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EQUATION OF STATE AND THERMODYNAMIC PROPERTIES  
OF THE CONDENSED PHASE OF A PURE SUBSTANCE

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It is shown that the equation of state of a liquid obtained with the cell model contains three individual constants, determinable from experiment. The equation possesses good extrapolation properties.

In [1] the cell model of a liquid with (6-12) effective potential and variable parameters was used to obtain an equation of state

$$\frac{p}{NkT\rho} = 1 - 1.744 \frac{\epsilon_l}{kT} [(b_{\alpha}\rho)^2 - 0.4654 (b_{\alpha}\rho)^4], \quad (1)$$

which describes the thermal properties of the liquid phase with a high degree of accuracy and conveys the fundamental principles governing change in liquid micro- and macroproperties.

In contrast to the well-known Lennard-Jones-Devonshire [2] and Frenkel [3] theories in which a fixed liquid structure is postulated, [1] considered change in liquid structural characteristics with change in temperature, which agrees with experimental data on the temperature dependence of the coordination number of simple liquids [4]. This major assumption allows the model in question to approach a real liquid.

Moreover, for the pair potential a (6-12) effective potential dependent on the temperature through the parameters  $\epsilon(T)$  and  $\sigma(T)$  was used, which allows extension of this model to a wide class of complex liquids including polar ones.

In Eq. (1) each term has a definite physical meaning. The first term corresponds to the "ideal gas" state of a liquid, in which the mean distance between closest neighbors is equal to  $R_g$ . In this case the liquid density is equal to the orthometric value, i.e., the value obtained from the ideal gas curve (Fig. 1, point a). The second and third terms in Eq. (1) consider respectively the contributions of molecular attraction and repulsion, when the dis-

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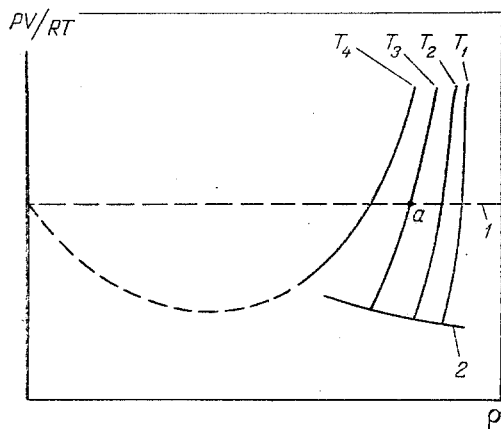


Fig. 1

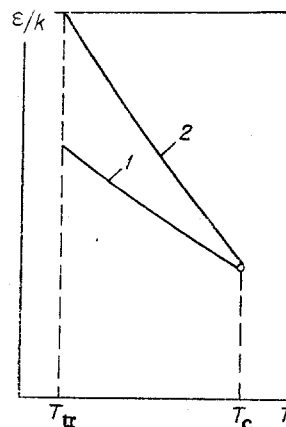


Fig. 2

Fig. 1. Liquid compressibility isotherms (generalized): 1) orthometric curve ( $z = 1$ ); 2) saturation line.

Fig. 2. Parameters  $\epsilon_l/k$  and  $\epsilon/k$  vs temperature (generalized): 1)  $\epsilon/k$ ; 2)  $\epsilon_l/k$ .

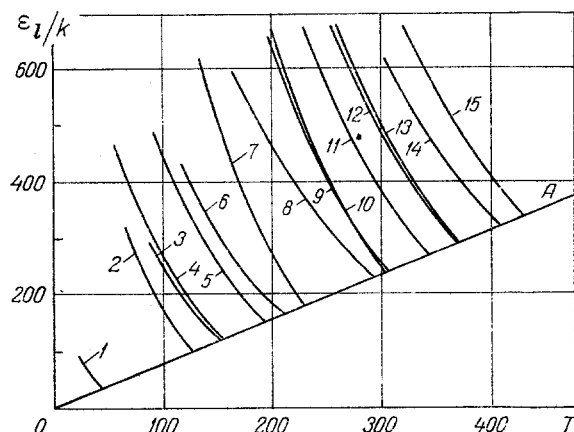


Fig. 3. Parameter  $\epsilon_l/k$  vs temperature, as found from PVT data for single phase liquids: 1) Ne ( $T_c = 44.4^\circ\text{K}$ ); 2)  $\text{N}_2$  (126.15); 3) Ar (150.65); 4)  $\text{O}_2$  (154.75); 5)  $\text{CH}_4$  (190.77); 6) Kr (209.39); 7) R14 (227.7); 8) Xe (298.74); 9) R13 (302.0); 10)  $\text{CO}_2$  (304.19); 11) R218 (345); 12) R22 (369.15); 13)  $\text{C}_5\text{H}_8$  (379.15); 14)  $\text{NH}_3$  (405.6); 15)  $\text{C}_4\text{H}_{10}$  (425.16); OA, line  $\epsilon_l/k = 0.794 T$ .  $\epsilon_l/k$ ,  $^\circ\text{K}$ ,  $T$ ,  $^\circ\text{K}$ .

tance between neighbors differs from the equilibrium value ( $R \neq R_e$ ). Depending upon which of these effects dominates, the system density will be less or more than the orthometric value.

The parameters of equation of state (1)  $\epsilon_l$  and  $b_{0l}$  depend on temperature and contain information on the character of the intermolecular interaction and structural characteristics of the liquid:

$$\epsilon_l = \epsilon \frac{\bar{Z}}{Z_0}, \quad b_{0l} = b_0 \frac{\gamma_0}{\gamma}, \quad b_0 = \frac{2}{3} \pi N \sigma^3. \quad (2)$$

It is evident that the parameter  $\epsilon_l$  must be a decreasing function of temperature, since with increase in  $T$  from the triple point temperature to the critical point, the intensity of the molecular interaction ( $\epsilon$ ) and coordination number ( $\bar{Z}$ ) decrease (Fig. 2). Without considering in detail the methods used for determination of  $\epsilon_l$  and  $b_{0l}$  from experimental PVT data of a liquid, it should be noted that for all the substances considered herein (more than 30), including polar liquids, the dependence of  $\epsilon_l$  on temperature was identical in character (Fig. 3), and is well described by a straight line in semilogarithmic coordinates. Consequently, the function  $\epsilon_l(T)$  can be represented in the form

$$\frac{\varepsilon_l}{k} = \frac{\varepsilon_c}{k} \exp \left[ c \left( 1 - \frac{T}{T_c} \right) \right]. \quad (3)$$

The  $\varepsilon_l(T)/k$  curves of Fig. 3 are located in order of increasing critical temperature upon progression from one material to another (the end points of the curves correspond to the temperatures  $T_{tr}$  and  $T_c$ ). For identical or similar  $T_c$  values, the curves practically coincide in the region of  $T_c$ , but have different slopes (characterized by the parameter  $c$  of the material), they diverge for  $T < T_c$ . Consequently, the critical temperature value uniquely defines the intensity of the intermolecular interaction in the liquid, characterized by the parameter  $\varepsilon_c$ .

We may thus propose the existence of a universal function relating the parameter  $\varepsilon_c$  to the critical temperature:  $\varepsilon_c = f(T_c)$ . It has been established that with an error of less one percent for all materials studied it is true that

$$T_c = 1,26 \frac{\varepsilon_c}{k}. \quad (4)$$

In [5] Barker et al. studied the possibility of obtaining critical parameter values with the aid of a virial series and calculated various  $T_c^*$  values for a Lennard-Jones potential as a function of number of virial coefficients considered. With consideration of the third, fourth, and fifth virial coefficients  $T_c^*$  values of 1.44, 1.30, 1.29 were obtained. The published results of this study show good agreement between the data of [5] and Eq. (4). Apparently inclusion of higher terms of the virial expansion would lead to even closer agreement of  $T_c^*$  values.

Returning to Eq. (3), with consideration of Eq. (4) we can obtain the form of the temperature dependence of  $\varepsilon_l$ :

$$\frac{\varepsilon_l}{k} = 0,795 T_c \exp \left[ c \left( 1 - \frac{T}{T_c} \right) \right]. \quad (5)$$

With the aid of Eq. (1) we can easily establish the relationship between the parameter  $b_0 \zeta$  and the orthometric density, if we set the term in square brackets equal to zero:

$$b_0^{-1} \zeta = 0,6822 \rho_{id}. \quad (6)$$

Since a linear change in orthometric density with temperature is characteristics of all the liquids, we find the form of the dependence of  $b_0 \zeta$  or  $\sigma^3 \zeta$  ( $b_0 \zeta = 2\pi N \sigma^3 \zeta / 3$ ) on  $T$ :

$$\sigma_l^{-3} = a - bT. \quad (7)$$

It should be noted that this linear density change along the orthometric curve has been established not only for simple and slightly polar liquids, but also for polar substances (except water) such as R21, R22,  $NH_3$ , R23, and R152, which have significant dipole moments ( $\mu = 1,29, 1,41, 1,47, 1,64, 2,23$  D). For these materials, on the basis of Eq. (1) [Eq. (6)] a linear change of  $\rho_{id}$  with  $T$  was also established.

With consideration of Eqs. (5) and (7) it becomes obvious that equation of state (1) contains three constants ( $a, b, c$ ). These are determined so as to best describe experimental PVT data of the liquid, so that the method used may vary depending on the form of the original experimental information.

The technique developed were used to create a calculation program for a large number of liquid systems including liquified noble gases, hydrocarbons, freons, and polar liquids. In all cases the error in describing the experimental thermal data is  $\delta\rho = 0,01-0,2\%$ . Table 1 presents values of  $a, b, c$  for several liquids, together with mean and maximum errors in describing experimental (tabular) data, and the temperature and pressure ranges for which the parameters of the equation of state were established.

The excellent extrapolation capabilities of Eq. (1) should be noted, these being due to the theoretically correct density dependency. The sequence of powers to which  $\rho$  is raised (0, 2, 4) is not dictated by empirical considerations, but is determined by lattice theory and the mathematical structure of the (6-12) potential used therein. The extrapolation properties of Eq. (1) were tested for a number of liquids (Ar,  $N_2$ ,  $O_2$ ,  $CH_4$ ,  $CO_2$ , etc.), by determining parameters over a relatively narrow pressure (density) range. Subsequent calculation of thermodynamic properties at higher pressures (extrapolation) showed good agreement

TABLE 1. Parameters of the Equation of State (1)

Material	$a \cdot 10^2$	$b \cdot 10^3$	$c$	$\delta\rho_{\text{min}}, \%$	$\delta\rho_{\text{max}}, \%$	$\Delta T, \text{K}$	$P_{\text{max}}, \text{MPa}$	Ref.
Ar	3,9651	9,516	2,12	0,06	0,17	85—150	100	[8]
O <sub>2</sub>	4,1025	9,895	2,22	0,04	0,14	60—160	33	[6]
R13	1,7660	2,400	2,95	0,07	0,24	100—300	30	[11]

TABLE 2. Comparison of Calculated and Reference [6, 7] Liquid Oxygen Density Values (kg/m<sup>3</sup>)

T, K	Pressure, MPa											
	10		20		30		50		70		100	
	[6]	calc.	[6]	calc.	[6]	calc.	[7]	calc.	[7]	calc.	[7]	calc.
60	1294,1	1294,0	1304,8	1304,4	1314,2	1314,8	1330,2	1333,9	—	—	—	—
80	1207,0	1207,9	1222,7	1223,1	1236,7	1237,1	1261,4	1262,2	1283,3	1284,5	1313,2	1313,9
100	1115,8	1116,3	1138,2	1138,1	1157,5	1157,3	1190,5	1190,5	1218,9	1218,6	1257,0	1254,5
120	1015,0	1014,6	1048,9	1047,6	1075,9	1074,7	1118,9	1118,4	1153,7	1153,5	1198,0	1196,5
140	892,8	893,2	950,8	949,1	990,3	988,5	1047,1	1046,1	1089,7	1089,3	1140,8	1140,0
160	—	—	839,4	837,9	898,8	898,3	975,2	974,1	1027,2	1026,3	1086,1	1084,7

TABLE 3. Comparison of Calculated and Reference [8, 9] Values of H and S for Liquid Argon on 140°K Isotherm

P, MPa	$\delta S, \text{kJ/kg} \cdot \text{deg K}$	$\delta H, \text{kJ/kg}$	Ref.
10	0,0016	0,073	[8]
20	0,0023	0,204	[8]
50	0,0028	0,231	[8]
100	0,0006	-0,145	[8]
120	0,0110	0,016	[9]
140	0,0092	-0,145	[9]
160	0,0075	-0,334	[9]
180	0,0077	-0,505	[9]
200	0,0070	-0,668	[9]
240	0,0071	-0,878	[9]
280	0,0063	-0,924	[9]

TABLE 4. Comparison of Calculated and Experimental Argon Parameters on Solid-Liquid Phase Equilibrium Line

T, K	P, MPa	$v^l \cdot 10^3, \text{calc. m}^3/\text{kg}$	$v^l_{\text{ex}} \cdot 10^3, \text{m}^3/\text{kg}$	$\delta v, \%$	$\Delta v_{\text{calc.}}, \text{m}^3/\text{kg}$	$\Delta v_{\text{ex}}, \text{m}^3/\text{kg}$	$q_f(\text{calc.}), \text{kJ/kg}$	$q_f(\text{exp.}), \text{kJ/kg}$
100	68,44	0,6757	0,6744	0,19	0,0702	0,0696	31,15	30,29
110	114,2	0,6595	0,6606	-0,17	0,0607	0,0611	33,54	31,67
120	162,6	0,6455	0,6481	-0,40	0,0550	0,0558	34,96	33,04
130	213,3	0,6332	0,6363	-0,49	0,0507	0,0511	35,43	34,17
140	266,2	0,6224	0,6261	-0,59	0,0469	0,0483	37,63	36,45
150	321,3	0,6131	0,6163	-0,52	0,0446	0,0456	38,43	38,30

between extrapolated and experimental data. An example is presented in Table 2, which above shows calculated density values for liquid oxygen, obtained with Eq. (1), constructed with data from [6] for the pressure range to 33 MPa. Comparison of calculated values with tabular data from [7] shows good agreement even at higher pressures ( $p = 30\text{--}100$  MPa). This apparently explained by the fact that the temperature dependence of structural characteristics on which Eq. (1) is based is manifested more clearly than the density dependence. On the other hand, at higher pressures the quasicrystalline approach upon which the liquid model is based becomes ever more justifiable.

Equation of state (1) can be used to calculate and extrapolate caloric properties of liquids, as is evident from Table 3, which presents calculated and tabular [8, 9] values of argon enthalpy and entropy, including an extrapolation range.

The good extrapolation properties of Eq. (1) allow determination of thermodynamic properties of the condensed phase on the solidification line with acceptable accuracy, as well as calculation of volume and thermal effects upon liquid-solid phase transition, if the density and caloric properties of the solid phase on the fusion line are known. Table 4 presents a comparison of calculated Ar density values on the solidification line and values of  $\Delta v$  and  $q_f = T\Delta S$  with data from [9]. To determine the volume change  $\Delta v = v^L - v^S$  and entropy change  $\Delta S = S^L - S^S$  Eq. (1) was used with constants from Table 1 ( $v^L$  and  $S^L$ ) and data from [10] for the solid phase ( $v^S$  and  $S^S$ ). Agreement between calculated and experimental values is acceptable.

Values of the thermodynamic properties of Kr, Xe, and  $CH_4$  on the solidification line were obtained in a similar manner, and the results of [10] were then used to find data on  $\Delta v$  and  $q_f$  of these materials.

#### NOTATION

$P$ ,  $\rho$ ,  $T$ , pressure, density, temperature;  $z = P/RT\rho$ ;  $T_t$ , triple point temperature;  $T_c$ , critical temperature;  $N$ , Avogadro's number;  $k$ , Boltzmann's constant;  $Z$ , coordination number;  $\gamma$ , structural factor;  $\bar{Z}_0$ ,  $\gamma_0$ , structural characteristics at critical temperature;  $\epsilon$ ,  $\sigma$ , potential parameters;  $\rho_{id}$ , orthometric density;  $v^L$ ,  $s^L$ , liquid volume and entropy on solidification line;  $v^S$ ,  $s^S$ , solid volume and entropy on fusion line.

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