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APPROXIMATE DEPENDENCE BETWEEN THE THERMODYNAMIC
QUANTITIES OF A FLUID ON THE SATURATION LINE

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It is shown in the approximation of additivity of the molecule interaction potential in a fluid that the relationship $uv \approx \text{const}$ is satisfied approximately on the saturation line. The deviation from experiment is 10-30% for the majority of fluids, and 5% for crystalline argon. The mentioned deviation of uv from experiment is explained by multiparticle molecule interaction not being taken into account in fluids, consequently, the role of the multiparticle interaction in condensed media can be assessed according to the magnitude of the deviation from experiment.

The following dependence between the internal heat of evaporation of a substance and its density is set up empirically in [1]

$$u = A \left(\frac{\rho_l - \rho_v}{\rho_k} \right)^n, \quad (1)$$

where ρ_l , ρ_v , ρ_k are, respectively, the fluid and vapor densities on the saturation line and at the critical point, A , n are constants characteristic for this substance. In conformity with the data in [1], the relationship (1) agrees with 2-3% accuracy with experiment for a number of substances with the exception of oxygen, where the exponent n varies in the narrow 1.1-1.2 band and in this sense is universal, which is, apparently, the "echo" law of corresponding states. The purpose of this paper is 1) to give a theoretical foundation of the empirical relationship (1) by starting from modern representations on the nature of fluids, and 2) to show that the investigation of the dependence of the heat of fluid evaporation u on its specific volume v on the saturation line yields valuable information about the non-additive component of the molecule interaction potential in the fluid.

If the fluid properties are described by using the radial distribution function $g(r)$, then the relationship

$$u \sim \frac{1}{v} \int_0^{\infty} \Phi(r) g(r) r^2 dr, \quad (2)$$

will be valid for the energy, where $\Phi(r)$ is the pairwise potential of molecule interaction at a distance r . The main contribution to the integral of the relationship (2) yields a domain of distances $r = r_1$ corresponding to the first maximum of the radial distribution function $g(r)$. Indeed, for $r < r_1$ the function $g(r)$ drops quite rapidly to 0 and becomes a small interaction potential $\Phi(r)$ at the distance r_2 corresponding to the second coordinate sphere of $g(r)$. Consequently, we can write

TABLE 1. Comparison of the Theoretical Dependence (4) with Experiment for Different Fluids on the Saturation Line

\bar{T}	\overline{uv}								
	O ₂	C ₂ H ₄	H ₂ O	CCl ₄	CH ₄	NH ₃	N ₂	Ar	CO ₂
0,351	1,000	—	—	—	—	—	—	—	—
0,368	0,993	1,000	—	—	—	—	—	—	—
0,422	0,969	0,974	1,000	—	—	—	—	—	—
0,455	0,961	0,960	0,976	1,000	—	—	—	—	—
0,475	0,956	0,954	0,964	0,990	1,000	—	—	—	—
0,482	0,954	0,952	0,960	0,986	0,995	1,000	—	—	—
0,500	0,950	0,946	0,951	0,971	0,985	1,000	1,000	—	—
0,556	0,937	0,924	0,925	0,949	0,962	0,996	1,000	1,000	—
0,602	0,929	0,905	0,906	0,927	0,941	0,986	0,998	0,991	—
0,658	0,919	0,877	0,882	0,901	0,920	0,966	0,977	0,970	—
0,712	0,906	0,859	0,857	0,875	0,902	0,940	0,952	0,947	1,000
0,753	0,888	0,826	0,835	0,839	0,883	0,916	0,930	0,918	0,971
0,796	0,862	0,797	0,809	0,794	0,868	0,887	0,904	0,883	0,939
0,849	0,802	0,755	0,783	0,764	0,854	0,836	0,843	0,830	0,894
0,865	0,788	0,735	0,752	0,738	0,841	0,807	0,818	0,811	0,875

TABLE 2. Comparison of the Theoretical Dependence (4) with Experiment for Crystalline Argon

\bar{T}	0	0,186	0,332	0,365	0,431	0,464	0,491	0,518	0,556
\overline{uv}	1,000	0,981	0,977	0,975	0,970	0,967	0,963	0,958	0,950

$$\int_0^{\infty} \Phi(r) g(r) r^2 dr \approx \int_0^{\infty} \Phi(r) g(r) r^2 dr \int_0^{\infty} \delta(r - r_1) dr = \text{const}, \quad (3)$$

where $\delta(r - r_1)$ is the Dirac delta-function. Therefore, the approximate dependence

$$uv \approx \text{const} \quad (4)$$

holds for this substance. The dependences (1) and (4) are actually identical at a sufficient distance from the critical point where $\rho_\ell \gg \rho_v$. A small difference (10-20%) in the exponent is related, as will be shown below, to the fact that multiparticle molecule interactions were not taken into account in a fluid in the derivation of (4). Let us note that relationships of the type (1) and (4) are valid if and only if the derivatives of the thermodynamic characteristics of the substance are continuous, i.e., within the domain of parameters under consideration, there are no triple points or structural phase transitions.

We now examine how much the relationship (4) agrees with experiment. We use the handbook data in [4-6]. Experimental values of the product uv are presented in Table 1 as a function of the referred temperature \bar{T} (measured in fractions of the critical temperature) for different substances on the saturation line above the triple point (u and v are referred to the fluid parameters at the triple point). As is seen from the tables, the maximal deviation of the theoretical dependence (4) from experiment is around 10-30% for the substances considered, where the dependence decreases with temperature. These facts can be explained if the non-additive nature of the intermolecular interaction in fluids is not taken into account. Indeed, its density increases as the fluid temperature diminishes, and therefore, the role of multiparticle interaction should grow, as is also described by known theories [7]. For instance, taking account of three-particle molecule interaction in a fluid results in 15% attenuation of the pairwise dispersion interaction in Ar and N₂, 20% in CH₄, and 33% in CCl₄. The experimental data in Table 1 yield 19% for Ar, 18% for N₂, 16% for CH₄, and 26% for CCl₄. As we see, the deviation of theory from experiment is 17-27% and this result can be considered satisfactory by taking account of the complexity of the phenomena being investigated. Let us note that for $\bar{T} > 0.865$ the nearness of the critical point (the condition $\rho_\ell \gg \rho_v$, ceases to be satisfied) starts to be felt for the substances investigated, consequently, the relationship (4) is not applicable in this domain.

A comparison between the theoretical dependence (4) and experiment [4, 5] is presented in Table 2 for argon in the domain below the triple point. Here the parameters u and v are referred to the substance parameters at absolute zero, where there are no structural phase

transitions in argon in the domain mentioned. The data of Table 2 indicated that the agreement between theory and experiment is even better for crystalline argon than for a fluid and is 5% although the role of multiparticle interactions for the crystals should seemingly be greater since they possess greater density. However, it is well known [7] that for a suitable selection of the pairwise molecule interaction potential parameters crystals are described better in the additivity approximation than are fluids. This is explained by the intrinsic behavior of the multiparticle forces at different distances, which can result in their mutual compensation. Very much weaker dependences $u(T)$ and $v(T)$ for crystals are a result, which indeed assures better agreement between the theoretical relationship (4) and experiment for them.

In conclusion, let us note that the obtained relationship (4) is its own kind of indicator of the role of multiparticle molecule interactions in condensed media and, consequently, an investigation of the dependence of the heat of substance evaporation on its volume yields information about the non-additive component of the substance potential energy.

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THERMAL CONDUCTIVITY OF N-ALKANES AND 1-ALKENES.

UNDISTORTED BY RADIANT ENERGY TRANSPORT.

I. RESULTS OF EXPERIMENTAL STUDY

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Results are presented from an experimental study of molecular thermal conductivity of liquid n-alkanes and 1-alkenes using the hot wire method. Measurements were performed at pressures up to 50 MPa and at temperatures from 300 to 640 K. The new experimental data appear to be low by 10% or more when compared to accepted values.

1. The majority of organic compounds, including n-alkanes and 1-alkenes are among the materials which are semitransparent in the IR range of the spectrum. The thermal conductivity process in such substances is always accompanied by radiant energy transport, as a result of which the thermal flux is determined not by the temperature gradient at a given point, but by the temperature field over the entire system, and Fourier's law is not satisfied. As a consequence the effective thermal conductivity proves to depend not only on the properties of the medium, but also the system geometry.

Current reference data [1, 2] on thermal conductivity of organic liquids is based on experimental material obtained by traditional methods (coaxial cylinders, plane layer, hot

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