

Volodymyr Kislenko, Liliya Oliynyk and Valentyn Serheyev

SOME RELATIONS BETWEEN DENSITY AND VISCOSITY OF LIQUID, SATURATION VAPOR PRESSURE, AND SURFACE TENSION

*Lviv National Polytechnic University
12, Bandera str., 79013 Lviv, Ukraine*

Received: July 15, 2010 / Revised: November 23, 2010 / Accepted: March 12, 2011

© Kislenko V., Oliynyk L., Serheyev V., 2011

Abstract. Kinetic scheme of formation of molecule fluctuations in gas and liquid phases is proposed. Distribution of molecule number in molecule fluctuations on the number of molecule fluctuations in the unit volume of the system is calculated. Correlation equations for surface tension, liquid viscosity and molecule number in molecule fluctuations in gas and liquid phases as well as correlation equation between saturation vapour pressure, liquid density and temperature are proposed.

Keywords: correlation equation, liquid, saturation vapour pressure, surface tension, viscosity.

1. Introduction

Investigation of equilibrium between liquid and vapor for pure substances is interesting to understand the dynamics and structure of molecule fluctuations in liquid and gas phases. It enables theoretical description of the appearance of interface between gas and liquid and of some properties of liquids such as viscosity. Models of molecule behavior in gas and liquid are described by multy-Yukawa hard-sphere fluid [1], replica Ornstein-Zernike equations for polydisperse quenched-annealed fluids [2], fractional dynamics from the ordinary Langevin equation [3], subordinated Brownian motion and its fractional Fokker-Planck equation [4] and local and cluster critical dynamics of 3D random-site Osong model [5]. These models show formation of fluctuations of molecule density in gas and liquid phases and they can explain the changes in liquid viscosity at difference temperatures. Unfortunately these theories need many correction coefficients for numerical calculations of the values of experimentally obtained parameters. There are well-known empirical equations describing dependences between surface tension and liquid density [6]:

$$P = \frac{M}{(r_1 - r_g) \cdot S^{1/4}}$$

where P is parahor, ρ_l and ρ_g are densities of liquid and gas, σ is surface tension. Parachor of molecule can be calculated as the sum of productions of the constants of different atoms on atom numbers in this molecule:

$$P = ax + by + cz + \dots$$

where a , b , and c are constants describing atom contribution in parahor, x , y , z are the number of atoms in molecule.

The aim of this article is to create a kinetic model of formation of molecule fluctuations in liquid and gas phases and to obtain equations binding saturation vapor pressure, liquid density, liquid viscosity, and surface tension between gas and liquid phases.

2. Results and Discussion

Formation of interface between gas and liquid phases takes place under the critical point for simple substances. However optical density of the system in this point is much greater than optical density of liquid or gas. It is evidently bound with the formation of stable microdrops of liquid or stable fog formation. Therefore, there is no visible interface between gas and liquid at critical point, but evidently there is an interface between liquid microdrops of liquid and gas. Some difference between the density of liquid microdrops and the density of gas found from the saturation vapor pressure at the critical point can be expected. Molar volume of real gases is less than ideal gas that can be explained by formation of intermediate molecule fluctuation where molecules are bound by hydrogen, Van-der-Waals or other binds. Average molecule number in these fluctuations is equal evidently to the ratio of molar volume of real gas to molar volume of ideal gas:

$$N_{gas} = \frac{V_M P}{RT} \quad (1)$$

where R is absolute gas constant, T is temperature, V_M is molar volume if ideal gas.

Liquid forms microdrops with molecule number greater than in fluctuations in gas phase taking into account

that in critical point gas and liquid are present in one phase. Number of molecules in microdrops is greater than in gas phase, so in the first approximation average molecule number in drop can be estimated as the ratio of molar density of the system to the molar volume of ideal gas:

$$N_{liq} = \frac{V_M \rho}{M} \quad (2)$$

where ρ is the density of the system in the critical point, M is the molecular mass of a simple substance.

Fig. 1 shows that the dependence between the molecule number in molecule fluctuations in gas and liquid phases and temperature are close to linear for the most of simple substances. Correlation coefficients of straight lines are 0.72 and 0.71 for gas and liquid correspondingly. The ratio of average molecule number in liquid microdrops and in molecule fluctuations in gas phase is evidently close to constant for the most of simple substances (Fig. 2). This dependence can be described by straight line with correlation coefficient 0.919. The tangent of the slope angle of straight line equals to 3.05.

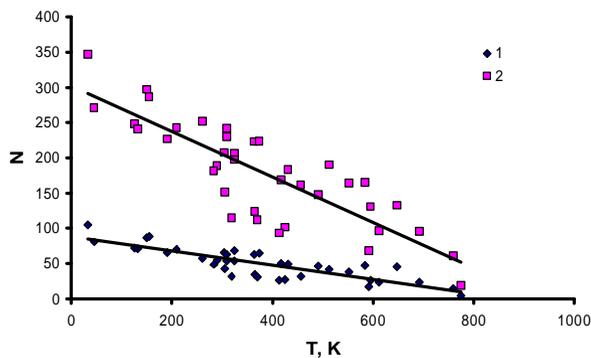


Fig. 1. Dependence of the molecule number in molecule fluctuations in gas (1) and liquid (2) phases on temperature

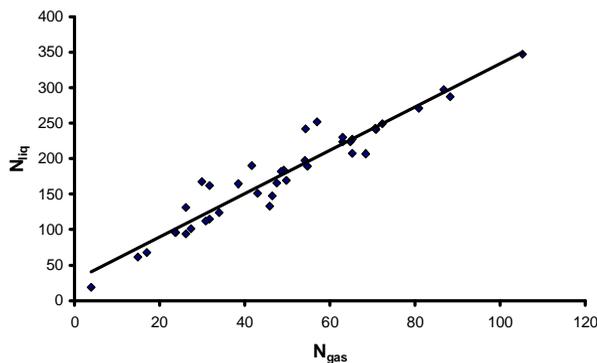


Fig. 2. Relationship between molecule number in fluctuation in gas phase and liquid phase

Therefore the mechanism of formation of molecule fluctuations in gas and liquid phases is evidently identical and can be described by equations:

$$2F_1 = F_2 \quad (3)$$

$$F_1 + F_2 = F_3 \quad (4)$$

$$2F_2 = F_4 \quad (5)$$

$$F_1 + F_3 = F_4 \quad (6)$$

$$F_i + F_j = F_{i+j} \quad (7)$$

where F_i is the molecule fluctuation containing i molecules.

The number of molecule fluctuations in the unite volume of the system in equilibrium state can be described by the system of equations:

$$KN_1 \sum_{k=1}^n N_k = \sum_{k=2}^n N_k \quad (8)$$

$$KN_2 \sum_{k=1}^n N_k = \sum_{k=3}^n N_k \quad (9)$$

$$KN_3 \sum_{k=1}^n N_k = \sum_{k=4}^n N_k \quad (10)$$

$$KN_i \sum_{k=1}^n N_k = \sum_{k=2}^n N_k \quad (11)$$

where K is equilibrium constant.

The overall number of molecule fluctuations in the unit volume in the system equals to:

$$N = \sum_{k=1}^n N_k \quad (12)$$

The number of molecules in the unit volume of system equals to:

$$N_0 = \sum_{k=1}^n kN_k \quad N_0 = \sum kN_k \quad (13)$$

The number of fluctuations containing k molecules in the unit volume of the system can be obtained from Eqs. (8)–(13).

$$N_1 = \frac{N}{KN + 1} \quad (14)$$

$$N_2 = \frac{KN^2}{(KN + 1)^2} \quad (15)$$

$$N_n = \frac{K^{n-1} N^n}{(KN + 1)^n} \quad (16)$$

The equation of the average number of molecules in the fluctuation was obtained taking into account Eqs. (12)–(16).

$$\frac{N_0}{N} = \frac{1 + 2[KN/(KN + 1)] + 3[KN/(KN + 1)]^2}{KN + 1} + \frac{(n+1)[KN/(KN + 1)]^n}{KN + 1} \quad (17)$$

If the formation of molecule fluctuations takes place, the value of $K > 0$ and $[KN/(KN + 1)] < 1$. In this case the

raw (18) is limited and the numerical calculation of Eq. (17) transforms into Eq. (19).

$$1 + 2[KN / (KN + 1)] + 3[KN / (KN + 1)]^2 + \dots + (n + 1)[KN / (KN + 1)]^n \quad (18)$$

$$\frac{N_0}{N} = 1 + KN \quad (19)$$

The distribution of the number of molecule fluctuation on the number of molecules in one fluctuation in this case can be described by Eq. (20):

$$P(k) = \frac{k(a - 1)^{(k-1)}}{a^k} \quad (20)$$

where $\alpha = N_0/N$.

Fig. 3 shows the distribution of the number of molecule fluctuations on the number of molecules in one fluctuation in gas and liquid phases at critical temperature (a) and temperature lower than critical (b). These two curves cross in all cases and there is a common area for liquid and gas curves. Its surface area decreases when the temperature of the system decreases. Therefore interface between gas and liquid phases appears at definite ratio of average number of molecules in fluctuations in gas and liquid phases. Surface tension between these phases increases when the difference between the number of fluctuations in liquid and gas phases out of common area between two distribution curves increases. The absciss of cross point of these two curves can be found from Eq. (21):

$$k_c = \ln[(N_{0gas} / N_{gas} - 1) / (N_{0liq} / N_{liq} - 1)] / \ln[N_{0gas} / N_{gas} - 1] \times \dots \times (N_{0log} / N_{lig}) / [(N_{0gas} / N_{gas}) (N_{0liq} / N_{lig} - 1)] \quad (21)$$

where N_{0gas} and N_{gas} are the numbers of molecules and molecule fluctuations in gas, N_{0liq} and N_{liq} are the numbers of molecules and molecule fluctuations in liquid, respectively.

The number of fluctuations in the unit volume of liquid phase common with the number of fluctuations in the unit volume of liquid phase can be calculated by integration of the area under liquid curve (Fig. 3) till the value of k_c .

$$N_{cg} = N_g \int_0^{k_c} k(N_{0liq} / N_{lig} - 1)^{(k-1)} / (N_{0log} / N_{lig})^k \quad (22)$$

where N_g is the number of fluctuations in the unit volume of gas phase.

The number of fluctuations in the unit volume of liquid phase common with the number of fluctuations in the unit volume of gas phase can be calculated by integration of the area under gas curve (Fig. 3) from the value of k_c .

$$N_{cg} = N_l \int_{k_c}^{\infty} k(N_{0gas} / N_{gas} - 1)^{(k-1)} / (N_{0gas} / N_{gas})^k \quad (23)$$

where N_l is the number of fluctuations in the unit volume of liquid phase.

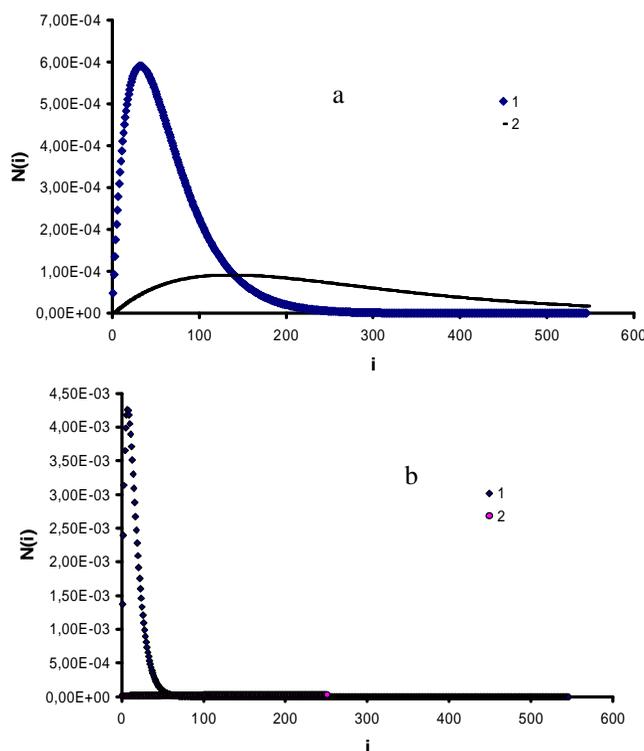


Fig. 3. Distribution of the fluctuation number in the unit volume on molecule number in gas (1) and liquid (2) for NH_3 at critical temperature of 405.4 K (a) and 323 K (b)

Dependence of surface tension on the difference between the number of fluctuations in the unit volume of liquid out of common area and gas phases out of common area can be described by Eq. (24):

$$\ln S = A_s + B_s \ln[(N_l - N_{c1}) - (N_g - N_{cg})] \quad (24)$$

where A_s and B_s are constants for individual compounds.

Fig. 4 shows that experimental data on the surface tension at different temperatures for simple compounds lie on straight line. Values of correlation coefficients and constants are presented in Table 1.

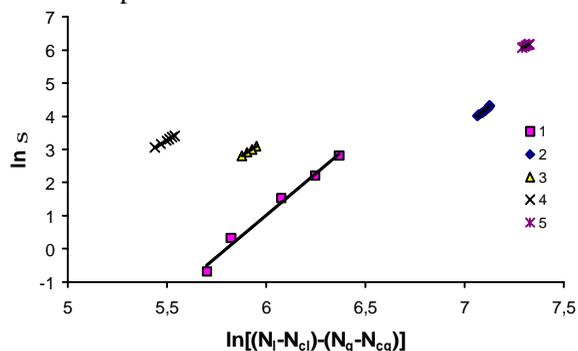


Fig. 4. Dependence of surface tension between liquid and saturated vapor on the difference between the number of fluctuations in the unit volume of liquid and the number of fluctuations in the unit volume of gas phases out of common area for CO_2 (1), H_2O (2), ethanol (3), benzene (4), and Hg (5)

Table 1
Correlation coefficients and values of constants
in Eqs. (24) and (25)

Substance	R	A_s	B_s	R	A_n	B_n
Hg	1	2.84	-14.62	0.995	0.358	-3.92
CO ₂	0.987	5.03	-29.18	-	-	-
H ₂ O	0.976	4.98	-31.19	0.997	0.338	-2.82
Benzene	1	3.60	-16.54	0.986	0.563	-8.31
Ethanol	1	3.81	-19.61	0.740	0.027	-0.28

Liquid moving can be described as a displacement of liquid fluctuation in gas phase taking into account that the part of liquid molecule fluctuations contains the number of molecules equal to that in gas phase. Therefore liquid viscosity may be proportional to the division of the number of fluctuations in the unit volume of liquid out of common area on the number of fluctuations in the unit volume of gas phases out of common area and can be described by equation:

$$\ln h = A_n + B_n \ln[(N_l - N_{cl}) / (N_g - N_{cg})] \quad (25)$$

where A_n and B_n are constants for individual compounds.

Dependence of the viscosity at different temperatures on the division of the number of fluctuations in the unit volume of liquid out of common area on the number of fluctuations in the unit volume of gas phases out of common area are described by the straight lines (Fig. 5). The values of correlation coefficients and the constants are presented in Table 1.

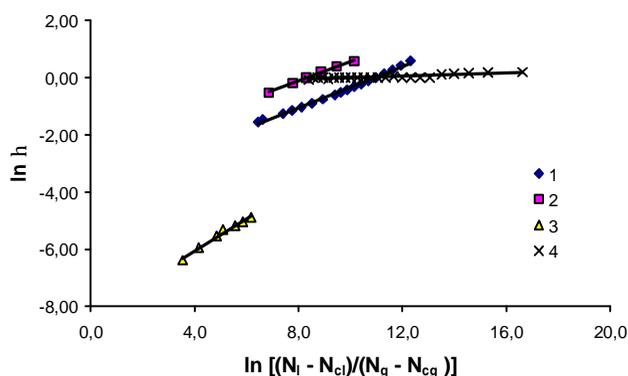


Fig. 5. Dependence of liquid viscosity on the division of the number of fluctuations in the unit volume of liquid on the number of fluctuations in the unit volume of gas phases out of common area for H₂O (1), ethanol (2), benzene (3), and Hg (4)

Destruction of one molecule fluctuation of liquid phase leads to the formation of several numbers of molecule fluctuations of gas phase and this process needs some quantity of energy. Therefore dependence between the value of liquid phase density and the saturated vapor pressure can be described by equation:

$$\ln(P) - \alpha * \ln(r) = A_p + B_p / T \quad (26)$$

where P is saturation vapor pressure over the liquid of substance, α is the constant describing the numbers of molecule fluctuations of gas phase formed from one molecule fluctuation of liquid phase, ρ is the density of liquid phase, A_p and B_p are temperature coefficients, T is the temperature.

Fig. 6 shows that experimental data lie on the straight lines in coordinates of Eq. (23). There is a break on the straight line for system containing CO₂ in the point of replacement of liquid carbon dioxide into solid state. Values of correlation coefficients of straight lines and constants are presented in Table 2.

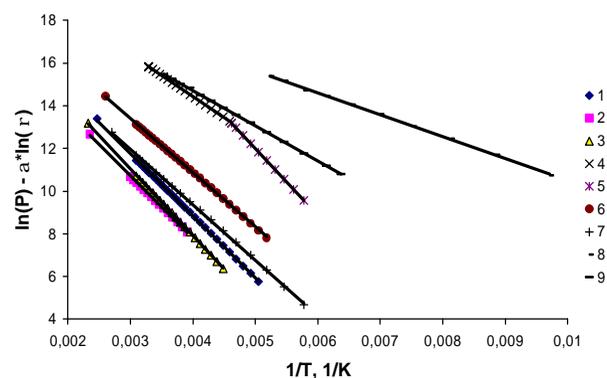


Fig. 6. Relationship between saturation vapor pressure, liquid density and temperature in coordinates of Eq. (23) for NH₃ (1), *n*-butane (2), SO₂ (3), CO₂ liquid (4), CO₂ solid (5), CF₂Cl₂ (6), CHF₂Cl (7), CH₄ (8) and ethylene (9)

Table 2
Correlation coefficients and values
of constants in Eq. (26)

Substance	R	α	A_p	B_p
NH ₃	1	0.3	-2904	20.5
SO ₂	1	0.3	-3128	20.4
CO ₂ (liquid)	1	0	-1983	22.4
CO ₂ (solid)	1	0	-3113	27.6
CH ₄	0.999	0	-1025	20.7
Ethylene	1	0	-1653	21.3
<i>n</i> -Butane	0.999	0.3	-2903	19.4
CF ₂ Cl ₂	1	0.1	-2536	21.0
CHF ₂ Cl	0.999	0.3	-2594	19.7

3. Conclusions

The proposed kinetic scheme of formation of molecule fluctuations in gas and liquid phases allows to obtain distribution of molecule number in molecule fluctuations on the number of molecule fluctuations in the unit volume of the system, correlation equations for surface

tension, liquid viscosity and molecule number in molecule fluctuations in gas and liquid phases as well as correlation equation between saturation vapor pressure, liquid density and temperature.

References

- [1] Kalyuzhnyi Y. and Hlushak S.: J. Chem. Phys., 2006, **125**, 3450.
- [2] Sokolowski S., Patrykiewicz A., Ilnytskyi J. and Pizio O.: J. Phys. Chem. B, 1999, **103**, 868.
- [3] Stanislavski A.: Phys. Rev. E., 2003, **67**, 1.
- [4] Stanislavski A.: Phys. Scripta, 2003, **67**, 265.
- [5] Ivaneyko D., Ilnytskyi J., Berche B. and Holowatch Y.: Physika A, 2006, **370**, 163.
- [6] Knynanz I. (Ed.): Khimicheskaya Encyclopedia, V. 3. Sovetskaya encyclopedia, Moskwa 1964.

ДЕЯКІ ЗАЛЕЖНОСТІ МІЖ ГУСТИНОЮ І В'ЯЗКІСТЮ РІДИНИ, ТИСКОМ НАСИЧЕНОЇ ПАРИ І ПОВЕРХНЕВИМ НАТЯГОМ

Анотація. Запропонована кінетична схема утворення флуктуацій молекул у газах та рідинах. Розрахований розподіл числа молекул у молекулярній флуктуації від числа флуктуацій в одиниці об'єму системи. Запропоновані кореляційні рівняння для поверхневого натягу, в'язкості рідини від числа молекул в молекулярній флуктуації в газовій і рідкій фазах, як і кореляційне рівняння між тиском насиченої пари, густиною рідини і температурою.

Ключові слова: кореляційне рівняння, рідина, тиск насиченої пари, поверхневий натяг, в'язкість.