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# CALCULATION OF ATOM WORK FUNCTIONS FROM LIQUID INTO GAS WITHIN THE MOLECULAR-KINETIC THEORY

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On the basis of model representations, the analysis of the first equation of the Bogolyubov—Born—Green—Kirkwood—Yvon (BBGKY) chain of equations for the equilibrium two-phase dielectric “liquid — gas” system is performed. The asymptotic values of the monatomic potential in liquid and gas are calculated. The expression for an atom work function from liquid to gas is obtained. Model calculations of the atom work function for many dielectric liquids with application of the Lennard—Jones (LJ) potential and the Barker—Henderson (BH) and Weeks—Chandler—Andersen (WCA) models for a radial distribution function along the saturation line from melting temperatures to critical temperatures are performed. Within the framework of model calculations, the effect of the atom density profile near the liquid-gas interface on the atom work function from liquid into gas is analyzed. For comparison, in the first order of thermodynamic perturbation theory, the estimation of the entropy contribution to the liquid-gas phase transition heat is carried out. The relationship between the atom work function and the liquid stability criterion is discussed.

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## Introduction

Knowledge of properties of two-phase liquid-gas systems is important for many areas of science, engineering, and technology. In spite of achievements in the molecular theory of equilibrium and kinetic properties of liquids and gases [1–6], the problem of constructing a microscopic theory for the properties of two-phase liquid-gas systems remains an actual one. Though the general statement of the problems on two-phase interfaces is known, solving those meets the insufficient knowledge of the density distribution and binary correlations in surface layers. The basic functions to solve the problem are the unary and binary distribution functions for atoms at the two-phase interface [2–6]. From the point of view of mathematics, the main barriers in investigation of the interface properties are in a noncentral character of the binary distribution function for atoms in the surface layer and the insufficient knowledge of possible consequences of the uncoupling of atom distribution functions. Study of the

behavior of the unary and binary distribution functions for atoms in the surface layer in some approximations [2–6] is usually applied to the calculation of surface energy and surface tension at the interface. At that, there are no attempts to apply such results to calculate the thermodynamic characteristics of first-order phase transitions.

Thermodynamic approaches [7–9] do not describe the properties of two-phase systems in terms of the molecular structure of the substance. Some phenomenological approaches to find the fitting formulae are proposed, for instance, to explain the existing experimental material on evaporation heat [8, 9]. As usual, phenomenological approaches are aimed to get the formulae relating the surface properties of a phase interface to volumetric characteristics of the phases. There is no common method to describe different experimental data as a result of those approaches, though it is possible to describe some features of temperature dependences of the thermodynamic characteristics.

The energy characteristics of various activation processes in condensed media related to behavior of separate atoms are determined by the character of self-consistent monatomic potential patterns. The temperature, volumetric, and concentration dependences of activation processes in condensed media are determined by the monatomic potential dependences on respective macroscopic parameters. The character of motive forces for many processes taking place under equilibrium and non-equilibrium conditions and determined by monatomic processes is not enough studied and needs a direct calculation of self-consistent monatomic potentials for different condensed media under different macroscopic conditions.

The aim of this work is to calculate the atom work function from liquid into gas within molecular-kinetic theory for the liberation of atoms from ordinary dielectric liquids to gas with application of statistical thermodynamics and to perform model calculations

of the atom work function in a wide range of temperatures, from the melting point to the critical one, for different dielectric liquids. The main point of the approach elaborated is in the application of monatomic potentials affecting the atoms in a two-phase system. Such an approach differs from available statistical thermodynamical approaches by the explicit account of a monatomic potential at the two-phase interface and its dependence on a specific structure of the interface. This approach makes it possible to study the character of the mechanisms of interface formation and its energy characteristics in more detail.

## 1. Calculation of the Work Function

Let us consider a flat equilibrium liquid-gas interface. The Hamiltonian of a two-phase system of atoms with a central interaction is

$$H = \sum_{i=1}^N \frac{\mathbf{P}_i^2}{2M} + \frac{1}{2} \sum_{i \neq j=1}^N \Phi(\mathbf{R}_i - \mathbf{R}_j), \quad (1)$$

where  $N$  is the number of atoms of the two-phase system;  $\mathbf{P}_i$ ,  $M$  — the momentum and the mass of atoms;  $\Phi(\mathbf{R})$  — potential energy for the atom-atom interaction. The atom distribution functions for the inhomogeneous two-phase system satisfy the BBGKY chain of equations [2–6]. The unary distribution function for atoms in liquid,  $F_1(z)$ , satisfies the equation [2–6]

$$k_B T \frac{\partial}{\partial z} F_1(z) + \frac{1}{v_0} \int d^3 R_1 F_2(z, z_1, \rho^{\parallel}) \times \\ \times \frac{\partial}{\partial z} \Phi(z, z_1, \rho^{\parallel}) = 0, \quad (2)$$

where  $k_B$ ,  $T$  — the Boltzmann constant and temperature;  $v_0$  — volume per atom in liquid;  $F_2(z, z_1, \rho^{\parallel})$  — two-particle distribution function of atoms;  $\rho^{\parallel} \equiv \mathbf{R}^{\parallel} - \mathbf{R}_1^{\parallel}$  — difference of the vector components parallel to the surface; the  $0z$  axis is chosen in the direction normal to the surface. The two-particle atom distribution function satisfies the following equation of the BBGKY chain of equations. On the consideration of Eq. (2) for the two-particle atom distribution function  $F_2(z, z_1, \rho^{\parallel})$ , the following representation is used:

$$F_2(z, z_1, \rho^{\parallel}) = F_1(z) F_1(z_1) g(z, z_1, \rho^{\parallel}), \quad (3)$$

where  $g(z, z_1, \rho^{\parallel})$  is the two-particle correlation function.

In view of (3), we can rewrite Eq. (2) in the integral form as

$$F_1(z) = \exp \left\{ \frac{1}{k_B T v_0} \int_0^{\infty} dR_{12} \frac{\partial \Phi(R_{12})}{\partial R_{12}} \times \right.$$

$$\left. \times \int_{-\infty}^z dz_1 \int_{z_1 - R_{12}}^{z_1 + R_{12}} dz_2 (z_2 - z_1) F_1(z_2) g(z_1, z_2, \rho_{12}^{\parallel}) \right\}. \quad (4)$$

The integral in (4) acts as a self-consistent potential  $U(z)$ , in which a motion of atoms takes place. To estimate asymptotic values of this potential at large distances from the interface, the approximation  $g(z_1, z_2, \rho_{12}^{\parallel}) \approx g_0(R_{12})$ ,  $F_1(z_2) \approx \Theta(-z_2)$  is chosen for the two-particle correlation function and the unary distribution function, where  $g_0(R_{12})$  is the two-particle correlation function in the volume of liquid, and  $\Theta(z)$  — the Heaviside step function. For the “liquid – vacuum” system, the asymptotic values of the potential  $U(z)$  in liquid and in vacuum are equal to

$$\lim_{z \rightarrow -\infty} U(z) = 0, \\ \lim_{z \rightarrow \infty} U(z) = \frac{4\pi}{3v_0} \int_0^{\infty} dR \frac{\partial \Phi}{\partial R} g_0(R) R^3. \quad (5)$$

In the same way, one can obtain the expressions for the asymptotic values of the monatomic potential in the gas phase.

With regard for those approximations, the atom work function from liquid into gas can be given as

$$A_{1-g} = \frac{4\pi}{3} \int_0^{\infty} dR \frac{\partial \Phi(R)}{\partial R} R^3 \left[ \frac{1}{v_0} g_0(R) - \frac{1}{v_1} g_1(R) \right], \quad (6)$$

where  $v_1$ ,  $g_1(R)$  — volume per atom in gas and the two-particle correlation function for the atoms of gas at large distances from the liquid-gas interface.

## 2. Model Calculations

For model calculations and numerical estimation of the work function, we use the LJ potential

$$\Phi(R) = 4\varepsilon \left[ \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^6 \right], \quad (7)$$

with the parameters  $\varepsilon$  and  $\sigma$  taken from [1]. The two-particle correlation functions of atoms in liquid and in gas are simulated with the use of 1) a solid sphere distribution function in the Percus–Yevick approxima-

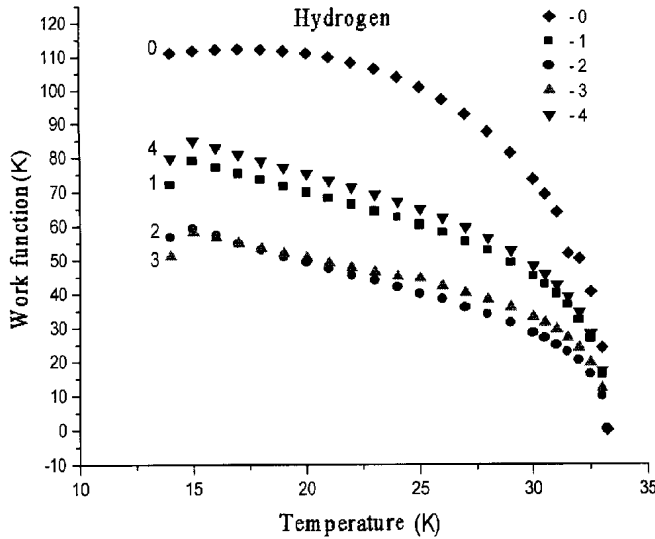


Fig.1. Results of calculations for the atom work function in hydrogen in the BH approximation: 1 -  $\epsilon = 37.00$  K,  $\sigma = 2.928$  Å; 2 -  $\epsilon = 29.2$  K,  $\sigma = 2.87$  Å; 3 -  $\epsilon = 33.3$  K,  $\sigma = 2.968$  Å; 4 -  $\epsilon = 38.00$  K,  $\sigma = 2.915$  Å. 0 - experiment

tion with the solid sphere diameter  $d$  chosen according to BH [4, 5, 10] as

$$d = \int_0^\sigma \left( 1 - \exp\left(-\frac{\Phi(R)}{k_B T}\right) \right) dR, \quad (8)$$

where  $\sigma$  is the first zero in the atom-atom interaction potential  $\Phi(R)$ , 2) atom distribution functions in the WCA approximation [4, 5, 11, 12].

Calculations of the work function are completed for a number of ordinary liquids along the saturation line in the temperature range from the melting temperature to the critical one. For calculations, we take the experimental data on the equilibrium densities of liquid and its saturated vapor [13]. To compare the calculated values for the atom work function to experimental ones, the data on evaporation heat [13] are recalculated to the respective data for a single atom (in Kelvin degrees).

In Fig. 1, the temperature dependences of the atom work function from normal hydrogen with the use of different parameters of the LJ potential are given for the case of the BH approximation being used for the two-particle atom distribution. In Fig.2, one can see analogous results for the atom work function from normal hydrogen for the case of the WCA approximation.

The use of the BH approximation for all elements except for hydrogen leads to negative values of the work function. In Fig. 3, the results of calculations for the

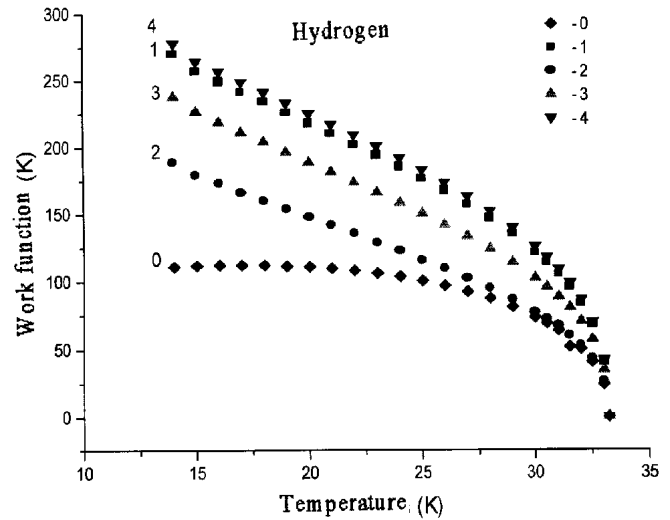


Fig.2. The same as in Fig. 1, in the WCA approximation

work function from argon are shown with the WCA approximation applied (curves 1–3) and with the BH approximation (curve 4). The results of calculations of the work function for krypton and xenon with the WCA approximation being used for the two-particle distribution and different values of the LJ potential parameters are given in Figs. 4 and 5.

### 3. Estimation of the Effect the Density Profile of Atoms on the Work Function

While obtaining the computational formula (6), the atom density profile at the liquid-gas interface is considered to be stepped. One can suppose that this approximation can be good enough for the atom density profile near the melting temperature. The results of numerical computations are obtained for a wide temperature range, from the melting temperature to the critical one. According to (6), the atom work function from liquid to gas is the difference of two components: the atom work function from liquid to vacuum and that from gas to vacuum. A substantial difference in the specific volumes of liquid and gas is observed up to temperatures close to the critical one (Table 1). Accordingly, the two-particle atom distribution functions for liquid and gas differ considerably up to temperatures close to the critical one. Near the critical temperature, it is not possible to neglect the difference of the atom density profile in liquid and in gas from the

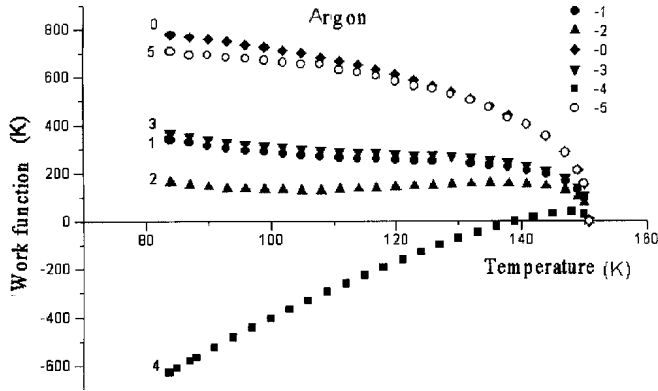


Fig.3. Results of calculations for the atom work function in argon: 1 –  $\varepsilon = 119.8$  K,  $\sigma = 3.405$  Å in the WCA approximation; 2 –  $\varepsilon = 116$  K,  $\sigma = 3.465$  Å in the WCA approximation; 3 –  $\varepsilon = 124$  K,  $\sigma = 3.418$  Å in the WCA approximation; 4 –  $\varepsilon = 38.00$  K,  $\sigma = 2.915$  Å in the BH approximation. 0 – experiment. 5 – calculation of the heat of vaporization with  $\varepsilon = 124$  K and  $\sigma = 3.418$  Å in the WCA approximation

step-like one. Though, because formula (6) contains the difference of two values tending to zero as  $v_0 \rightarrow v_1$ , we can expect the mutual compensation of the inputs from the density profiles in liquid and in gas in the calculation of the atom work function from liquid to gas. Thus, the numerical value of the difference of the inputs due to the atom density profile is to be negligible. In Table 1, the data on specific volumes of liquid and gas and the results of calculations for the liquid-vacuum work function  $A_{l-v}$ , gas-vacuum work function  $A_{g-v}$ , and liquid-gas work function  $A_{l-g}$  for argon along the saturation line are given. As seen from the table, the work functions  $A_{l-v}$  and  $A_{g-v}$  take values of the same order only in the several-degree vicinity of the critical temperature.

We note that there is no common point of view on the character of the atom density profile behavior based on the solution of the first equation of the BBGKY chain near the free liquid-gas interface [6]. The discussion relates to the character of approximations and to the monotonic or oscillating character of the density profile behavior obtained as a result of the solution. To estimate the contribution of a density profile to the work function  $A_{l-g}$ , we use a model two-parameter atom concentration profile in the surface layer in the form

$$\begin{aligned} \rho(z) = & \rho_0[\Theta(-z)(1 - 0.5 \exp(z/M)) + \\ & + 0.5\Theta(z) \exp(-z/M)] + \rho_1[\Theta(z)(1 - 0.5 \exp(-z/L)) + \\ & + 0.5\Theta(-z) \exp(z/L)], \end{aligned} \quad (9)$$

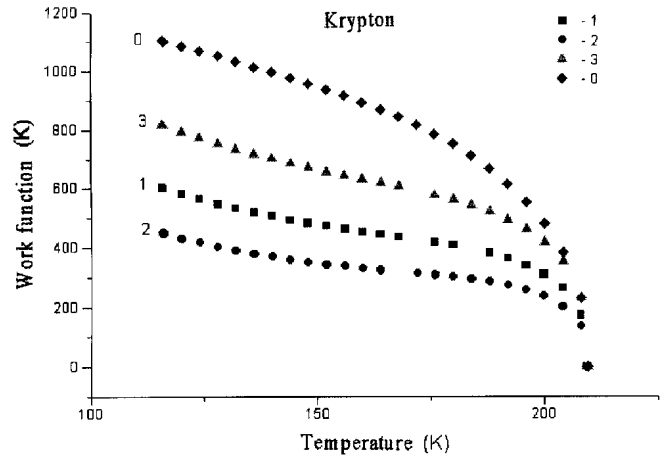


Fig.4. Results of calculations for the atom work function in krypton in the WCA approximation: 1 –  $\varepsilon = 171$  K,  $\sigma = 3.6$  Å; 2 –  $\varepsilon = 158$  K,  $\sigma = 3.597$  Å; 3 –  $\varepsilon = 190$  K,  $\sigma = 3.61$  Å. 0 – experiment

where  $\rho_0 = 1/v_0$ ,  $\rho_1 = 1/v_1$  – atom concentrations in liquid and in gas, respectively;  $M, L$  – parameters with dimension of length which characterize the decrease rate of the atom density from the value in the volume of a homogeneous liquid to the value corresponding to a

**Table 1.** Results of calculations for values  $A_{l-v}$ ,  $A_{g-v}$ , and  $A_{l-g}$  (6) in argon in the WCA approximation for the potential parameters  $\varepsilon = 124$  K and  $\sigma = 3.418$  Å

T, K	$V_0$ (dm <sup>3</sup> /kg)	$V_1$ (dm <sup>3</sup> /kg)	$A_{l-v}$ , K	$A_{g-v}$ , K	$A_{l-g}$ , K
83.78	0.7068	246.9	367.25	3.77	363.48
84	0.7075	241.2	366.33	3.85	362.48
87	0.7171	178.0	354.56	5.18	349.38
90	0.7270	134.2	344.38	6.82	337.56
93	0.7372	103.0	335.59	8.81	326.78
96	0.7480	80.46	328.94	11.18	317.76
99	0.7593	63.77	323.75	14.00	309.75
102	0.7713	51.21	320.28	17.28	303.00
105	0.7838	41.60	317.86	21.10	296.76
108	0.7970	34.14	316.52	25.49	291.03
111	0.8116	28.27	317.57	30.52	287.05
114	0.8270	23.59	319.15	36.25	282.90
117	0.8440	19.81	322.44	42.78	279.66
120	0.8624	16.73	326.54	50.19	276.35
123	0.8828	14.19	331.83	58.60	273.23
126	0.9053	12.07	337.76	68.19	269.57
129	0.9306	10.29	344.37	79.13	265.24
132	0.9595	8.776	351.59	91.70	259.89
135	0.9929	7.473	359.04	106.29	252.75
138	1.031	6.339	365.66	123.46	242.20
141	1.080	5.336	373.07	144.11	228.96
144	1.145	4.428	379.64	170.17	209.47
147	1.245	3.547	383.86	206.47	177.39
149	1.358	2.907	381.71	244.00	137.71
150	1.464	2.525	375.56	272.98	102.58
150.86	1.867	1.867	336.76	336.76	0

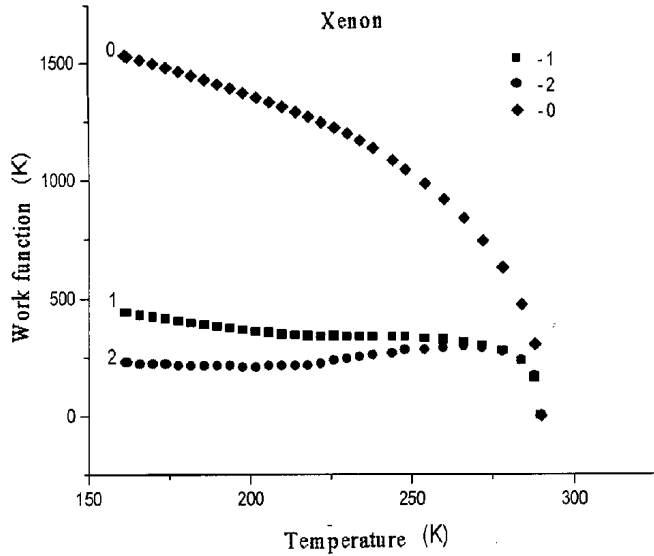


Fig.5. Results of calculations for the atom work function in xenon in the WCA approximation: 1 –  $\epsilon = 217$  K and  $\sigma = 3.963$  Å; 2 –  $\epsilon = 229$  K and  $\sigma = 4.055$  Å. 0 – experiment

homogeneous gas. The two-parameter form of (9) is related to the fact that the character of a decrease in the atom concentration from the value in the volume of liquid to the value in gas can be “nonsymmetric”. At large distances from the surface, we have

$$\lim_{z \rightarrow -\infty} \rho(z) = \rho_0, \quad \lim_{z \rightarrow \infty} \rho(z) = \rho_1. \quad (10)$$

By using (9) to calculate the asymptotic form of a monatomic potential in liquid and in gas, we get a contribution to the work function of atoms from liquid to gas,

$$\Delta A_{1-g} = 4\pi \int_0^\infty dR \frac{\partial \Phi(R)}{\partial R} \times \left[ \frac{1}{v_0} g_0(R) M^3 - \frac{1}{v_1} g_1(R) L^3 \right], \quad (11)$$

additionally to (6). As a partial case, (11) includes the result for a one-parameter profile with  $L = M$ . Let us point out that result (11) corresponds to the model choice (9) and cannot be universal, though it can be used for estimations. The parameters of the density profile are to be found either by solving the first equation of the BBGKY chain or within variation procedures for the free energy of an inhomogeneous two-phase system.

From (11), it is easily seen that, as temperature approaches the critical one, the difference in the integrand tends to zero because  $v_0 \rightarrow v_1$ ,  $g_0(R) \rightarrow$

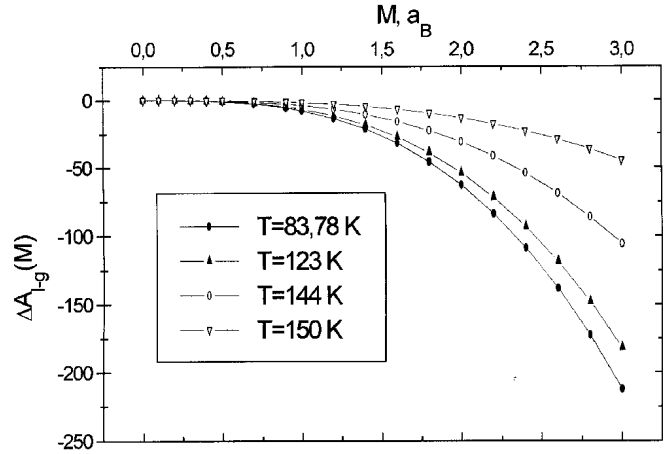


Fig.6. Results of calculations for the dependence  $\Delta A_{1-g}(M)$  in argon with the potential parameters  $\epsilon = 124$  K and  $\sigma = 3.418$  Å in the WCA approximation

$g_1(R)$ , the atom concentration profile becomes more and more “symmetric”, and  $L \approx M$ . This means that the use of (6) near the critical temperature becomes possible.

We note that, for the “symmetric” density profile with same parameters  $L = M$ , numerical computations indicate the negative sign of the contribution, whose absolute value increases by the cube law. In Fig. 6, the results of calculations of  $\Delta A_{1-g}(M)$  for argon in the WCA approximation are shown at different temperatures with the use of the “symmetric” density profile with  $L = M$ .

The calculation of corrections to the atom work function with regard for the density profile can be executed only after solving the problem on determining the density profile proper.

#### 4. Comparative Calculation of Evaporation Heat within Statistic Thermodynamics

During the last decades, a considerable progress is achieved in the description of the structure of liquids and gases [5, 10–12, 15] within statistic thermodynamics, due to the use of the thermodynamic perturbation theory. The best version of thermodynamic perturbation theory was proposed in [11, 12]. The results of calculations of the thermodynamic properties of liquids and gases in the WCA approach coincide with a high level of accuracy with the molecular–dynamical results. This is due to the successful choice of the so-

called “reference system” of solid spheres, and the good convergence of the series in thermodynamic perturbation theory. For most equilibrium properties of liquids, it is sufficient to use the first order of perturbation theory [11, 12].

Within statistical thermodynamics, evaporation heat is related to the entropies of phases being in equilibrium [7],

$$q = T (s_1 - s_0), \quad (12)$$

where  $s_1, s_0$  are the phase entropies.

In the calculation of the phase transition heat, one must take into account that the entropy is not the average value of some additive dynamical value, cannot be expressed through the low-order correlation functions [1, 2, 14], but is directly expressed through the highest-order correlation function of a statistical system [2]. In indirect way, the entropy can be found if the temperature dependence of the atom radial distribution function is known [2, 15]. The derivative of the atom radial distribution function for liquid with respect to temperature is expressed through the high-order correlation functions [15].

To calculate the heat of the liquid-gas transition, we apply the WCA approach. In the first order of thermodynamic perturbation theory, the free energy of liquid or gas per particle can be written [11, 12] as

$$\frac{F}{N} = \frac{F_{id}}{N} + k_B T \frac{4\eta - 3\eta^2}{(1 - \eta)^2} + \frac{2\pi}{v} \int_0^\infty dr r^2 g_0(r) \varphi_1(r), \quad (13)$$

where

$$\frac{F_{id}}{N} = -k_B T \left\{ 1 + \ln \left[ \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} v \right] \right\} \quad (14)$$

is the free energy of perfect gas;  $v$  — volume per particle;  $\eta = \pi d_{WCA}^3 / 6v$  — packing parameter for an auxiliary system of solid spheres;  $d_{WCA}$  — solid sphere diameter determined by the WCA procedure;  $g_0(r)$  — radial distribution function for particles, according to WCA;

$$\varphi_1(r) = \Phi(r_{min}) \Theta(r_{min} - r) + \Phi(r) \Theta(r - r_{min}) \quad (15)$$

is the perturbation potential in the WCA approach; and  $r_{min}$  — point of the potential minimum. The second term in (13) takes account of the non-point nature of solid spheres, and the third one takes account of the first order of thermodynamic perturbation theory.

Entropies of liquid and gas are determined numerically, after the free energies of liquid and gas being calculated, by the formula

$$S = - \left( \frac{\partial F}{\partial T} \right)_V. \quad (16)$$

The results of calculations of the free energy, entropies for liquid and gas, and evaporation heat for argon in the temperature range from the melting point to the critical one are given in Table 2. Those for the heat of vaporization are also given in Fig. 3 (curve 5).

As seen from Table 2, the calculated results for the evaporation heat as a function of temperature in the first order of thermodynamic perturbation theory are lower than the experimental data by 10% at temperatures close to the melting temperature, and are close to the experimental data at temperatures about the critical temperature. The increase in the accuracy of calculations with temperature is explained by a decrease of the difference in specific volumes of liquid and gas. The comparative calculation of the evaporation heat allows us to conclude on the need in parallel calculations of energy characteristics, in the case being allowed by the problem, within the method of correlation functions with the use of single-particle potentials and within the framework of statistical thermodynamics as well. Such parallel calculations will make it possible to correct the model calculations of single-particle energy characteristics of condensed systems.

## 5. Relation between the Atom Work Function and the Liquid Stability Criterion

The calculated asymptotic values (5) of a monatomic potential enable a novel view on the stability criterion for liquid. A classification of the limiting stability points of a homogeneous phase by the characteristic of their isolation or unisolation is given in [2]. The condition for that a homogeneous phase loses its stability at the so-called limiting point of the first type (by the Fisher classification) is written [2] as

$$\frac{4\pi}{3v_0 k_B T} \int_0^\infty \Phi'(r) g_0(r) r^3 dr = 1, \quad (17)$$

where the prime at the atom interaction potential denotes the derivative. From the comparison of equality (17) to asymptotic values of the monatomic potential (5), one can see that condition (17) corresponds to the requirement of equality of the atom work function from liquid to vacuum and the average kinetic energy of atoms. With this equality being realized, the liquid loses its stability, its atoms can leave the liquid due to their

**Table 2. Results of calculations for the free energy and entropy of liquid and gas, and evaporation heat in argon in the WCA approximation for the potential parameters  $\epsilon = 124$  K and  $\sigma = 3.418$  Å**

$T, \text{K}$	$F_0/Nk_B, (\text{K/atom})$	$F_1/Nk_B, (\text{K/atom})$	$S_0/Nk_B, (1/\text{atom})$	$S_1/Nk_B, (1/\text{atom})$	$q/Nk_B, (\text{K/atom})$ calc.	$q/Nk_B, (\text{K/atom})$ exp. [13]
83.78	-685.41	-1286.38	8.41	16.84	705.83	777.32
84	-687.61	-1288.15	8.42	16.82	705.41	776.84
87	-717.79	-1312.70	8.58	16.56	694.79	767.23
90	-748.59	-1337.60	8.63	16.33	693.36	758.58
93	-780.01	-1362.74	8.77	16.11	682.66	748.01
96	-812.22	-1388.25	8.87	15.91	675.71	736.48
99	-845.19	-1414.00	8.94	15.72	671.00	724.95
102	-879.04	-1439.99	9.07	15.54	659.60	711.50
105	-913.69	-1466.18	9.15	15.37	652.32	697.09
108	-949.24	-1492.54	9.17	15.22	652.06	682.68
111	-986.05	-1519.04	9.38	15.06	629.68	666.82
114	-1023.86	-1545.65	9.50	14.91	616.64	649.53
117	-1063.05	-1572.30	9.62	14.76	602.16	630.79
120	-1103.54	-1598.99	9.79	14.63	581.73	610.13
123	-1145.64	-1625.66	9.93	14.50	561.23	588.03
126	-1189.43	-1652.22	9.98	14.34	549.11	564.01
129	-1235.21	-1678.69	10.13	14.20	525.30	537.11
132	-1283.39	-1704.96	10.27	14.05	499.78	508.28
135	-1334.41	-1730.94	10.42	13.90	470.64	475.14
138	-1385.50	-1756.54	10.70	13.79	425.43	439.10
141	-1448.18	-1781.62	10.75	13.57	397.52	397.31
144	-1515.37	-1805.93	10.95	13.37	347.60	349.27
147	-1597.38	-1828.62	11.21	13.10	278.22	282.01
149	-1670.59	-1841.95	11.45	12.84	207.65	209.46
150	-1723.89	-1847.68	11.62	12.63	151.32	149.41
150.86	-1850.10	-1850.10	12.14	12.14	0	0

thermal energy. This condition can be achieved through extension of liquid. We note that equality (17) in [2] was obtained as the result of analysis of the asymptotic behavior of the two-particle distribution function for atoms of a homogeneous liquid. Conditions for equality (17) to be valid arise at an abrupt decrease of the pressure in liquid to the pressure of saturated vapor at a given temperature, which corresponds to the formation of cavitation bubbles in liquid.

## 6. Discussion

The developed microscopic theory for the atom work function from liquid into gas is not ultimate. The following improvement should concern with the consideration of both a noncentral character of the binary distribution function for atoms and the atom density profile in the surface layer within a self-consistent procedure.

Model calculations indicate a rather strong dependence of the results of calculations for the work function on a choice of parameters of the LJ potential. Among the parameters of the potential, one can find those being better from the viewpoint of correspondence with experimental data. This means a high sensitivity of

the atom work function to parameters of the interaction potential. No parameter fitting has been performed, though it is possible to pose the problem on the parameter choice optimization to achieve the best accordance between the results of calculations and experiments. We note that the use of the effective LJ potential with central symmetry to simulate molecular systems can be insufficient. The contribution from the noncentral component of the interaction potential for diatomic molecules can be noticeable.

The obtained relation (6) takes the equal account of liquid and gas. In this case, the account of two-particle atom-atom correlations is of great importance. The WCA approximation shows a more accurate consideration of “softness” of the interaction potential of atoms comparing to the BH approximation. The binary distribution function in the WCA approximation reaches its maximal value near the potential minimum, and this fact is critical for the calculations of a work function. The high sensitivity of the atom work function calculations to the interatomic potential parameters and the shape of the binary distribution function can be used to choose the best models for potentials and respective binary distribution functions of atoms.

The approach developed in this work is mainly based on the method of correlation functions and makes it possible to account the dynamical and multiparticle mechanisms of formation of equilibrium characteristics in detail. Upon the description of equilibrium properties of homogeneous phases, the method of correlation functions is equivalent to the general description of the system in terms of Gibbs ensembles [1, 2, 4, 5].

The results obtained make it possible to give also a simple physical interpretation to the stability criterion for liquid. The equality of the atom work function from liquid into vacuum and the energy of thermal motion means the absolute instability of the system that has to disintegrate into separate atoms. The study of the liquid instability lines in phase diagrams will be the subject of another work.

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#### РОЗРАХУНОК РОБОТИ ВИХОДУ АТОМІВ З РІДИНИ В ГАЗ В РАМКАХ МОЛЕКУЛЯРНО-КІНЕТИЧНОЇ ТЕОРІЇ

Я. С. Кайм

Резюме

На основі модельних уявлень виконано аналіз першого рівняння ланцюжка рівнянь Боголюбова—Борна—Гріна—Кірквуда—Івона для рівноважної двофазної системи діелектрична рідина—газ. Розраховано асимптотичні значення одноатомного потенціалу в рідині та газі. Отримано вираз для роботи виходу атомів з рідини в газ. Виконано модельні розрахунки роботи виходу атомів для ряду діелектричних рідин з використанням потенціалу Леннарда—Джонса та радіальної функції розподілу в моделях Баркера—Хендерсона та Уїкса—Чандлера—Андерсона вздовж лінії насичення від температур плавлення до критичних температур. В рамках модельного розрахунку проаналізовано вплив профілю щільності атомів поблизу межі поділу рідина—газ на роботу виходу атомів з рідини в газ. Для порівняння у першому порядку термодинамічної теорії збурень наведено оцінку ентропійного внеску до теплоти фазового переходу рідина—газ. Обговорено зв'язок роботи виходу атомів та критерію стійкості рідини.