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The key role of Mendeleev's forces in intermolecular interactions

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Abstract

In this paper, it is shown that a physically correct description of the thermophysical properties of liquid hydrocarbons is possible only when non-covalent long-range bond forces are taken into account

The results of detailed studies of the physical nature of intermolecular forces in organic systems, presented in the works [1-8], in particularly [9], lead to the need for a detailed analysis of issues related to taking into account long-range noncovalent recognition supramolecular binding forces leading to the association of particles and the formation of a special cluster structure of matter [10].

Under these conditions, it is quite natural to analyze the equations [11-14] characterizing the relationship between the thermophysical properties of a substance with its molecular structure and peculiarities of the nature of intermolecular forces on the basis of the thermodynamic equation of state, which reproduces the fundamental relationship between the thermal and caloric properties of a substance. It should be noted that equation (1), obtained within the framework of the discrete-continual model [13], reproduces the features of such a relationship for condensed systems with an atom-atom mechanism of intermolecular interaction.

A fundamentally important parameter of equation (1) is the energy of intermolecular forces entering into E_p

$$T \left(\frac{\partial p}{\partial T} \right)_V = \frac{NkT}{V} - \frac{E_p}{V}, \quad (1)$$

which characterizes the degree of bonding of the particles of the condensed system. It should be noted that for a wide range of state parameters, equation (1) coincides with the well-known empirical Lewis formula [15], which, far from the critical point, adequately reproduces the relationship between the heat of vaporization and the elastic and caloric properties of a liquid.

Assuming that the pairwise interaction of "atomic" centers is realized by the Lennard-Jones potential, and the energy of the pairwise interaction of long-range bonding forces of particles is proportional to the critical temperature, the total energy of intermolecular forces is determined by the sum of 3 terms:

$$E_p = -B\rho^2 + a\rho^4 - b\rho^{1/3}. \quad (2)$$

Here $-B\rho^2$ is the energy of dispersive forces of attraction;

$+a\rho^4$ is the energy of repulsive forces;

$-b\rho^{1/3}$ is the long-range bond energy.

The constants of dispersion forces B and binding forces b per unit mass are closely related to the critical parameters of a substance, are determined by the formulas below

$$\left(\frac{\partial P}{\partial T}\right)_{cr} = \frac{B\rho_{cr}^3}{T_{cr}} + \frac{R}{M}\rho_{cr}, \quad b = \frac{RT_{cr}}{2M\rho_{cr}^{1/3}}.$$

The repulsive force constants a are empirically related to the binding force constant $a\rho_b^4 = b\rho_b^{1/3}$.

Table 1

B 0,543		b 4424,6	
T,K	$Ep[16]$	$Ep(2^*)$	Err,%
280	416	415	-0,3
285	412	411	-0,2
290	408	407	-0,1
295	404	404	-0,1
300	400	400	0,0
305	396	396	0,0
310	392	392	0,0
315	388	389	0,0
320	385	385	0,1
325	381	381	0,1
330	377	377	0,1
335	373	373	0,1
340	369	369	0,1
345	365	365	0,1
350	361	362	0,2
355	357	358	0,2

In practical terms, a very interesting relationship that determines the energy of intermolecular interaction of a unit mass liquid hydrocarbon, which is a special case of formula (2), is the relationship (2*) are presented below

$$|E_p| = B\rho^2 + b\rho^{1/3} \cdot \left[1 - \left(\frac{\rho}{\rho_b} \right)^{11/3} \right]. \quad (2^*)$$

Here ρ_b is the density of the liquid at normal boiling point.

From formula (2*) it follows that at temperatures exceeding the normal boiling point, the energy of intermolecular forces is determined mainly by the dispersion forces of attraction. To get an idea of the degree of reliability of the values of the energy of intermolecular forces predicted by formula (2*) Table 1 is given with data on the value of the energy of intermolecular forces for liquid benzene on the equilibrium curve in the range from the normal boiling point to a temperature close to the crystallization temperature.

Differentiating (2) by volume, and assuming that the energy of intermolecular forces of the vapor phase is determined by a similar relationship, we obtain a formula that determines the vapor pressure, including on the equilibrium curve.

$$p_s = \frac{1 + \delta}{2} \frac{RT}{M} \rho - \delta \frac{1}{3} b \rho^{4/3} - 2B\rho^3 + \delta 4a\rho^5 \quad (3)$$

Formula (3) takes into account the action of each of these three forces by its derivatives from the energy caused by each of them. The association of vapor particles caused by the Mendeleev forces and the effects connected with it are controlled by the dissociation coefficient δ and the chemical equilibrium constant K , which depend on the binding energy

$$K = C \rho T^{-3/2} \exp(T_{cr}/T) = \frac{1 - \delta^2}{4\delta^2} \Rightarrow \delta = \frac{1}{\sqrt{4K + 1}} \quad (4)$$

The above formulas (3) and (4) are used to estimate the pressure of saturated vapors of hydrocarbons and others, including noble substances. For example, in the graph presented the results of calculating the pressure of saturated xenon vapors, carried out for the liquid-vapor equilibrium curve, including the critical point, are presented. The values of vapor density and other data required for calculations were taken from the NIST website [16]. The value of the constant C, which is included in the ratio for the constant of chemical equilibrium K , was determined by normalizing the value δ by $\frac{1}{2}$ at the critical point. The obtained values of the vapor pressure are in full agreement with the experimental values [16], excluding critical region. This is demonstrated by the graph shown in the figure.

$p, \text{ bar}$

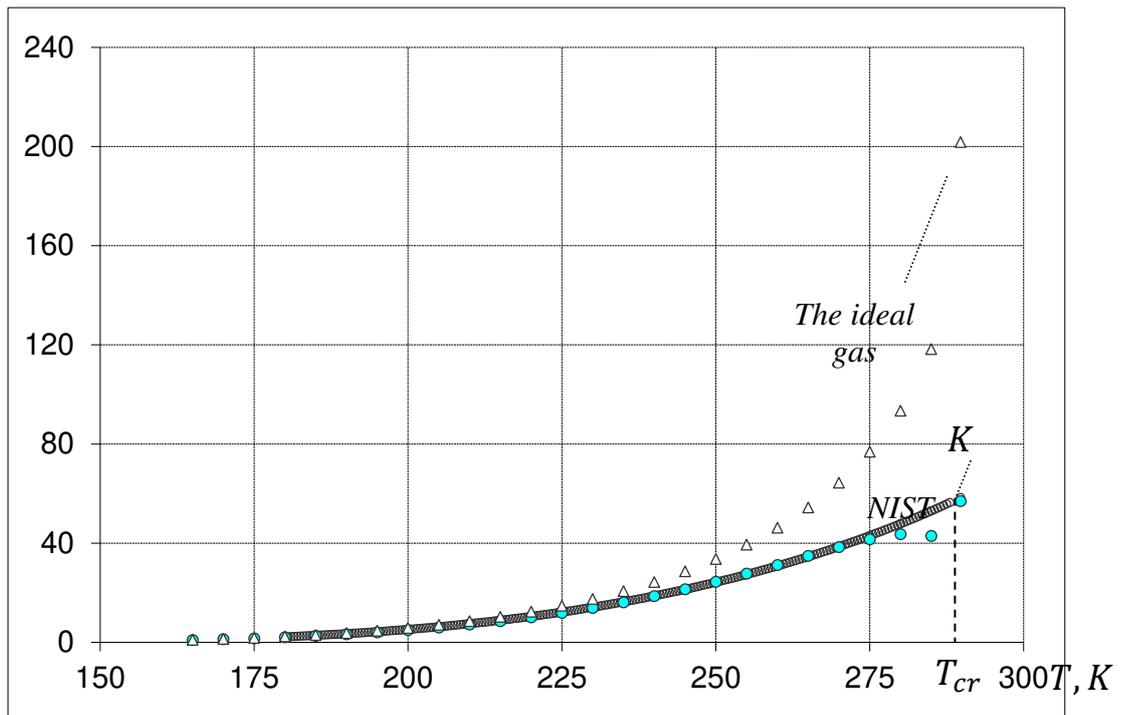


Fig. 1

Full agreement of the pressure values of saturated vapors of xenon and other liquids calculated using equation (3) with experimental data and taking into account the fact that the energy of intermolecular forces is a function of density makes it possible to use equation (1) to study the dependence of pressure on temperature after separation from the equilibrium curve both in liquid and vapor phases, along two isochores at temperatures and pressures exceeding critical values. In this case, to calculate the pressure on the isochores of the liquid and vapor phases, the following relation can be used, obtained by integrating equation (1) with a fixed volume. For the liquid phase, the equation has the form

$$p_l = p_s + B\rho^3 \ln(T/T_s) + \frac{1+2\delta_l}{2} \frac{R}{M} \rho(T - T_s)$$

Here p_s, ρ_s, T_s, B_s is the pressure, density, temperature and constant B on the equilibrium curve, δ_l is the liquid phase dissociation coefficient.

$$B = B_s(1 + \alpha(T - T_s)).$$

$$\alpha = 1,0 \cdot 10^{-3} \text{ K}^{-1}.$$

The nature of the pressure versus temperature dependence of the vapor and liquid n-hexane isochores formed after separation from the equilibrium curve at 400 K is shown in Table 2. The observed high degree of agreement with the data presented by the NIST website was achieved by taking into account the thermal expansion of dimmer complexes of liquid caused by the action of non-covalent recognition binding forces - by Mendeleev's forces.

Table 2

T, K	$\rho = 550.08 \text{ kg/m}^3$			$\rho = 14.046 \text{ kg/m}^3$		
	<i>cal (bar)</i>	[16] (bar)	<i>err, %</i>	[16] (bar)	<i>cal (bar)</i>	<i>err, %</i>
400	4.66	4.66	0.0	4.7	4.7	0.0
410	4.82	4.83	-0.2	43.0	42.4	-1.4
420	4.97	4.99	-0.3	81.3	80.1	-1.5
430	5.13	5.15	-0.4	119.6	117.7	-1.6
440	5.29	5.31	-0.4	157.8	155.3	-1.6
450	5.45	5.47	-0.4	196.0	192.8	-1.6
460	5.60	5.63	-0.4	234.1	230.3	-1.6
470	5.76	5.78	-0.4	272.1	267.9	-1.6
480	5.92	5.94	-0.3	310.0	305.4	-1.5
490	6.08	6.09	-0.2	347.8	342.9	-1.4
500	6.23	6.24	-0.2	385.5	380.5	-1.3
510	6.39	6.40	-0.1	423.1	418.1	-1.2
520	6.55	6.55	0.0	460.5	455.7	-1.1
530	6.71	6.70	0.1	497.8	493.3	-0.9
540	6.86	6.85	0.2	535.0	531.0	-0.8
550	7.02	7.00	0.3	572.1	568.7	-0.6
560	7.18	7.15	0.4	609.0	606.5	-0.4
570	7.34	7.30	0.5	645.8	644.3	-0.2

580	7.49	7.44	0.6	682.4	682.2	0.0
590	7.65	7.59	0.7	718.9	720.1	0.2
600	7.80	7.74	0.8	755.3	758.1	0.4

The results presented here allow us to draw a number of fundamentally important nontrivial conclusions. The first of them is the conclusion that the list of fundamental forces characterizing intermolecular interaction should include non-covalent chemical recognition long-range binding forces - Mendeleev's forces with energy proportional to the critical temperature of the substance. As a second, that it is necessary to take into account the relationship between the constants of dispersion forces B and Mendeleev's forces b with critical parameters, which makes it possible to adequately reproduce the relationship of pVT -parameters with each other in a wide range of parameters of the state of matter. As a final conclusion, the statement about the correctness of Van der Waals's remark about the absence of fundamental differences between liquid and vapor [1] should be considered, and therefore the use of a discrete-continuum model is quite enough for solving pVT -problems.

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