

STUDY OF MULTIATOMIC MOLECULAR INTERACTION POTENTIALS
IN LIQUIDS USING PERTURBATION THEORY.

1. CALCULATION METHOD AND COMPARISON OF RESULTS WITH
LENNARD-JONES POTENTIAL

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An algorithm is presented for calculation of the thermodynamic properties of a liquid whose molecules interact in accordance with a specified model potential, using the methods of perturbation theory.

1. Perturbation theory is at present one of the most dependable methods used in the physics of the liquid state, permitting description of the properties of dense liquids with satisfactory accuracy at sufficient distance from the critical point on the basis of the intermolecular interaction potentials [1, 2]. For model systems with a Lennard-Jones interaction potential, many results have been obtained with perturbation theory, including calculation of the liquid-gas coexistence curve [3]. Comparison of these calculations with pseudo-experimental data (obtained by computer simulation of the given system) and with data for Ar [4, 5] has shown good agreement between calculated and experimental values.

The great majority of studies using perturbation theory have treated Lennard-Jones systems, sometimes with various (for example, dipole) additions. Occasional studies which have used other potentials [6, 7] have not given very good results, which, in addition, are dependent on a large number of parameters.

At the same time, as was shown in [8, 9], all liquids of the nonassociated class can be adequately described by a simple three-parameter spherically symmetric effective intermolecular interaction potential of the form

$$\frac{u}{\epsilon} = f\left(\frac{r}{\sigma}, \alpha\right), \quad (1)$$

where $\alpha = d/\sigma$, d is the size of the molecule as a whole, and ϵ is the characteristic interaction energy (for globular molecules σ is the Van der Waals diameter of the peripheral atom, d is the diameter of the globule, ϵ is the depth of the atom-atom interaction potential well. For more complex molecules σ and α must be treated as certain mean values). It is of importance that all parameters in Eq. (1) can be calculated commencing from the molecular structure, i.e., the potentials used are model ones.

The present study will be dedicated to an investigation of a number of model potentials of the form of Eq. (1) using the methods of Wicks-Chandler-Andersen perturbation theory in the Verlet-Weis formulation [3]. The potentials used were constructed on the basis of the Lennard-Jones potential, i.e., $f(r/\sigma, 0) = (r/\sigma)^{-12} - 2(r/\sigma)^{-6}$.

Since, as is evident from the concrete form of the potentials to be studied (see, for example, [10]), the transition from $\alpha = 0$ to $\alpha \neq 0$ leads to a narrowing of the potential well and production of an impenetrable core, perturbation theory of the given type should converge better than with a Lennard-Jones system. The extremely detailed description of the calculation algorithm presented in [3] makes writing and debugging the corresponding program relatively easy. Use of the more refined methods of [11, 12] would require consideration of their applicability and determination of the concrete form of the corresponding equations. Although appearing quite promising, construction of a perturbation theory using a Lennard-Jones fluid as the reference system, for which a large amount of computation material has been accumulated (see, for example, [13]), will require separate study. At the same time, the Verlet-Weis

method, which is sufficiently reliable over a quite wide temperature range, gives interesting results, although of less value, with relatively low computer time expenditures.

2. In the Verlet-Weis theory [3] a division of the potential, typical of Wicks-Chandler-Andersen perturbation theory, into a reference and perturbation potential is used:

$$u_0(r) = \begin{cases} u(r) + u_{\min}, & r \leq r_{\min} \\ 0, & r > r_{\min} \end{cases},$$

$$u_1(r) = \begin{cases} -u_{\min}, & r \leq r_{\min} \\ u(r), & r > r_{\min} \end{cases},$$

$$u(r_{\min}) = -u_{\min} = \min.$$

The function $u_0(r)$ is used to construct an equivalent system of rigid spheres with a diameter dependent on temperature and density. This system acts as a reference; for its radial distribution function we use a corrected Wertheim-Tillet solution of the Percus-Yevick equation [14, 15] for a system of rigid spheres. Then with the aid of the function $y(r) = e^{\beta u(r)} g(r)$ for the reference system we calculate the first-order perturbation for the free energy F_1 , for which approximants are constructed. By differentiation of the latter we also obtain the compressibility factor $z = PV/RT$. Approximants are also constructed for the various functions characterizing the reference system.

The authors have introduced some changes into the technique of [3]. First, since the potentials to be studied differ significantly from Lennard-Jones, the quantities directly dependent on the form of the potential function were not considered by the approximants presented in [3], but by exact expressions. At the same time, having calculated the reference system sphere diameter for given temperatures and densities, we can use the approximants of [3] to calculate the properties of the system.

Second, to calculate the first-order perturbation to the free energy and the compressibility factor we have used the method of [16], in which integration of the potential with a weight of $g(r)$ in coordinate space is replaced by integration in Laplace transform space. This method is simpler in realization and significantly more accurate, inasmuch as the Wertheim-Tillet solution [14, 15] can be written in a simple form, convenient for integration in just this space.

Other than these changes, the method used here follows the algorithm of [3]. The integrals needed for calculation of the system thermodynamic characteristics were calculated with Gaussian quadratures [17, 18] for finite segments and with Gauss-Laguerre quadratures for semiinfinite intervals [17]. The number of nodes required was determined by the condition of constancy of the calculated integral value to a specified accuracy when the number of nodes is changed. It was shown that with use of 16 nodes in the Gaussian quadratures and 12 in the Gauss-Laguerre quadratures typical integral values could be calculated to a relative accuracy of 10^{-3} - 10^{-4} or better.

Thus, using the method described above, for each state T, ρ we obtain values of F and z , i.e., the equation of state for the dense liquid. To compare the results of perturbation theory calculations with empirical material, it is very desirable to obtain the critical constants by perturbation theory. Unfortunately, the inaccuracy of perturbation theory in the region close to the critical point made it impossible to find these constants directly. Therefore, a method based on determination of the critical constants from the liquid-vapor coexistence curve, using empirical material, was chosen [8]. Moreover, obtaining the coexistence curve was of interest in its own right, since its form is very sensitive to change in the characteristics of the intermolecular interaction [8].

To calculate the gas phase coexistence curve (whose properties cannot be obtained with perturbation theory) either a gas with nonzero second and higher virial coefficients, or an ideal gas was considered.

The coexistence curve was constructed in the following manner. The liquid-vapor equilibrium condition

$$T = T_V, P = P_V, \mu = \mu_V \quad (2)$$

(where the subscript V refers to the gas phase, and the subscriptless quantities describe the liquid) was rewritten in the form

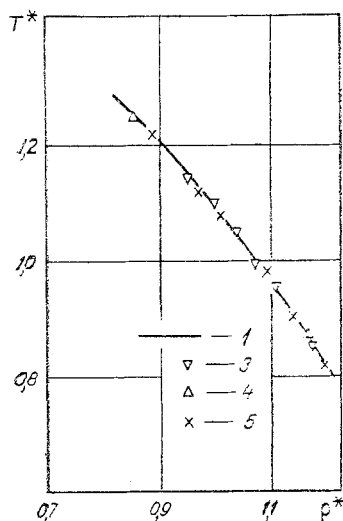


Fig. 1

Fig. 1. T, ρ projection of coexistence curve: 1) perturbation theory; 3) Lennard-Jones fluid [4]; 4) same [5]; 5) Ar [19]. $T^* = kT/\epsilon$; $\rho^* = \rho\sigma^3$.

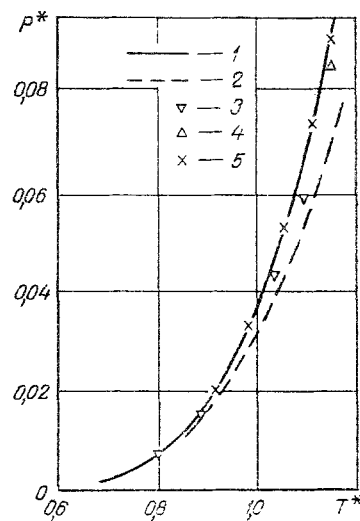


Fig. 2

Fig. 2. P, T projection of coexistence curve: 1) Perturbation theory, for vapor with $B \neq 0$; 2) same, but $B \equiv 0$; 3) Lennard-Jones fluid [4]; 4) same [5]; 5) Ar [9], $P^* = P\sigma^3/\epsilon$; $T^* = kT/\epsilon$.

$$T = T_v \equiv T, \rho z = \rho_v z_v, \beta F + z = \beta F_v + z_v. \quad (3)$$

For a gas with nonzero second and higher virial coefficients

$$z_v = 1 + \rho_v B, \beta F_v - (\beta F_v)^{id} = \rho_v B.$$

(The superscript *id* indicates an ideal gas.) Considering that $(\beta F)^{id} = \beta F_0(T) + \ln \rho$, system (3) reduces to the equation

$$\beta F_1 + z - \ln \left(\frac{z}{1 + B\rho_v} \right) - 1 - 2B\rho_v = 0, \quad (4)$$

where

$$\rho_v = (\sqrt{4Bz\rho + 1} - 1)/2B \quad (5)$$

is the vapor density in the given approximation. Equation (4) with condition (5) was solved numerically. The solution consisted of values of ρ , ρ_v , z , z_v , βF , βF_v , etc. for each temperature T .

3. Computer Realization of the Method. The program to calculate thermodynamic properties of liquids by the perturbation theory method was written in the input language of the TA-1M translator (subset of ALGOL-60) and tested on a BESM-4M computer. Preliminary testing of the program using the Lennard-Jones potential showed almost complete correspondence of intermediate calculation results with similar values from [3]. The time required for calculation of one state (at given T, ρ) was 20-40 sec. Time required for calculation of a point on the coexistence curve was of the order of 3 min with a good initial approximation. The program comprises some 400 lines, so will not be presented here.

4. Calculation Results for Lennard-Jones Potential. The coexistence curve calculated by perturbation theory methods is shown in the coordinates T, ρ and P, T , respectively, in Figs. 1 and 2 (solid lines). The corresponding pseudoexperimental (Monte Carlo) data points are shown by symbols 3 ([4]) and 4 ([5]). The dashed curve of Fig. 2 is the coexistence curve calculated with the assumption of an ideal gas phase (i.e., $B(T) \equiv 0$). The behavior of these curves demonstrates the necessity, and in the first approximation, the sufficiency, of considering only the second virial coefficient for calculation of vapor properties over a quite wide range of states. In Fig. 1 the difference between the solid and dashed curves is significantly less, so the latter is not shown.

The points 5 in Figs. 1 and 2 correspond to the equation of state of Ar [19], with parameters $\epsilon/k = 118^\circ\text{K}$, $\sigma = 0.382 \text{ nm}$ [4]. These parameters give the best agreement of the experimental data on Ar (second virial coefficient, viscosity) with corresponding calculated data using the Lennard-Jones potential.

It can be concluded from study of Figs. 1 and 2 that perturbation theory adequately describes the properties of a liquid with a specified interaction potential, which for monoatomic molecules in the first approximation may be the Lennard-Jones potential.

5. Critical Constants. As was indicated previously, in the form used here perturbation theory cannot describe the critical state with satisfactory accuracy. Therefore, to calculate the critical constants of the model fluid the following algorithm [8] was used, based on generalization of empirical material.

Let T_1, ρ_1, P_1, z_1 and T_2, ρ_2, P_2, z_2 be the characteristics of two points on the coexistence curve. Then ρ_c can be defined with the aid of the expression

$$\frac{\rho_i}{\rho_c} = \frac{-1.1635 + 1.7866 \lg z_i}{1 + 6.444 \lg z_i} \quad (6)$$

The subscript i may take on the values 1 or 2. The quantities T_c and A are defined in the following manner:

$$\lg A = -0.4575 + 0.5125 \frac{T_2}{T^+} - \left(1.20 - 0.35 \frac{T_2}{T^+}\right) \lg z^+ - 0.206 (\lg z^+)^2, \quad (7)$$

$$T_c = \frac{T^+}{0.03803 + \sqrt{1.8791 - 1.5815 \lg A}}, \quad (8)$$

where

$$T^+ = \frac{T_1 T_2}{T_1 + T_2} \left[0.098805 + \sqrt{0.0097625 + \dots} \right] + 2.46737 \frac{T_1 + T_2}{T_2 - T_1} \times \left(\lg \frac{P_2}{P_1} - 3.9726 \lg \frac{T_2}{T_1} \right), \quad (9)$$

$$\lg \frac{P^+}{P_2} = 3.9726 \lg \frac{T^+}{T_2} + \left(\frac{T^+}{T_2} \right) \left(0.3252 + 0.40529 \frac{T^+}{T_2} \right), \quad (10)$$

$$z^+ = P^+ / \rho_2 T^+.$$

Calculation for the Lennard-Jones potential gives $\rho_c^* = 0.443$; $T_c^* = 1.28$; $A = 3.97$. Calculation with Eq. (10) and $T_2^* = T_c^*$ gives $P_c^* = 0.1664$. Correspondingly, $z_c = P_c^* / \rho_c^* T_c^* = 0.294$. The pseudoexperimental values of the corresponding constants for the Lennard-Jones fluid comprise: $\rho_c^* = 0.51$; $T_c^* = 1.36$; $z_c = 0.31$ [3]. For Ar with the parameters indicated, $\rho_c^* = 0.450$; $T_c^* = 1.283$; $A = 3.94$; $P_c^* = 0.1683$; $z_c^* = 0.292$. It is known [4] that the pseudoexperimental binodal differs significantly from the Ar binodal in the peak region, although the region far from the critical point is described well; in other words, the Lennard-Jones potential is inadequate for description of the near-critical region. In complete agreement with this, the critical constants calculated by the method of [8] from a portion of the coexistence curve far from the critical region for the Lennard-Jones fluid (which coincides well with the analogous segment of the curve for Ar coexistence) are close to the corresponding values for Ar, and not those for the Lennard-Jones fluid.

From this we conclude that processing of the coexistence curve in the region sufficiently far from the critical point ($z \sim 10^{-3} - 10^{-2}$) is a completely acceptable method of obtaining the critical constants of model fluids.

NOTATION

u , intermolecular interaction potential; ϵ , characteristic interatomic interaction energy; σ , peripheral atom size; d , molecular size; $g(r)$, radial distribution function; T , temperature; ρ , density; P , pressure; V , specific volume; z , compressibility factor; F , free energy; μ , chemical potential; $B(T)$, second virial coefficient; β , inverse temperature; P_c, T_c, ρ_c, z_c , critical constants.

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