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STUDY OF MODEL INTERACTION POTENTIALS OF MULTIATOMIC MOLECULES IN LIQUIDS BY PERTURBATION THEORY II. MODEL POTENTIALS FOR CCl_4

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The results of calculation of thermodynamic properties of liquids with intermolecular potentials modeling CCl_4 are presented.

The possibility of using perturbation theory in the Verlet—Weis formulation for the study of effective pair interaction potentials of molecules in liquids has been considered in [1]. Below we use this method to study various model potentials whose parameters correspond to the characteristics of the CCl_4 molecule. The term model, as also used earlier in [2-4], is understood to comprise potentials where all parameters are determined from the molecular structure and the physical interaction model under consideration, and do not contain adjustable parameters. Methods of determining model potential parameters from the molecular structure have been discussed in [2]. The molecule CCl_4 is particularly suitable for this type of analysis since it has been studied in detail [5, 6] and hence there is abundant data for comparison; also the symmetry of the molecule eliminates certain ambiguities in what is meant by "peripheral atoms" and "center of the molecule" which occur in the determination of model potential parameters in [2, 4, 7]. Also the CCl_4 molecule significantly differs from a point force center as can be seen by the value determining the similtude number A [8, 9] which is equal to 2.06 for this material (recall that $A = 4$ for an inert gas).

In the present paper, we study potentials selected from a number of forms considered earlier [2, 4] by different methods [7]. The potentials considered here have the form

$$\frac{u}{\varepsilon} = f_{12}\left(\frac{r}{\sigma},\ \alpha\right) - 2f_6\left(\frac{r}{\sigma},\ \alpha\right), \tag{1}$$

where $f_{12}(t, 0) = t^{-12}$; $f_6(t, 0) = t^{-6}$. The parameters ε, σ, and α corresponding to the CCl_4 molecule are given by

$$\sigma = \sigma_{Cl} = 3.55\,\mathring{A}\ [7], \tag{2}$$

$$d_{C-Cl} = 1.766\mathring{A},$$

$$\alpha = d/\sigma = 2d_{C-Cl}/\sigma = 1{,}00, \tag{3}$$

$$\varepsilon = c/\sigma^6,$$

$$c = (4\sqrt{c_{Cl}} + \sqrt{c_C})^2,$$

$$\sqrt{c_{Cl}} = 2.36;\ \sqrt{c_C} = 1.14\ [7], \tag{4}$$

and hence

$$\varepsilon/k = 6726\,K.$$

The following functions were taken for f_n:

$$f_n^{ss} = \frac{1}{(n-2)(n-3)\,\alpha^2 R}\,P^{(n-3)}(R,\ \alpha) \tag{5}$$

(spherical shell potential)

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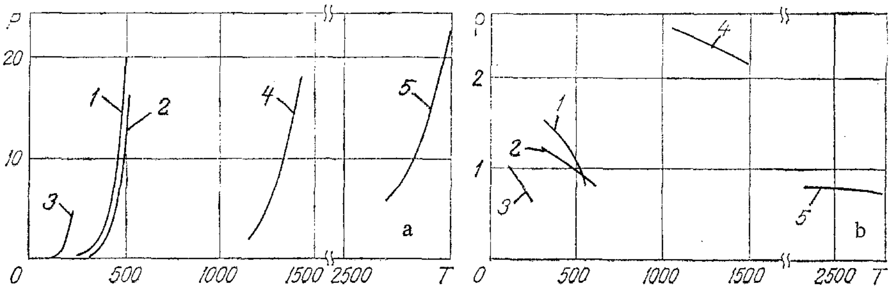

Fig. 1. P—T projection (a) and ρ—T projection (b) of the liquid—gas coexistence curve for model potentials and CCl_4: 1) experiment, 2) spherical shell potential (Eq. (9)); 3) model potential 9 (Eq. (11)); 4) model potential 1 (Eq. (10)); 5) Kihara potential (Eq. (12)). P) bar; ρ) g/cm³; T) °K.

$$P^k(R,\ \alpha)=\left(\frac{1}{R-\alpha}\right)^k+\left(\frac{1}{R+\alpha}\right)^k-2\left(\frac{1}{R}\right)^k,$$

$$f_n^{\mathrm{MP1}}=\left(\frac{1}{R^2-\alpha^2}\right)^{\frac{n}{2}} \tag{6}$$

(model potential 1 from [2], which is equivalent to the Smith—Tekker potential)

$$f_n^{\mathrm{K}}=\left(\frac{1}{R-\alpha}\right)^n \tag{7}$$

(the Kihara potential, which is one of the more popular three-parameter potentials). In (5)-(7)

$$R=r/\sigma. \tag{8}$$

The potentials under consideration have the following forms:

$$\frac{u_{\mathrm{CO}}}{\varepsilon}=f_{12}^{\mathrm{SS}}-2f_6^{\mathrm{SS}}, \tag{9}$$

$$\frac{u_{\mathrm{MP1}}}{\varepsilon}=f_{12}^{\mathrm{MP1}}-2f_6^{\mathrm{MP1}}, \tag{10}$$

$$\frac{u_{\mathrm{MP9}}}{\varepsilon}=f_{12}^{\mathrm{SS}}-2f_6^{\mathrm{MP1}}, \tag{11}$$

$$\frac{u_{\mathrm{K}}}{\varepsilon}=f_{12}^{\mathrm{K}}-2f_6^{\mathrm{K}}. \tag{12}$$

As shown in [2, 4], the first three model potentials are among the best from the point of view of the methods employed in [2, 4, 7] while the Kihara potential (12) is unsatisfactory from this point of view.

For ease in comparison with the empirical data and for greater clarity the values $P^*=P\sigma^3/\varepsilon$, $T^*=kT/\varepsilon$, $\rho^*=\rho\sigma^3$ obtained by perturbation theory are expressed in terms of macroscopic units using formulas which follow from (2)-(4):

$$P=2{,}075\cdot 10^4 P^*, \tag{13}$$

$$T=6726\,T^*, \tag{14}$$

$$\rho=5.707\rho^*, \tag{15}$$

The (P, T) and (ρ, T) projections of the coexistence curve are shown in Fig. 1. Clearly the degree of correspondence with the empirical curve is very different for different model potentials. The spherical shell potential follows the experimental data considerably better than the others; this was also found to be the case earlier in a study by different methods of the relation between the potential parameters and the macroscopic characteristics [2]. The Kihara potential is seen to be completely unsatisfactory; this corresponds also to the conclusions in [2]. The model potentials determined according to (10) and (11) and denoted as model potentials 1 and 9, are nearly equivalent to the spherical shell potential from the point of view of the methods used in [2], but describe the properties of CCl_4 much more poorly than does the latter.

Thus we see that perturbation theory is an effective tool in the calculation of several of the simplest thermal properties of model liquids. Effective molecular interaction potentials, determined a priori from molecular structure data and containing no adjustable parameters, describe in diverse fashion empirical macroscopic data. The optimal (in the sense of a closeness to the empirical data) and also the best from the a priori point of view of the models considered is the spherical shell model, corresponding to a uniform "smearing" of force centers over a sphere of radius d/2 where d is the size of the molecule (twice the distance from the center of the molecule to the center of a peripheral atom).

It must be noted that we have not exhausted all of the possibilities for refining the spherical shell model. For example, one may consider the interaction of shells whose elements interact with a more refined potential function than the simple 12-6 Lennard-Jones potential. However, even without these refinements we can assert that an effective intermolecular pair potential exists that describes the properties of real liquids sufficiently well; a completely satisfactory first approximation to this potential is the spherical shell potential. Physical models based on different model potentials lead to significant differences in the macroscopic behavior; this allows at this stage a unique determination of an adequate model.

NOTATION

u, molecular interaction potential; f_{12}, repulsive part of potential; f_6, attractive part of potential; ε, characteristic interaction energy; σ, peripheral atom size; c, sum of atom-atom interaction increments; k, Boltzmann constant; P, pressure; T, temperature; ρ, density.

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