tilt angle.

To confirm that the transition is truly of the continuous type and thus exhibits critical behavior, the temperature dependence of the energy and heat capacity C were examined. The energy curve displayed a continuous sigmoidal shape

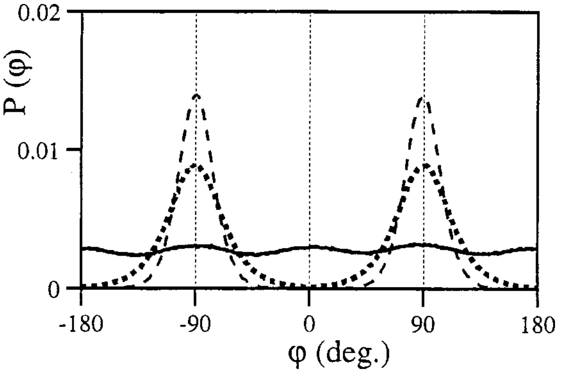

FIG. 2. The azimuthal angle (φ) distribution for $T = 10\,\mathrm{K}$ (dashed), 20 K (dotted), and 30 K (solid).

throughout the phase transition. No evidence of a discrete jump in energy at the transition was found. The heat capacity, shown in Fig. 3, was calculated from the energy fluctuations and displays a characteristic λ divergence with a peak at $T_c = 25.3\,\mathrm{K}$. This value is comparable to the transition temperature (27 K) of an orientational transition observed in the N_2/graphite system.[14] Away from the transition temperature the heat capacity approaches its baseline value of $5R/2$, which is consistent with each molecule having five degrees of freedom (x,y,z,θ,ϕ) contributing to the total potential energy. We conclude that the transition is indeed continuous.

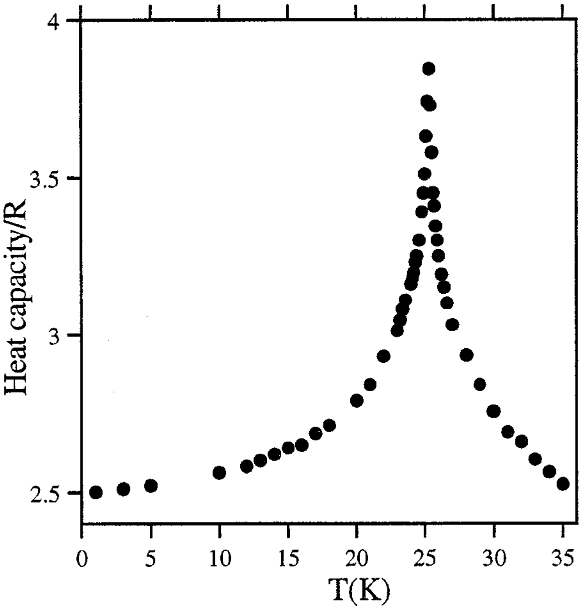

FIG. 3. The heat capacity as a function of temperature. The peak occurs at $T_c = 25.3\,\mathrm{K}$.

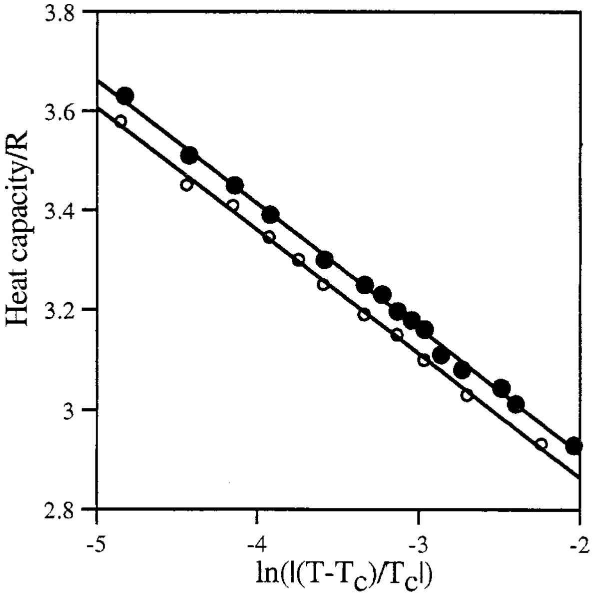

FIG. 4. The heat capacity as a function of ln(t). The solid (open) circles are for temperatures below (above) T_c. The solid circles span the temperature range 22–25.1 K from right to left while the open circles span 25.5–28 K from left to right.

To the best of our knowledge, the form of a divergence in the heat capacity for the *XY* model with cubic anisotropy is unknown. Owing to the fourfold symmetry imposed by the substrate, the transition might be similar to that of the four-state clock model and exhibit Ising-like behavior. The heat capacity will then have a logarithmic divergence of the form $C/R = -A\ln(t) + B$, where $t = |(T_c - T)/T_c|$ is the absolute value of the reduced temperature, R is the gas constant, and A and B are nonuniversal constants which have the same values above (+) and below (−) T_c, e.g., $A^+ = A^- = 0.989$ and $B^+ = B^- = -0.613$ for the four-state clock model. In Fig. 4 the heat capacity as a function of ln(t) is plotted for temperatures above and below T_c for the N_2/NaCl(001) system. In both cases there is a linear dependence of C on ln(t) that can be expressed as

$$C^-/R = -0.250\ln(t) - 0.087 + 2.5 \quad \text{for } T < T_c,$$

$$C^+/R = -0.247\ln(t) - 0.131 + 2.5 \quad \text{for } T > T_c,$$

where the background heat capacity of $2.5R$ is shown explicitly and the errors in $A^\pm$ and $B^\pm$ are 0.004 and 0.015, respectively. Note that within these error limits the amplitude A is the same above and below the transition temperature. As may be inferred by the offset of the two heat capacity lines in Fig. 4, the values of the intercepts $B^\pm$ are not the same above and below T_c. This difference might be due to the anisotropy[15] of the molecular interactions which would affect the value of B^- but not B^+ due to the averaging of the molecular orientations in the disordered phase. The error assigned to the intercepts is large because they are sensitive to the value of T_c used to construct the reduced temperature. Preliminary results from a 3600 particle system indicate that the heat capacity still diverges logarithmically and gives $T_c = 25.1\,\mathrm{K}$, $A^- = 0.250$, and $B^- = -0.212$ with the caveat that these values are extracted from runs of only 0.2 Mc/s in length preceded by an equilibration period of 0.1 Mcycles. The decrease (1%) in T_c with an increase in size is expected for a finite system with periodic boundary conditions.[16] The value of A^- is unchanged and is thus possibly insensitive to finite-size effects whereas B^- changes significantly. For comparison, recent heat capacity measurements of the CO/graphite system give values of $A = 0.340$ and $B = 0.157$ for the head-tail disordering transition[17] at $T_c = 5.18\,\mathrm{K}$ while work on the pinwheel to disorder transition[18] at $T_c = 35.2\,\mathrm{K}$ found values of $A = 0.940$ and $B = 0.344$.

In conclusion, it is predicted that N_2 adsorbed on the (001) face of an NaCl crystal will form an epitaxial monolayer of tilted molecules ($\theta = 29°$) with an ordered $p(2 \times 1)$ structure containing two molecules per unit cell at temperatures below 25.3 K. Above this temperature the monolayer is predicted to undergo a continuous transition into an azimuthally disordered phase. The transition should exhibit a logarithmic divergence in the heat capacity and might have nonuniversal values for the critical exponents of the order parameter, susceptibility, and correlation length. Investigations on larger systems are currently underway in the hope of extracting these values and will be reported upon in the near future. The predictions presented here can be tested experimentally via low-energy electron diffraction, HAS, induced IR, and heat capacity measurements.

Financial support came from the Natural Sciences and Engineering Research Council of Canada and computational support from SGI/CRAY.

---

*Corresponding author. Electronic address: david@planck.concordia.ca

[1] H. Kawamura and Y. Sakamoto, Phase Transit. **53**, 165 (1995).

[2] J. V. José, L. P. Kadanoff, S. Kirkpatrick, and D. R. Nelson, Phys. Rev. B **16**, 1217 (1977).

[3] N.-T. Vu, A. Jakalian, and D. B. Jack, J. Chem. Phys. **106**, 2551 (1997).

[4] N.-T. Vu and D. B. Jack, J. Chem. Phys. **108**, 5653 (1998).

[5] J. Heidberg, E. Kampshoff, and M. Suhren, J. Chem. Phys. **95**, 9408 (1991).

[6] D. Schmicker, J. P. Toennies, R. Vollmer, and H. Weiss, J. Chem. Phys. **95**, 9412 (1991).

[7] M. Schick, Physica B **109 & 110**, 1811 (1982).

[8] M. E. Fisher, S.-K. Ma, and B. G. Nickel, Phys. Rev. Lett. **29**, 917 (1972).

[9] E. Bayong and H. T. Diep, Phys. Rev. B **59**, 11 919 (1999).

[10] D. J. Dai, J. Chem. Phys. **104**, 2461 (1996).

[11] G. E. Ewing, Int. Rev. Phys. Chem. **10**, 391 (1991).

[12] A. K. Sallabi and D. B. Jack, J. Chem. Phys. **112**, 5133 (2000).

[13] C. Graham, J. Pierrus, and R. E. Raab, Mol. Phys. **67**, 939 (1989).

[14] A. D. Migone, H. K. Kim, M. H. W. Chan, J. Talbot, D. J. Tildesley, and W. A. Steele, Phys. Rev. Lett. **51**, 192 (1983).

[15] L. Onsager, Phys. Rev. **65**, 117 (1944).

[16] A. E. Ferdinand and M. E. Fisher, Phys. Rev. **185**, 832 (1969).

[17] H. Wiechert and K. D. Kortmann, Surf. Sci. **441**, 65 (1999).

[18] Y. P. Feng and M. H. W. Chan, Phys. Rev. Lett. **71**, 3822 (1993).