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Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

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To cite this Article Waseda, Y. and Suzuki, K.(1976) 'Pair potentials and properties of simple liquids from the pair correlation function', *Physics and Chemistry of Liquids*, 5: 2, 93 – 102

To link to this Article: DOI: 10.1080/00319107608084109

URL: <http://dx.doi.org/10.1080/00319107608084109>

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Pair Potentials and Properties of Simple Liquids from the Pair Correlation Function

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(Received September 10, 1975)

The Born-Green equation was numerically analyzed to derive the intermolecular potentials from the observed structural data for liquified rare-gases (Ne, Ar, Kr and Xe). In all cases the Lennard-Jones type potentials were found. The surface tension, surface energy, energy of vapourization, viscosity coefficient and self-diffusion coefficient were calculated and a comparison of calculated values with experimental data was made. Adequate agreement was obtained.

1 INTRODUCTION

In the last few years much theoretical effort has been devoted to develop the molecular theories of liquids and to understand the electronic properties of liquid metals.¹ Three approximate equations connecting the pair correlation function $g(r)$ with the pair potential function $\phi(r)$ have been used in the study of simple liquids; there are the Born-Green (BG), Percus-Yevick (PY), and hypernetted chain (HNC) equations. Particularly, the work of Johnson, Hutchinson and March² gave us the first information of the effective ion-ion interaction in liquid metals which had a long-range oscillatory characteristics contrary to the Lennard-Jones type potential such as the pair potential of liquid Ar. More recently BG equation was numerically solved to derive the effective ion-ion interaction for liquid alkali metals by a linearized simultaneous equation method.³ In this result the effective ion-ion interaction in liquid metals showed the long-range oscillatory characteristics again.

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However, BG equation is based on the so-called superposition approximation of Kirkwood⁴ and it is deduced that the accuracy of this approximation is not fully quantitative, especially in dense fluids. Nevertheless the pair potentials^{2,5} derived from the observed structural data frequently indicate moderately good agreement with that formerly predicted⁶⁻⁸ within the framework of pair theory. For these reasons, it would be desirable to re-examine the derivation of the pair potential of liquified rare-gases from the available structural data by solving the Born-Green equation, because it is theoretically discussed that the pair potential of these elements is the Lennard-Jones type potential. In this work, the Born-Green equation was solved to derive the pair potentials for rare-gas elements (Ne, Ar, Kr, and Xe). Besides, as the check of the validity of the pair potentials obtained, the calculation of some molecular properties such as viscosity, self-diffusion and so on, were performed according to the kinetic theory of fluids and a comparison of calculated values with experimental data was made. The results are discussed below.

2 METHOD FOR DERIVATION OF PAIR POTENTIAL

According to the Born-Green theory⁹ the pair potential $\phi(r)$ is given by the following relation;

$$\phi(r) = U(r) + \frac{k\rho_0}{r} \int_0^\infty \frac{d\phi(s)}{ds} g(s) ds \int_{-s}^{+s} (s^2 - t^2)(t+r) [g(|t+r|) - 1] dt, \quad (1)$$

$$U(r) = -kT \ln g(r), \quad (2)$$

where ρ_0 is the average number density of atoms, $g(r)$ is the pair correlation function obtained by diffraction experiments, k is the Boltzmann constant and T is the absolute temperature.

As shown in our previous paper¹⁰ the Equation (1) for $\phi(r)$ was numerically solved by the linearized simultaneous equation method. The practice of numerical computation was performed on NEAC-2200, Model-700 in Computer Center, Tohoku University.

3 RESULTS AND DISCUSSION

3.1 Pair potentials

The pair potentials $\phi(r)$ were determined with recent structural data by X-ray and neutron diffraction experiments for liquified rare-gases, Ne^{11,12}, Ar^{13,14}, Kr¹⁵ and Xe¹⁶.

Figure 1 shows the results obtained from three states of liquid Ar. They

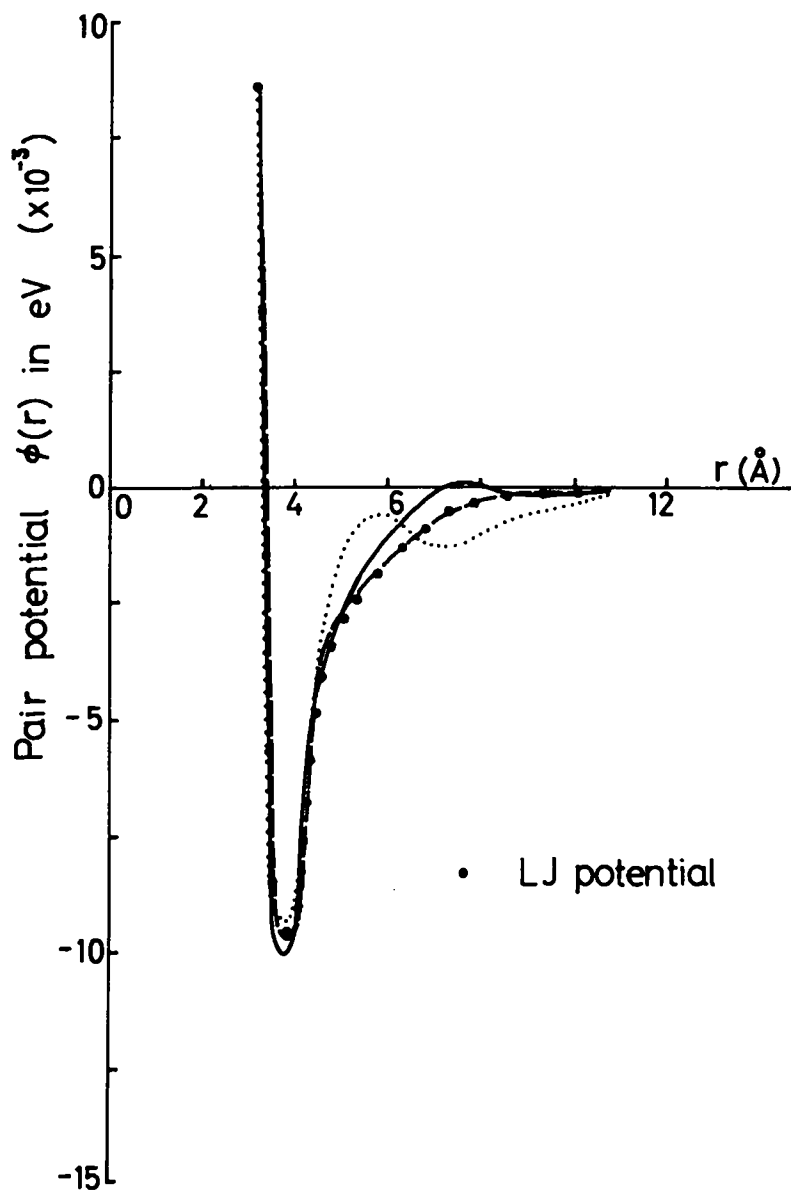


FIGURE 1 Pair potentials derived from three states of liquid Ar. (.....) 84K, 0.02130 atoms/ \AA^3 ; (—) 148K, 0.00808 atoms/ \AA^3 ; (---) 163K, 0.00422 atoms/ \AA^3 .

are in adequately agreement with the Lennard-Jones (LJ) potential as given by Dobbs and Jones.¹⁷ In the case of the result at 84 K the pair potential indicates the deviation from LJ type potential curve in the region followed the usual potential minimum corresponding to the nearest neighbour distance. This behaviour was also found in the direct correlation function which was closely related to the pair potential by Enderby and March¹⁸ (they used the same structural data in this work). Recently, Mikolaj and Pings¹⁹ reported the density dependence of the pair potential for liquid Ar using the PY and HNC equations. This was also found in our previous calculation using the BG equation.²⁰ In our previous calculation,²⁰ the fairly

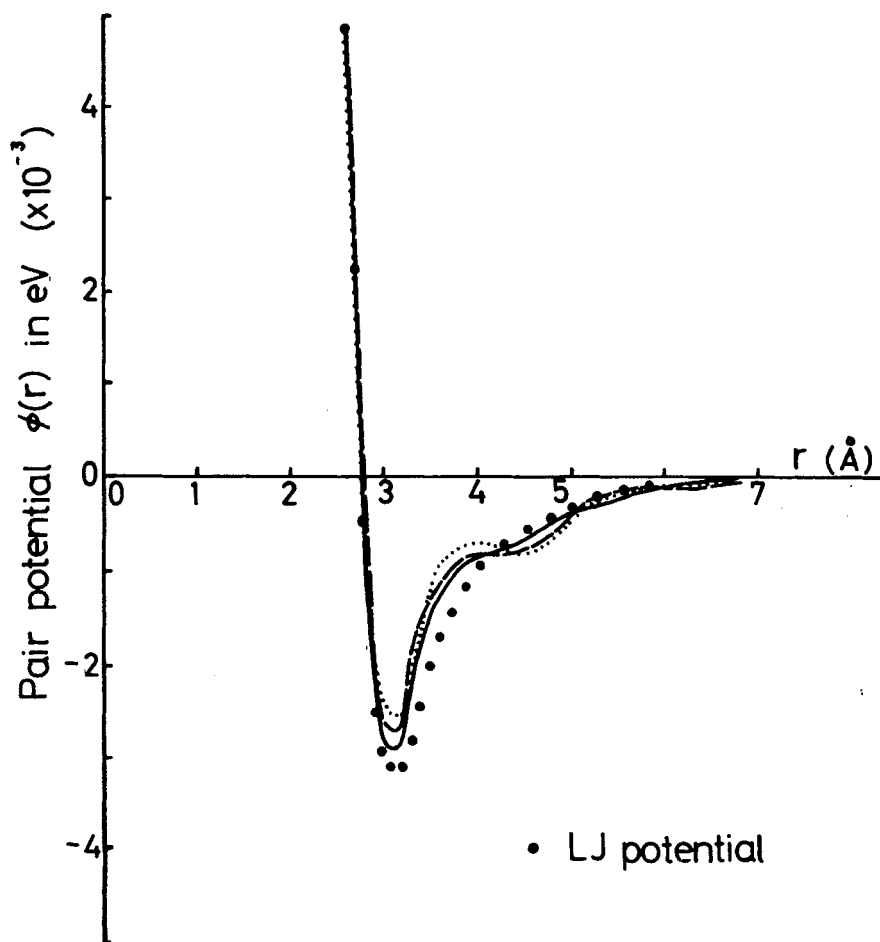


FIGURE 2 Pair potentials derived from three states of liquid Ne (—) 35K, 0.03169 atoms/Å³; (---) 35K, 0.03338 atoms/Å³; (.....) 35K, 0.03469 atoms/Å³

large repulsive positive part and subsequent small oscillations toward zero which followed the potential minimum were found in the case of higher density. But these large positive part was considerably reduced when introducing the accurate re-calculation, for example the numerical calculation in double precision arithmetic.

As shown in Figure 1 the results for liquid Ar obtained in this work essentially indicate the LJ type potential formerly predicted⁶⁻⁸ as those of rare-gas elements. The deviation from the LJ potential curve observed at 84K and the small positive part observed at 148K may be caused by the following factors. Many-body effect seems to be increasingly important at higher density state and the BG equation based on the superposition approximation in which the triplet correlation function is expressed by the product of the pair correlation functions does not completely represent the distribution of atoms in liquids. Besides it should be kept in mind in this numerical calculation that the ambiguous error arising from the difficulty which is indispensable in solving the simultaneous linear equations with many unknowns seems to be included.

Figure 2 shows the pair potential of liquid Ne calculated from the structural data recently observed by de Graaf and Mozer.¹² The density dependence of the pair potential is observed as also found in liquid Ar. But they support the shape of the LJ type potential, which de Graaf and Mozer¹² also pointed out using the PY and HNC equations. Figure 3 shows the results for liquid Ne, Kr and Xe using the experimental structural data (Ne¹¹, Kr¹⁵, Xe¹⁶). The same behaviour of deviation from the LJ potential curve was found and this seems to be caused by the same reasons above-mentioned. But it is also found that they are not to be apart from the LJ type potential. From these results, it may be safely said that the pair potentials of rare-gas elements derived from the structural data give the LJ type potential formerly predicted.⁶⁻⁸

It is well known that the Lennard-Jones type potential is given by the following form;

$$\phi(r) = 4 \epsilon [(\sigma/r)^{12} - (\sigma/r)^6], \quad (3)$$

where ϵ is the depth of the potential at its minimum and σ is the finite value of r for which $\phi(r) = 0$. Therefore, adopting as an initial function the solution obtained by the linearized simultaneous equation method the parameters, ϵ and σ , are determined using the iteration approximation. Table I gives the values of the parameters obtained by the procedure above-mentioned. The results are similar to those found by Shoemaker *et al.*²¹ who calculated the parameters from the pressure or the internal energy equation with the pair correlation functions observed experimentally.

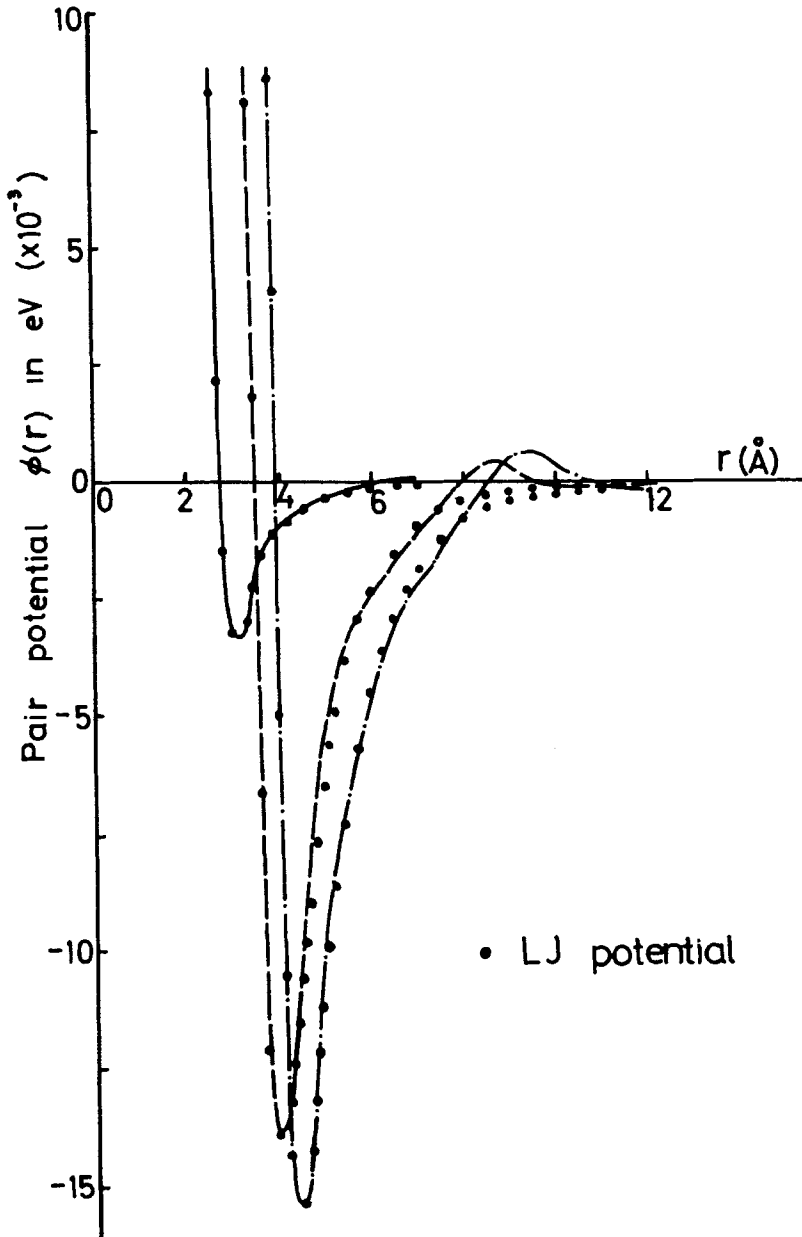


FIGURE 3 Pair potentials of liquid Ne, Kr and Xe (—) Ne 44.2K, 0.01999 atoms/Å³; (---) Kr 210K, 0.00750 atoms/Å³; (-·-) Xe 161.5K, 0.01417 atoms/Å³.

TABLE I

Parameters for pair potentials obtained in this work

	this work		Shoemaker <i>et al.</i> ²¹	
	σ (Å)	E/k (°K)	σ (Å)	E/k (°K)
Ne	2.760	39.77	2.761	34.44
Ar	3.280	112.5	3.255	147.23
Kr	3.570	164.4	3.599	168.51
Xe	3.940	180.3	3.750	230.69

k: Boltzmann constant

3.2 Application to some properties

As a check of the pair potentials determined in this work, we made calculations of several properties of bulk liquids. According to the kinetic theory of fluids, surface tension (γ), surface energy (U^s), energy of vapourization (E^v) and viscosity coefficient (η) are expressed by the pair correlation function $g(r)$ and the pair potential $\phi(r)$ in the following equations;²¹⁻²³

$$\gamma = \frac{\pi}{8} \rho_0^2 \int_0^\infty g(r) \frac{d\phi(r)}{dr} r^4 dr, \quad (4)$$

$$U^s = -\frac{\pi}{2} \rho_0^2 \int_0^\infty g(r) \phi(r) r^3 dr, \quad (5)$$

$$E^v = N_0 [kT - 2\pi\rho_0 \int_0^\infty g(r) \phi(r) r^2 dr], \quad (6)$$

$$\eta = \frac{2\pi}{15} (m/kT)^{1/2} \rho_0^2 \int_0^\infty g(r) \frac{d\phi(r)}{dr} r^4 dr, \quad (7)$$

where m is atomic mass and N_0 is Avogadro's number.

Table II shows the results calculated by Equations (4)–(7) together with the values observed experimentally. The infinite integral in above equations was truncated at a finite upper value at which the pair potential $\phi(r)$ was sufficiently reduced and showed the absolute value of 1×10^{-4} eV (about four times the atomic diameter). Besides, the pair correlation function $g(r)$ is unity in the region larger than the values of four times the atomic diameter.

As shown in Table II, the calculated values of surface tension and energy of vapourization are in good agreement with the experimentally observed values. But those of surface energy are not as good. This may be related to the inadequacy of the step model by Fowler²² in Equation (5). This model neglects the contribution of the liquid-vapour transition and vapour phase. Viscosity coefficient of liquid Ar is in moderately good agreement with ex-

TABLE II

Comparison of calculated surface tension, surface energy, energy of vapourization and viscosity coefficient with experimental data

	temp. (K)	density (g/cm ³)	γ (dyne/cm)		U^s (erg/cm ²)		E^v (kcal/mole)		η (cP)	
			cal.	exp. ^a	cal.	exp. ^b	cal.	exp. ^c	cal.	exp. ^d
Ne	33.1	1.090	4.78	2.70	8.68	14.3	0.385	0.331	0.044	
	39.4	0.920	3.63		6.19		0.324		0.030	
	44.2	0.670	2.38		3.61		0.255		0.019	
Ar	84.0	1.413	13.5	13.2	22.0	35.0	1.21	1.42	0.11	0.24
	148.0	0.780	4.93		6.64		0.657		0.030	0.051
	163.0	0.536	2.77		3.17		0.451		0.016	
Kr	117.0	2.449	16.8	16.1	29.1	40.1	1.83	1.96	0.17	
	153.0	2.143	13.7		21.9		1.56		0.12	
	210.0	1.043	3.68		5.51		0.814		0.027	
Xe	161.5	3.090	16.5	19.3	30.0	50.0	2.13	2.75	0.16	

^aE. P. Buff and R. A. Levett, *Simple Dense Fluids* (H. L. Frisch and Z. W. Zalsburg, editors), Academic Press Inc., New York, 1968.

^bH. Renon, C. A. Eckert and J. M. Prausnitz, *Ind. Eng. Chem. Fundamentals* **6**, 52 (1967);

^cJ. S. Rowlinson, *Liquids and Liquid Mixtures*, Butterworths Sci. Pub. Ltd., London, 1959.

^dA. Lowry, S. A. Rice and P. Gray, *J. Chem. Phys.* **40**, 3673 (1964);

periments. But for other liquids the available experimental data seem not to be found. Hence we can not give any statement about comparison between calculations and experiments.

On the other hand, in principle the self-diffusion of liquids is expressed by the structure and pair potential. Rice-Kirkwood²⁴ and Helfand²⁵ attempted the self-diffusion calculation for liquid Ar using the knowledge only of the pair potentials, the pair correlation function and the number density. Hence, we derived the self-diffusion coefficient from the pair potential obtained in this work using the kinetic theory of fluids suggested by Rice-Kirkwood.²⁴

As pointed out by Helfand²⁵ and Rice-Allnatt,²⁶ we assume that the pair potential is approximately written in the following form which is expressed by the two parts (hard and soft parts),

$$\phi(r) = \phi^H(r) + \phi^S(r), \quad (8)$$

$$\left. \begin{aligned} \phi^H(r) &= \infty & \text{and} & & \phi^S(r) &= 0 & r &\leq \sigma \\ \phi^H(r) &= 0 & \text{and} & & \phi^S(r) &= \phi_A(r) & r &\geq \sigma \end{aligned} \right\}, \quad (9)$$

where σ is the core diameter being defined as the finite value of r for which $\phi(r) = 0$, and $\phi_A(r)$ is the additive part which follows the usual hard part in the pair potential.

The self-diffusion coefficient (D) is given by the relation;

$$D = kT/(\zeta^H + \zeta^S + \zeta^{SH}), \quad (10)$$

where ζ^H , ζ^S and ζ^{SH} are the friction coefficients due to the repulsive hard-core interaction, to the soft interaction between the neighbouring atoms and to the cross-effect between the hard and soft forces in the pair potential. They are given by the following relations;

$$\zeta^H = \frac{8}{3} \rho_0 g(\sigma) \sigma^2 (mkT)^{1/2}, \quad (11)$$

$$\zeta^S = \left[\frac{4\pi m \rho_0}{3} \int_{\sigma}^{\infty} \nabla_r^2 \phi^S(r) g(r) r^2 dr \right]^{1/2} \quad (12)$$

and

$$\zeta^{SH} = -\frac{1}{3} \rho_0 g(\sigma) (m/\pi kT)^{1/2} \times \int_0^{\infty} [Q \sigma \cos(Q\sigma) - \sin(Q\sigma)] \tilde{\phi}^S(Q) dQ, \quad (13)$$

where $g(\sigma)$ is the value of the pair correlation function at $r = \sigma$, Q is the wave-vector transfer and $\tilde{\phi}^S(Q)$ is the Fourier transform of the soft-part of the pair potential $\phi^S(r)$. Equation (12) is based on the small-step diffusion model by Rice-Kirkwood²⁴ and Equation (13) is formulated by Davies-Palyvos.²⁷ Here, we ignored the cross-effect due to a three-body correlation because Davies-Palyvos suggested that this is negligible small.

In Table III the results calculated in this work are shown. In all cases the magnitude of ζ^{SH} is comparable with that of ζ^H . Therefore ζ^{SH} was considerably important for the self-diffusion coefficient of liquified rare-gases

TABLE III

Comparison of calculated self-diffusion coefficient with experimental data

	temp. (K)	density (g/cm ³)	ζ^H	ζ^S	ζ^{SH}	cal. D	exp. ^a
Ne	33.1	1.090	0.449	1.56	0.324	1.96	
	39.4	0.920	0.439	1.39	0.266	2.59	
	44.2	0.670	0.338	1.20	0.183	3.54	
Ar	84.0	1.413	0.750	2.93	0.561	2.74	1.86
	148.0	0.780	0.585	2.12	0.248	6.92	
	163.0	0.536	0.392	1.60	0.151	10.5	
Kr	117.0	2.449	1.40	4.76	1.13	2.22	1.56
	153.0	2.143	1.46	4.30	0.900	3.17	
	210.0	1.043	0.925	3.06	0.415	6.59	
Xe	161.5	3.090	1.90	5.72	1.24	2.51	1.63

^aJ. Naghizadeh and S. A. Rice, *J. Chem. Phys.* **36**, 2710 (1962); S. A. Rice, J. P. Boon and H. T. Davis, *Simple Dense Fluids* (H. L. Frisch and Z. W. Salsburg, editors), Academic Press Inc., New York, 1968. Units of ζ are g sec⁻¹ × 10⁻¹⁰ and units of D are cm² sec⁻¹ × 10⁻⁵. ζ^H , ζ^S and ζ^{SH} are hard-part, soft-part and cross-effect friction coefficient, respectively.

though Helfand²⁵ and Rice–Allnatt²⁶ neglected this effect. However, ζ^S is larger than the sum of ζ^H and ζ^{SH} ($\zeta^S > \zeta^H + \zeta^{SH}$) and hence it is found that the effect of the soft part in the pair potential on the self-diffusion coefficient is very important. As shown in Table III the calculated values are in adequate agreement with the experimentally observed values. The detailed available experiments for self-diffusion in these liquids seem not to be reported, so we can not give any further comments to the calculated results. But it is found that the pair potentials obtained in this work are fairly useful for the presentation of some properties for bulk liquids.

From these results, we may suggest that the Born–Green equation with the superposition approximation is not necessarily sufficient for dense fluids but this approximate equation is still useful as a first approximation in molecular theory of fluids.

Acknowledgments

The authors are greatly indebted to Prof. M. Ohtani for his support and encouragement in this study. The assistance of Computer Center, Tohoku University is also gratefully acknowledged.

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