INVESTIGATIONS OF THE STEEPNESS OF A REPULSIVE POTENTIAL IN ACCORDANCE WITH THE EQUATION OF STATE AND LIGHT-SCATTERING SPECTRA

V.YU. BARDIK, K.S. SHAKUN[1]

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Taras Shevchenko Kyiv National University
(6, Academician Glushkov Prosp., Kyiv 03022, Ukraine; e-mail: vital@univ.kiev.ua),

[1]**Odesa State University**
(2, Dvoryans'ka Str., Odesa 65026, Ukraine; e-mail: mnp@normaplus.com)

The functional form of a repulsive potential is discussed on the basis of the results obtained by two approaches: the processing of statistical valid equations of state and the high-frequency asymptotics of depolarized light scattering. It is shown that the steepness parameter varies from 10 to 15 for a number of inert gases and up to $24 - 28$ in the liquid phase. The results yielded with the help of both the equation of state and molecular light scattering spectra well correlate.

The central idea of our study involves the assumption that a repulsive part of the intermolecular potential is a homogeneous function with the homogeneity exponent m, the Euler theorem on homogeneous functions being applied to the molecular potential as

$$U_r\left(s\bar{r}_1, ...s\bar{r}_n\right) = s^{-m}U_r\left(\bar{r}_1, ...\bar{r}_n\right).$$

For example, the function $U\left(\bar{r}_1, ...\bar{r}_n\right) = \sum_{1 \leq i \triangleleft j \leq N} \varphi\left(\bar{r}_i, \bar{r}_j\right)$ that describes the sum of pair potentials in the frame of the soft-sphere model $\varphi\left(\bar{r}\right) = \varepsilon\left(\frac{\sigma}{r}\right)^m$ must obey this theorem. In this case, the partition function of a system can be presented on the grounds of similarity $\bar{r} \rightarrow q\bar{r}$, $q^3 = \frac{V}{V_0} = \frac{\rho_0}{\rho}$, and $\rho_0 = \frac{N}{V_0}$ as a function of the variable $\left(\frac{(V^*)^{m/3}}{kT}\right)$. For this system, the generalized form of the equation of state is described by the expression

$$\frac{PV}{NkT} = 1 + \varphi\left(\frac{(V^*)^{m/3}}{kT}\right), \qquad (1)$$

where $V^* = \frac{V}{V_0}$. In the vicinity of some basic state (V_0, P_0) within the region of small compression, the function $\varphi\left(x\right)$ can be expanded in a series in $x = \frac{(V^*)^{m/3}}{kT}$. Hence, we obtain

$$P = \frac{NkT}{V} + \frac{NkT}{V}\varphi(x_0) + \frac{N}{V}\varphi'\left(x_0\right)\left[\left(\frac{V_0}{V}\right)^{m/3} - 1\right] +$$

$$+ \frac{N}{V}\frac{\varphi''\left(x_0\right)}{2!kT}\left[\left(\frac{V_0}{V}\right)^{m/3} - 1\right]^2 + ..., \qquad (2)$$

where $\varphi\left(x_0\right)$ is the unknown function. Taking into account that the argument $\left(\frac{(V^*)^{m/3}}{kT}\right)$ varies slightly in the region where the isothermal compressibility is low, we get $\left[\left(\frac{V_0}{V}\right)^{m/3} - 1\right] \ll 1$, and the terms higher than the first-order one can be ignored in (2). Assuming that the term $\frac{NkT}{V}\varphi(x_0)$ is the pressure in the reference state P_0 and allowing the temperature dependence for the term $\frac{N}{V}\varphi'(x_0)$, Eq.(2) can be modified as follows:

$$P - P_0 = \frac{NkT}{V} + B\left(T\right)\left[\left(\frac{V_0}{V}\right)^{m/3} - 1\right]. \qquad (3)$$

This equation of state contains two fitting constants, one of them being the homogeneity exponent m or the steepness parameter of the soft-sphere potential model. Note that a similar form of the equation of state and its modifications have been deduced within the thermodynamic perturbation theory methods in [1—4].

Thus, the statistical mechanics approach gives a possibility to establish a relation between the parameters of intermolecular potentials and the thermodynamic properties of substances. Setting such a relation allows one to calculate the homogeneity parameter m(the steepness parameter for the soft-sphere model) as a fitting constant of the statistical valid equation of state with the use of the processing of experimental PVT-data.

Partly, such a processing was carried out for inert gases [4], for liquid argon [3], and fullerenes [5]. As was shown in [4], the processing of PVT-data based on the equation of state led to the different values of the steepness parameters m varied from 10.5 to 17.5 for a number of inert gases, which does not match the value m=12 generally accepted in many potential models. In connection with this, one should refer to [3], in which the treatment of a theoretically based equation

of state for liquid argon gave the steepness parameter m equal to 28. This fact seems to be surprising to some extent, but the excellent agreement of experimental data with the equation of state encourages. Moreover, the majority of modern papers devoted to the equations of state yields the empirical equation of state containing a great number of fitting parameters, whose physical sense remained obscure and which can be apted as merely interpolation formulae for treating the experimental data.

The results obtained within the statistical mechanics method are in a quantitative agreement with the approach based on the high-frequency asymptotics of depolarized molecular light scattering for simple liquids which is briefly discussed in this paper.

As was shown in [6—8], the high-frequency asymptotics of molecular light scattering is formed by the collision-induced mechanism. The analysis of the binary collision contributions into the spectrum $I^{VH}(\omega)$ of depolarized light scattering leads to the expression

$$I^{VH}_{\omega\to\infty}(w) \sim \omega^p \exp\left(-(\omega\tau_*)^q\right),\qquad(4)$$

where

$$q = \frac{2m}{3m+2},\qquad(5)$$

$$p = \frac{1}{3} - 2\left(\frac{7}{9m+6} + \frac{2}{m+2}\right),\qquad$$

$$\tau_* = 16.32\frac{\sigma}{m}\left(\frac{\mu}{2kT}\right)^{\frac{1}{2}}\left(\frac{\varepsilon}{kT}\right)^{\frac{1}{m}}.\qquad(6)$$

Here, σ, m, and ε are the parameters of the potential $\varphi(\bar{r}) = \varepsilon\left(\frac{\sigma}{r}\right)^m$. From the physical point of view, the high-frequency asymptotics of the molecular light scattering spectra at the high shifts of frequencies is defined by the rate of the process running in a system. One can consider molecular collisions as a combination of soft and hard ones. Some of them are caused by the attractive and repulsive forces acting at distances which are comparable with the average interparticle spacing. Soft collisions result in many-particle interactions. With a satisfactory accuracy, hard collisions can be considered as a sequence of hard binary collisions. In this case, the simultaneous interaction between three and more molecules is improbable. The binary hard collisions are responsible for the high-frequency behaviour of spectra under the assumption that they are characterized by the smallest time of interaction in a system. Thus, if one
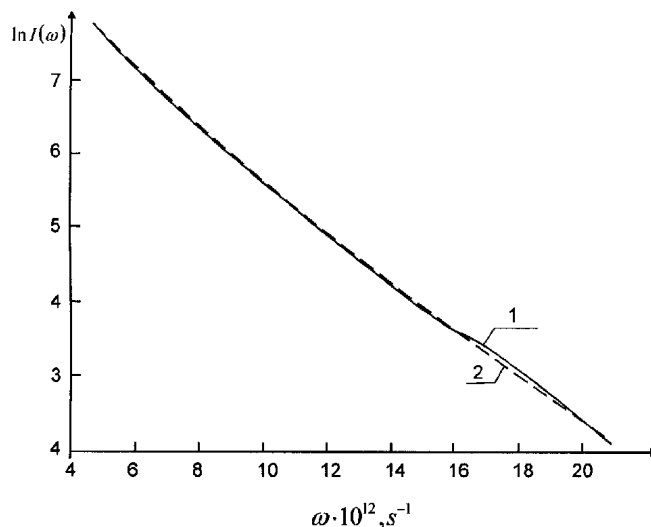
Comparison of experimental and theoretical results. Intensity of depolarized light scattering is shown as a logarithmic function of frequency. Experimental data — solid line *1*, theoretical data — dotted line *2*

takes into account the adduced arguments, two types of the characteristic times can be introduced:

$$\tau_s = \frac{\sigma}{v_T}\qquad(7)$$

and

$$\tau_H = \frac{\tau_s}{m}\qquad(8)$$

which describe soft and hard collisions. The first of them, τ_s, is the time interval corresponding to a smooth variation of the relative velocity in the binary collision, and τ_H characterizes a faster variation of the relative velocity near the stop point and therefore is called the hard-collision time. Correspondingly, the formula for τ_* can be rewritten as

$$\tau_* = a^{\frac{1}{q}}\tau_H,\qquad(9)$$

where

$$a^{\frac{1}{q}} = 16.32\left(\frac{\varepsilon}{kT}\right)^{\frac{1}{m}}.\qquad(10)$$

Then, expression (11) could be transformed to

$$I^{VH}_{\omega\to\infty}(\omega) \sim \omega^p \exp\left(-a\left(\omega\tau_H\right)^q\right).\qquad(11)$$

Expression (11) gives the prediction for the leading term of the high-frequency asymptotics. We expect also that this expression can be applied to the molecular light scattering spectra in liquids. To motivate this assertion, it would be well to assume: 1) binary hard collisions,

unlike soft collisions, are correctly defined both in gases and liquids; 2) it is improbable that three or more particles are involved in a hard collision simultaneously. To verify a qualitative agreement between theory and experiment and to evaluate the optimal values of the parameter m entering the repulsive part of the potential, we used the experimental data on the depolarized light scattering for argon [9].

The calculations were carried out in the frequency interval $4.6 \times 10^{12} - 1.7 \times 10^{13}$ s^{-1} which had minimal experimental error. The best coincidence is observed with such values of the parameters: $a = 8.67$, $q = 0.648$, $\tau_H = 6 \times 10^{-14}$ s (Figure), and the steepness parameter m was defined from Eq. (5). Its value equals 24 for liquid argon that is very close to the values of this parameter obtained in [3].

Thus, the main result of our work is the estimation of the steepness parameter for the repulsive potential in argon. The values of the parameter $m = 24 \div 28$ calculated on a basis of two approaches for liquid argon are essentially more in comparison with $m = 12$ for the well-known Lennard—Jones potential. It is possible that such a difference is connected with the relative narrowness of the pressure and temperature intervals for the equation of state which are used for the calculation of the parameter m in the thermodynamic approach. In other words, the applicability region for the standard Lennard—Jones potential can be only restricted by states corresponding to relatively low pressures. Unlike this, the asymptotic form of molecular light scattering manifests the most steep part of the intermolecular potential which was approximated by a power potential. It is not excluded that, for high-pressure states, the power model for the repulsive part of the intermolecular potential is inapplicable, or one can suggest that the steepness parameter in the frame of the inverse power model is a property of atoms and is a constant for each element.

1. *Boiko V.G., Mogel H.J., Sysoev V.M., Chalyj A.V.* // Uspekhi Fiz. Nauk. — 1991. — **161**, N2.— P.77.

2. *Sysoev V.M.* // Teor. Mat. Fiz. — 1983.— **55**, N2.— P.305.

3. *Bardik V.Yu.,Sysoev V.M.* // Low Temp. Phys. — 1998. — **24**, N8.— P.602—604.

4. *Atamas A.A., Bardik V.Yu., Sysoev V.M.* // Ukr. Zh. Fiz. — 2000.— **45**, N10.— P.1184.

5. *Bulavin L.A., Bardik V.Yu., Prylutskyy Yu.I., Sysoev V.M.* // Ibid. — 2002.— **47**, N5. — P.486.

6. *McTague P., Birnbaum G.*// Phys. Rev. Lett.— 1968.— **21**.— P.661.

7. *Volterra V., Bucaro J.A., Litovitz T.A.* //Ibid.—1971. — **26**.— P.55.

8. *Barocchi F, McTague J.P.* // Phys.Lett.A.— 1975.— **53**.— P.488.

9. *Levine H.B., Birnbaum G.* // Phys. Rev. Lett.— 1968.— **20**.— P.439.

ДОСЛІДЖЕННЯ ПАРАМЕТРА КРУТИЗНИ ПОТЕНЦІАЛУ СИЛ ВІДШТОВХУВАННЯ НА ОСНОВІ РІВНЯННЯ СТАНУ ТА ДАНИХ ЗІ СВІТЛОРОЗСІЯННЯ

В.Ю. Бардик, К.С. Шакун

Р е з ю м е

Обговорюється функціональна форма відштовхувального міжмолекулярного потенціалу, отримана на основі обробки p—V—T-даних за допомогою статистично-обгрунтованого рівняння стану та формули високочастотної асимптотики деполяризованого світлорозсіяння. Показано, що значення параметра крутизни змінюється від 10 до 15 в ряду інертних газів та сягає 24—28 у рідкому стані. Результати, одержані за допомогою рівняння стану та молекулярного світлорозсіяння, добре узгоджуються між собою.