1376 © 1989 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 62, 1376—1378 (1989) [Vol. 62, No. 4

A Lattice Gas Model for Neopentane

Masato Shinmi and Dale A. Huckaby*
Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, U.S.A.
(Received August 16, 1988)

Synopsis. A lattice gas model for neopentane on a bcc lattice was considered. The equation of state and critical point were calculated using a Guggenheim-McGlashan approximation. The liquid phase in the model exhibits the same type of short-range orientational ordering proposed by Nishikawa to exist in liquid neopentane.

Nishikawa recently carried out structure simulation studies for liquid neopentane[1] and reported that the X-ray diffraction intensities from the liquid observed by Narten[2] were reproduced well by a local body centered cubic (bcc) lattice structure model.[1] In this bcc cluster model, the central carbon atoms of the neopentane molecules occupy the sites of a bcc lattice, the molecules are all in the same orientation, and the four carbon-carbon bonds of each molecule point toward the central carbon atoms of neighboring molecules. This local orientational ordering was proposed to occur over a wide range of temperatures.[1] Nishikawa and Murata[3] previously used this bcc cluster model to accurately reproduce the X-ray diffraction intensities from liquid carbon tetrachloride. The X-ray diffraction intensities from liquid 1,1,1-trichloroethane have also been accurately reproduced using the bcc cluster model.[4]

Using a five force center Lennard-Jones potential, Mountain and Brown[5] carried out a molecular dynamics study of neopentane. Their results were consistent with radial distribution functions derived from Narten's diffraction data,[2] and their study indicated that long-range angular correlations in liquid neopentane are weak.[5]

The bcc cluster model[1,3] for short-range orientational ordering has the same local structure as does the long-range orientational ordering proved to exist in a lattice gas of tetrahedral molecules on a bcc lattice.[6,7] We[8] have previously fitted a Guggenheim-McGlashan approximation[9,10] of this lattice gas model to the properties of carbon tetrachloride at the critical point. The lattice gas has properties which are consistent with several aspects of the bcc cluster model[3,11] and provides a fairly good model for carbon tetrachloride.[8]

In the present work we use this bcc lattice gas of tetrahedral molecules as a model for neopentane. A lattice site in the model can be either vacant or occupied by a molecule in either of the two orientations in which the carbon-carbon bonds of the molecule point toward neighboring lattice sites. One such orientation is illustrated in Fig. 1. If two molecules occupy neighboring lattice sites, they repel with a steric bond-bond repulsion $\gamma>0$ if each points a bond toward the other, they attract with an energy $\varepsilon\leq 0$ if exactly one points a bond toward the other, and they attract with an energy $\delta\leq 0$ if neither points a bond toward the other.

An extension of the Peierls argument[12,13] has been used to prove that if $2\varepsilon<\gamma+\delta$, then at sufficiently low temperature and sufficiently high chemical potential an orientationally ordered phase exists in the lattice gas model in which most of the sites are occupied by molecules in a single orientation.[8] Within the Guggenheim-McGlashan approximation, this orientationally ordered structure was found to exist locally in the liquid phase of the lattice gas over a wide range of temperatures.[8]

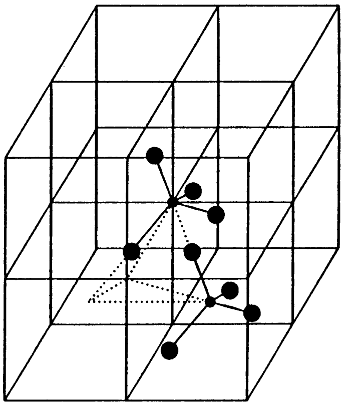

Fig. 1. One of two possible orientations of a neopentane molecule in the bcc lattice gas is shown. A tetrahedron is illustrated which is used in the Guggenheim-McGlashan approximation.

We shall now use a Guggenheim-McGlashan approximation of this bcc lattice gas[8] to model the properties of the liquid and vapor phases of neopentane. The approximation considers the interactions within the various molecular configurations possible on a cluster of sites and then approximates the interactions between various clusters on the lattice.

The following outline of the Guggenheim-McGlashan approximation is described in more detail in Ref. 8. The bcc lattice is composed of tetrahedra, one of which is illustrated in Fig. 1. We consider the set τ consisting of all translates of a single tetrahedron. Each lattice site is covered by a vertex from each of four tetrahedra in τ, and each first neighbor lattice bond is covered by an edge from exactly one tetrahedron in τ.

The set of possible molecular configurations about a tetrahedron in τ is illustrated in Fig. 2 of Ref. 8. For a configuration of type i, the energy ε_i, the number of molecules n_i, and the number of such configurations ω_i are listed in Table II of Ref. 8.

For a lattice of N sites containing M molecules, we let ψ_i be the probability that a given unit tetrahedron in τ has a molecular configuration i. The energy per lattice site is given as

$$E=\sum_i \varepsilon_i\omega_i\psi_i.$$

The entropy per lattice site is given in the

Guggenheim-McGlashan approximation as

$$S = N^{-1} k \ln \Omega_0 - k \sum_i \omega_i \psi_i \ln \psi_i.$$

Here there are N tetrahedra in τ, and Ω_0 in a constant which is determined by calculating S at extremely high temperatures.

At equilibrium the Helmholtz free energy, $A=E-TS$, is minimized at constant T, M, and N under the restrictions

$$\sum_i \omega_i \psi_i = 1$$

$$\sum_i n_i \omega_i \psi_i = \rho,$$

where $\rho=M/N$ is the number density of occupied sites. The order parameter ρ is sufficient to locate the liquid phase-vapor phase equilibrium and the associated critical point.

The Lagrange multiplier technique then gives expressions for the chemical potential μ, the pressure P, and the density ρ as functions of a parameter r.[8] These equations can be solved to obtain the phase diagram for the model. An iterative technique we developed[8] was used to locate the critical point in the model. For plotting purposes we define the reduced variables $P'=Pv_0/|\varepsilon|$, $T'=kT/|\varepsilon|$, $\gamma'=\gamma/|\varepsilon|$, and $\delta'=\delta/|\varepsilon|$. Here v_0 is the volume per lattice site.

Since steric repulsions are very strong between the methyl groups on neighboring molecules in the bcc cluster model for neopentane,[1] we consider here only the case of infinite bond-bond repulsion, $\gamma'\to\infty$, in the bcc lattice gas model. Using the experimental critical values[14] $P_c=31.545$ atm, $T_c=433.75$ K, and $\overline{V}_c=311$ cm^3 mol^{-1} for neopentane, the parameters δ', v_0, and ε in the lattice gas model can be fitted to experiment at the critical point.

The critical compressibility factor $Z_c=P_c'/(\rho_c T_c')$ for the lattice gas is plotted against δ' in Fig. 4 of Ref. 8. Since $Z_c=P_c\overline{V}_c/(RT_c)$, this quantity can be readily fitted to experiment. The best fit occurs at $\delta'=-0.78$.

For the case $\gamma'\to\infty$ and $\delta=0.78\ \varepsilon$, steric bond-bond repulsions are certainly central in producing the orientational ordering, for the two orientations of a pair of neighboring molecules which are attractive have nearly the same energy. The effect of steric repulsion on this ordering can be readily seen within the Guggenheim-McGlashan approximation, for packing considerations (see Fig. 2 of Ref. 8) even in a tetrahedral arrangement of four sites preclude all four sites from being occupied such that an attraction δ occurs in the tetrahedron without the simultaneous occurrence of a steric repulsion γ.

The critical parameters for the lattice gas model with $\gamma'\to\infty$ and $\delta'=-0.78$ were computed to be $P_c'=0.08922$, $T_c'=0.8558$, and $\rho_c=0.3784$. The volume per lattice site, v_0, was then fixed at the critical point using the equation $v_0=\rho_c\overline{V}_c/N_0$, where $\overline{V}_c$ is the experimental critical molar volume and N_0 is Avogadro's number. This gives a value $v_0=1.954\times10^{-22}$ cm^3, and a resulting first neighbor central carbon-central carbon separation of $r_{cc}=6.33$ Å. This compared quite well with the separations $r_{cc}=6.14$ Å at −17 °C to $r_{cc}=6.90$ Å at 150 °C which were used in the bcc cluster model[1] to accurately simulate the experimental X-ray diffraction intensities of the liquid at different temperatures under high pressure.[2]

The energy ε was fitted to experiment using the equation $|\varepsilon|=kT_c/T_c'$, where T_c is the experimental critical temperature. This yields $N_0|\varepsilon|=4.21$ kJ mol^{-1}. In order to compare the fitted value of $|\varepsilon|$ with experiment, we assume the liquid at the normal boiling point is ordered in the bcc local lattice structure. Then $N_0|\varepsilon| \approx \Delta\overline{E}_v/4=(\Delta\overline{H}_v-P\Delta\overline{V}_v)/4$. The experimental values[14] $\Delta\overline{H}_v=22.64$ kJ mol^{-1} and $\Delta\overline{V}_v=21893.4$ cm^3 mol^{-1} at the normal boiling point ($T_b=282.628$ K and $P=1$ atm) yields $N_0|\varepsilon|=5.11$ kJ mol^{-1}, which agrees fairly well with the fitted value.

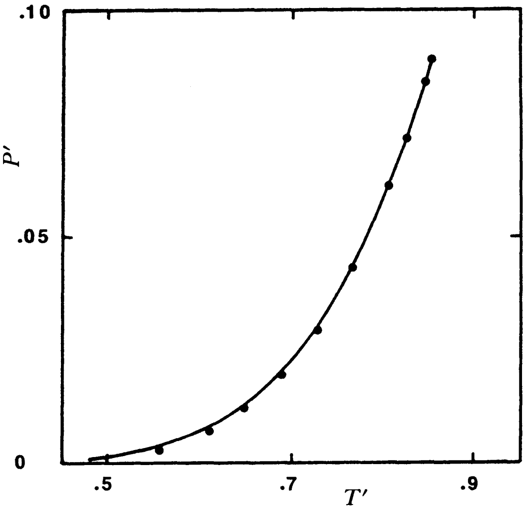

Fig. 2. The liquid-vapor coexistence curve in the (P', T') plane is plotted for the lattice gas case in which $\gamma'\to\infty$ and $\delta'=-0.78$. Several experimental points[14] are illustrated as dots in the figure.

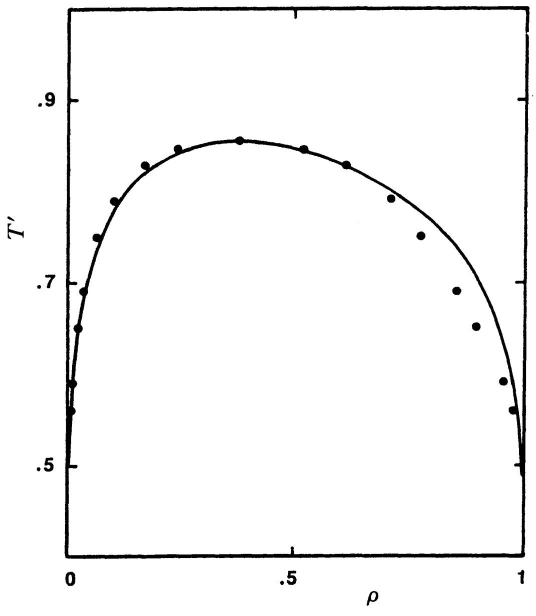

Fig. 3 The liquid-vapor coexistence curve in the (T', ρ) plane is plotted for the lattice gas case in which $\gamma'\to\infty$ and $\delta'=-0.78$. Several experimental points[14] are illustrated as dots in the figure.

The liquid-vapor coexistence curves in the (P', T') plane and in the (T', ρ) plane are plotted in Figs. 2 and 3, respectively, for the lattice gas case in which $\gamma' \to \infty$ and $\delta' = -0.78$. Using the equations $P' = Pv_0/|\varepsilon|$, $T' = kT/|\varepsilon|$, and $\rho = v_0 N_0/\overline{V}$, several experimental points[14] (P, T) and $(T, \overline{V})$ on the liquid-vapor coexistence curve were converted to (P', T') and (T', ρ) values and illustrated in Figs. 2 and 3, respectively.

In conclusion, the lattice gas model studied here is consistent with many aspects of Nishikawa's local bcc lattice structure model and seems to provide a fairly good model for neopentane.

This research was supported by the Robert A. Welch Foundation, grant P-446.

References

1) K. Nishikawa, *Bull. Chem. Soc. Jpn.*, **59**, 2920 (1986).
2) A. H. Narten, *J. Chem. Phys.*, **70**, 299 (1979).
3) K. Nishikawa and Y. Murata, *Bull. Chem. Soc. Jpn.*, **52**, 293 (1979).
4) K. Nishikawa and T. Iijima, *Bull. Chem. Soc. Jpn.*, **61**, 217 (1988).
5) R. D. Mountain and A. C. Brown, *J. Chem. Phys.*, **82**, 4236 (1985).
6) D. A. Huckaby, *J. Stat. Phys.*, **17**, 371 (1977).
7) D. A. Huckaby, A. M. Dougherty, and A. Pękalski, *Phys. Rev. A*, **26**, 3528 (1982).
8) M. Shinmi and D. A. Huckaby, *J. Chem. Phys.*, **84**, 951 (1986).
9) E. A. Guggenheim and M. C. McGlashan, *Proc. R. Soc. London*, **206**, 335 (1951).
10) G. M. Bell and D. A. Lavis, *J. Phys. A*, **3**, 568 (1970).
11) K. Nishikawa and T. Iijima, *Bull. Chem. Soc. Jpn.*, **58**, 1215, 1220 (1985).
12) R. Peierls, *Proc. Cambridge Philos. Soc.*, **32**, 477 (1936).
13) O. J. Heilmann, *Commun. Math. Phys.*, **36**, 91 (1974).
14) T. R. Das, C. O. Reed, Jr., and P. T. Eubank, *J. Chem. Eng. Data*, **22**, 16 (1977).