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Calculation of equilibrium and transport properties using modified hard-core potential models

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Abstract

We present in this paper a new method of modifying hard-core potentials to correctly predict the equilibrium and non-equilibrium properties of real fluids at low densities (specifically when $\rho \leqslant B/C$ where ρ is density, and B and C are the second and third virial coefficients) only by *one* set of potential parameters. Because the molecular diameter becomes smaller when temperature increases, we introduced a new expression for the variation of molecular diameter with temperature that incorporates this effect. The temperature dependence of the diameter was used in both Sutherland (ST) and square-well (SW) potential models to modify the second virial coefficient. Then we have shown that the experimental second virial coefficient fits into the modified Sutherland (MST) and modified square-well (MSW) quite well for the entire temperature range for which experimental data are reported, including the inversion temperature. Such fittings give the parameters of the modified potential models, which are used to calculate the non-equilibrium properties of He, Ne, N_2, O_2, CO, and NO, including viscosity, thermal conductivity, and self-diffusion coefficients. In comparison with experimental data, such modifications of the potential models give much better results than those obtained from the original ST and SW models, especially at high temperatures at which the deviations are reduced significantly. Therefore, there is no need to use two sets of potential parameters; one for the equilibrium and another for the non-equilibrium properties of real fluids, if we use the modified hard-core potential models.

Keyword: Modified hard-core potential models

1. Introduction

Hard-core potential models, including the hard-sphere (HS), square-well (SW), Sutherland (ST), and hard-core Lennard-Jones (HCLJ) are of great importance in fluid theories because of:

(A) Having analytical expressions for their radial distribution functions (RDF) at least at low-densities; hence their properties may be expressed and calculated analytically [1–4].
(B) The HS potential is usually used as a reference state in the perturbation theory of simple liquids.
(C) The behavior of all simple liquids approaches that of the hard-core fluids when temperature and density increase.

For these reasons their radial distribution functions (RDF), thermodynamic properties, and phase behavior are intensely investigated both analytically and by various computer simulation methods [5–15]. Despite these features, they have an incorrect behavior that must be improved. For instance, while these potential models correctly predict the behavior of the second virial coefficient $[B(T)]$ in the low temperature region, they show a significant deviation from experimental data at high

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temperatures. Specifically, they do not predict any maximum value for $B(T)$ versus T at any temperature, which may be called the inversion temperature [16,17], observed experimentally. In addition, it has been known for a long time that the potential parameters of any given model that give the best fit for non-equilibrium and equilibrium properties (such as viscosity, thermal conductivity, self-diffusion coefficient, and the second virial coefficient) are generally different [18]. Hence, for a simple potential model (like the Lennard-Jones), there is one specific set of potential parameters appropriate for each property. Our goal in this work is to modify these potential models in such a way that they can predict the behavior of the second virial coefficient $B(T)$ up to high temperatures, including the inversion temperature. Then, the modified potentials will be used to calculate the transport properties. The potentials used for this purpose are the square-well and Sutherland which we have analytical expressions for their RDFs. As will be shown in Sections 2 and 3, we can achieve this goal by modifying the hard-core diameter properly. In this way we are able to retain the hard-core potentials and their analytical RDFs for description of real simple fluids. Also it is shown that with these modified potential models, we can well represent the experimental data (equilibrium and non-equilibrium) only by *one* set of potential parameters at low densities.

2. The modified hard-core potential models

The Sutherland (ST) and square-well (SW) potential models are defined as

$$U(r) = \infty \quad (r \leqslant \sigma)$$
$$U(r) = -\varepsilon r^{-\gamma} \quad (r > \sigma)$$
$$U(r) = \infty \quad (r \leqslant \sigma)$$
$$U(r) = -\varepsilon \quad (\sigma < r \leqslant \lambda\sigma)$$
$$U(r) = 0 \quad (r > \lambda\sigma)$$

respectively.

The second virial coefficients of the ST and SW potentials are given [19] by

$$B = b_0[1 - \varepsilon/kT - \tfrac{1}{6}(\varepsilon/kT)^2 - \tfrac{1}{30}(\varepsilon/kT)^3 + \cdots] \tag{1}$$

and

$$B = b_0[1 - (\lambda^3 - 1)(\mathrm{e}^{\varepsilon/kT} - 1)] \tag{2}$$

respectively, where $b_0 = \frac{2}{3}\pi\sigma^3$, σ is the core diameter, λ is the width of the SW potential, ε is the depth of the potential well, and T is absolute temperature. For these potentials, the derivative of $B(T)$ with respect to T is always positive. Therefore these potentials can not show any maximum value which has been observed experimentally [20].

This difference in behavior is mainly due to the existence of a hard-core diameter in such potential models. However, the soft-core potential models like the Lennard-Jones model, can take into account this effect qualitatively. They are treated in the perturbation theories of liquids as having a hard-core. In the perturbation theories of liquids the potential, at the first step, is separated into two parts; repulsion and attraction. In the second step, it is shown that the fluid structure is mainly determined by the repulsion part which in turn may be represented by a conveniently chosen hard-sphere fluid, and the attractive part is treated as a perturb term. The hard-sphere fluid which is taken as the reference system has a temperature-dependent diameter. For instance, for the Barker–Henderson theory, it can be calculated by [19];

$$\sigma = \int_0^\infty (1 - \mathrm{e}^{-u(r)/kT})]\,\mathrm{d}r \tag{3}$$

in which $u(r)$ is the repulsive part of the potential. For the Lennard-Jones potential, Verlet and Weis used Eq. (3) to calculate the temperature-dependent diameter. The calculated diameter was fitted into [4];

$$\sigma_{vw} = \frac{aT + b}{cT + 1} \tag{4}$$

where $a = 0.3837$, $b = 1.068$, and $c = 0.4293$, which yields an error less than 2×10^{-4}. Therefore, one may expect that if temperature-dependence of the diameter is taken into account, the second virial coefficient given by a hard-core potential model would pass through a maximum. We may note that when temperature increases, real molecules are expected to penetrate more into each other, and hence the diameter is expected to become shorter. For instance, we may expect that at very low temperature the closest distance between the centers of two molecules is the molecular diameter, i.e., they just may touch each other. However, the distance decreases with temperature. We may include the above-mentioned character to improve these potential models without loosing their simple functional forms by supposing that the diameter is temperature-dependent. In this way, we are able to retain the hard-core potentials and their known properties for a description of real simple fluids. As mentioned previously, at high temperatures the real inter-particle potential becomes harder and harder, in other words with increasing temperature, molecules may penetrate into each other more and more. The amount of penetration depends on both the softness of outer shell and temperature. At low temperatures, the molecules may only touch each other, which in this situation the molecular diameter is indicated by its soft core diameter, σ_s. With increasing temperature, molecules penetrate into each other to the point that the repulsion forces overcome the thermal energy; which for the case of $T \to \infty$, the core diameter is given by the hard-core diameter σ_c. Since the hard-core diameter involves in the second virial coefficient via b_0, where $b_0 = \frac{2}{3}\pi\sigma^3$, the following equation may account for the temperature dependence of the core diameter:

$$b_0 = b_s + (b_c - b_s)\mathrm{e}^{-\alpha/T} \tag{5}$$

where $b_c = \frac{2}{3}\pi\sigma_c^3$, $b_s = \frac{2}{3}\pi\sigma_s^3$, and $\alpha = -\frac{d\ln(b_0-b_s)}{d(1/T)}$ is the rate of molecular penetration with temperature. Even though we could make use of Eq. (4) to take temperature-dependence of the diameter, but we prefer to use Eq. (5) which its parameters have clear physical meaning. Nonetheless, we have considered the Verlet–Weis form for completeness and comparison, which we may refer to them as ST–VW and SW–VW, respectively. Inserting Eq. (5) into Eqs. (1) and (2), one can reach to the following modified expressions for the second virial coefficients of the modified SW and modified ST potential models, respectively:

$$B = [b_s + (b_c - b_s)e^{-\alpha/T}][1 - (\lambda^3 - 1)(e^{\varepsilon/kT} - 1)] \qquad (6)$$

and

$$B = [b_s + (b_c - b_s)e^{-\alpha/T}] \times [1 - \varepsilon/kT - \tfrac{1}{6}(\varepsilon/kT)^2 - \tfrac{1}{30}(\varepsilon/kT)^3 + \ldots] \qquad (7)$$

The modified potential models which lead to Eqs. (6) and (7) will be called the MSW and MST models from now on, respectively. Now that the modified SW and ST potentials and their corresponding second virial coefficients have been introduced, we may test the ability of the modified potentials in predicting the equilibrium and non-equilibrium properties of real gases at low densities.

3. Experimental test for the second virial coefficients

In this work for some real gases (He, Ne, N_2, O_2, CO, and NO); we used the accurate reported data containing the inversion temperatures. For He we used the experimental data in [20] at the whole temperature range and for Ne, N_2 in [21–23] at low temperatures. For these two gases and for other gases at high temperatures we used the accurate reported data, based on the principle of corresponding states in [24,25]. The accurate reported data have been fitted into the modified second virial coefficients [Eqs. (6) and (7)], which for one of them, namely neon, we have plotted the second virial coefficients using the ST, MST, SW, and MSW potential models along with experimental data in Fig. 1. As may be seen, the experimental data are well fitted into the proposed MST and MSW models in whole temperature range for which the experimental data are reported, whereas the second virial coefficients calculated with the ST and SW potential models have meaningful deviations from experimental data, especially at high temperatures. In addition we see that the MST and MSW potential models can take into account the inversion temperature whereas the ST and SW potential models can not. Also, we have used the Verlet–Weis parameterization to calculate temperature-dependence diameter, which may be used to obtain the second virial coefficient via both ST and SW potential models. The deviation curve of Ne for the calculated second virial coefficient, obtained from the MST, MSW, ST–VW, and SW–VW are shown in Fig. 2.

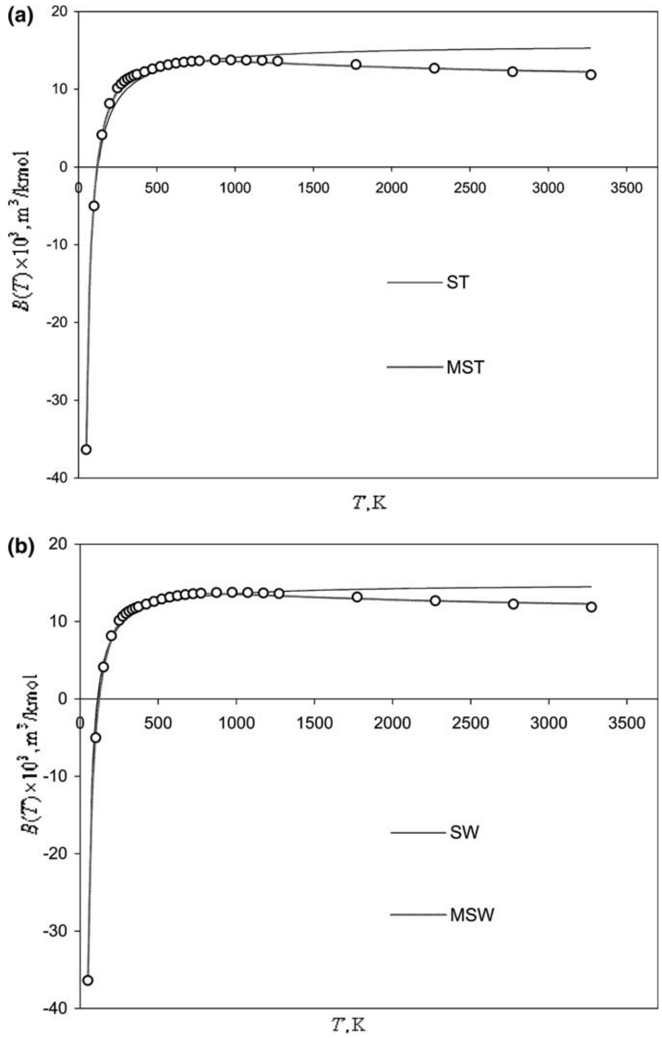

Fig. 1. (a) The experimental second virial coefficient of Ne fitted into Eqs. (1) and (6) for ST and MST Potential Models. (b) The experimental second virial coefficient of Ne fitted into Eqs. (2) and (7) for the SW and MSW potential models.

For other gases essentially similar results are obtained. Using the above-mentioned method of fitting, the parameters of the new potentials for the MST and MSW have been obtained which are given in Table 1. We may consider σ_s/σ_c as a quantity representing the extent of penetration and α as the rate of molecular penetration with temperature. A penetrable molecule has a smaller value for its ratio of σ_s/σ_c, and softer molecule has a larger value of α, hence its penetration with temperature is more. As one can see in the 6th and 15th rows of Table 1, when temperature increases the molecular diameter of all above-mentioned gases will decrease within 17–24% with one exception; helium with ~34% (due to its small diameter). In order to grasp the penetrability of different molecules, the ratio of $\sigma(T)/\sigma_s$ obtained from both MST and MSW is plotted versus T in Fig. 3. As shown in this figure, the penetrability for He has the highest values which means He is the softest species.

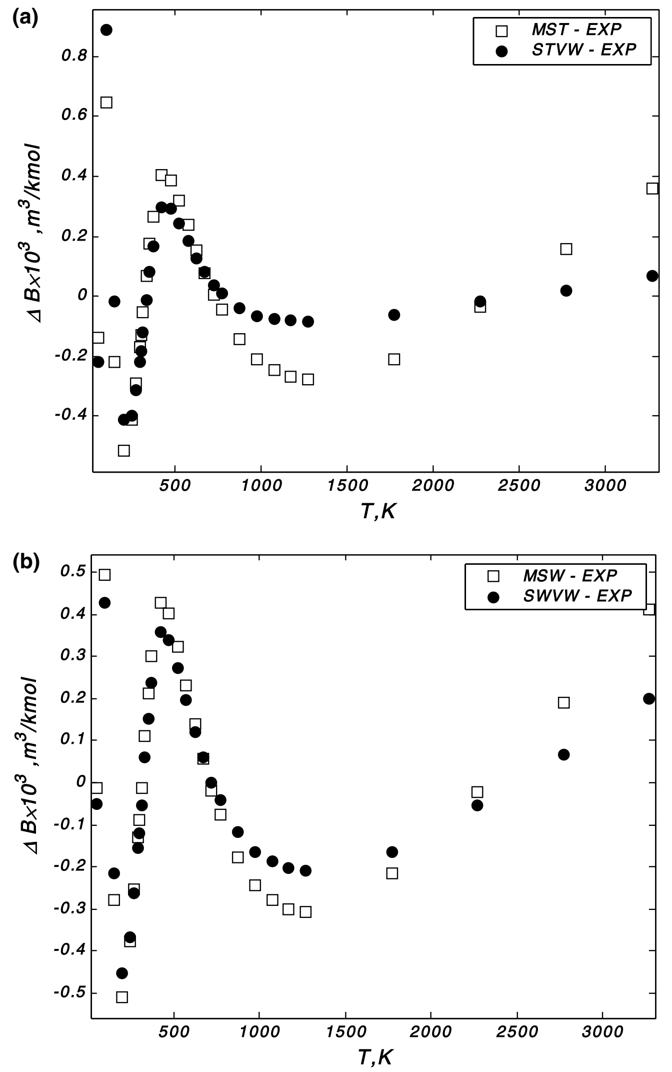

Fig. 2. (a) The deviation curves for the calculated second virial coefficient of Ne, Obtained from the MST and ST–VW. (b) Same as (a) for the MSW and SW–VW.

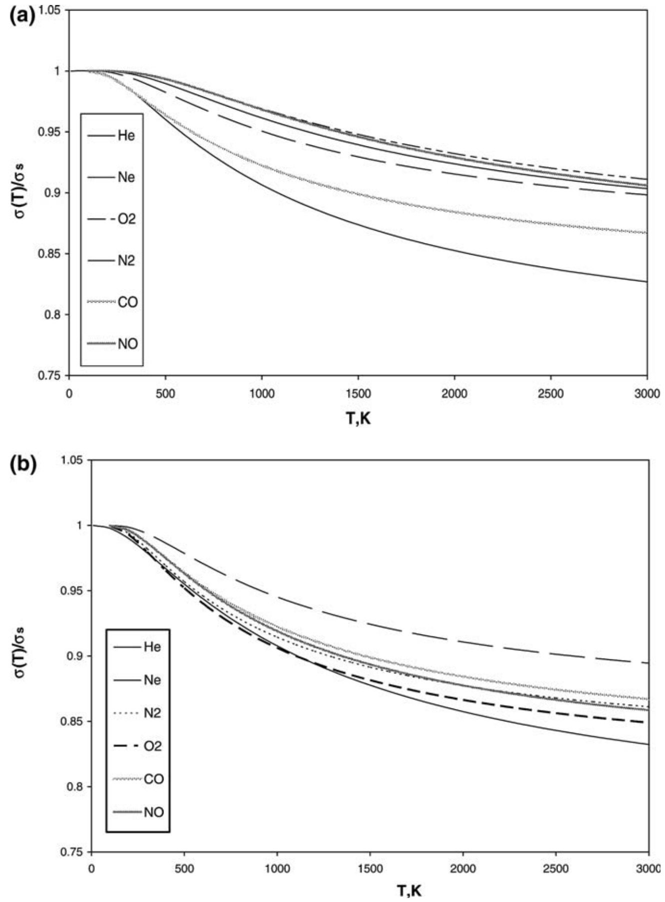

Fig. 3. (a) The penetrability ratio, $\sigma(T)/\sigma_s$, of various gases obtained from MST. (b) Same as (a) for the MSW.

4. Calculation of transport properties using the modified potentials

Now by having the potential parameters we can easily compute the transport properties of the gases, i.e., viscos-

Table 1
Potential parameters for the modified Sutherland and modified square-well potentials of some gases

Potential models	Gases parameters	He	Ne	N_2	O_2	CO	NO
ST	ε/k (K)	11.28 ± 4.5	106.8 ± 5.1	279.1 ± 7.4	343.4 ± 9.1	300.8 ± 10	360.7 ± 10
	b_0 (cm³/mol)	12.72 ± 0.73	15.81 ± 0.85	41.92 ± 2.14	34.06 ± 1.85	42.91 ± 5.56	36.45 ± 2.07
MST	ε/k (K)	11.42 ± 1.24	103.3 ± 1.3	269 ± 4.3	331.6 ± 4.5	283.2 ± 2.5	347.1 ± 4.4
	b_s (cm³/mol)	12.77 ± 0.20	17.62 ± 0.45	45.92 ± 1.66	37.82 ± 1.37	49.47 ± 0.95	40.6 ± 1.33
	b_c (cm³/mol)	5.526 ± 0.271	10.84 ± 1.12	27.38 ± 7	22.62 ± 4.84	28.42 ± 2.36	23.2 ± 5.04
	σ_s/σ_c	1.3221	1.1758	1.1881	1.1869	1.2029	1.2051
	α (K)	799.2 ± 49.4	1004 ± 312	1289 ± 730	1497 ± 787.2	953.8 ± 216.2	1542 ± 720
SW	ε/k (K)	61.81 ± 162.39	69.27 ± 21.54	118.2 ± 20.6	161.5 ± 34.8	137.7 ± 19.9	166.5 ± 33.7
	λ	1.029 ± 0.133	1.292 ± 0.122	1.478 ± 0.082	1.436 ± 0.092	1.44 ± 0.066	1.443 ± 0.088
	b_0 (cm³/mol)	12.35 ± 0.9	14.85 ± 0.9	40.32 ± 2.76	32.44 ± 2.23	40.07 ± 2.86	34.67 ± 2.47
MSW	ε/k (K)	68.39 ± 66.51	35.14 ± 10.34	66.14 ± 10.19	54.97 ± 34.92	91.33 ± 9.17	76.22 ± 23.09
	λ	1.024 ± 0.024	1.584 ± 0.145	1.739 ± 0.079	1.959 ± 0.384	1.605 ± 0.045	1.797 ± 0.163
	b_s (cm³/mol)	12.35 ± 0.34	17.91 ± 1.17	53.78 ± 3.05	47.35 ± 6.38	52.65 ± 2.76	48.24 ± 4.2
	b_c (cm³/mol)	5.393 ± 0.274	11.03 ± 1.13	29.7 ± 1.67	24.73 ± 1.28	29.33 ± 1.76	25.55 ± 1.39
	σ_s/σ_c	1.3390	1.1750	1.2189	1.2417	1.2153	1.2360
	α (K)	884.9 ± 96.6	903.8 ± 393.2	642.8 ± 170	624.2 ± 263.9	722.6 ± 195.7	743.2 ± 243.4

ity, thermal conductivity, and self-diffusion coefficients at low densities. It is well-known that at low densities, the Boltzmann equation gives explicit expressions for the viscosity, thermal conductivity, and self-diffusion coefficients as [18,19]:

$$\eta = \frac{5}{16}\frac{(\pi m k T)^{1/2}}{\pi\sigma^2\Omega^{(2,2)^*}} \tag{8}$$

$$\lambda = \frac{25}{32}\frac{C_v}{N}\left(\frac{\pi k T}{m}\right)^{1/2}\frac{1}{\pi\sigma^2\Omega^{(2,2)^*}} \quad \text{for monatomics} \tag{9a}$$

$$\lambda = \frac{5}{16N}\left(\frac{9}{4}R + C_v\right)\left(\frac{\pi k T}{m}\right)^{1/2}\frac{1}{\pi\sigma^2\Omega^{(2,2)^*}} \quad \text{for polyatomics} \tag{9b}$$

$$D = \frac{3}{8}\left(\frac{\pi k T}{m}\right)^{1/2}\frac{1}{\rho\pi\sigma^2\Omega^{(1,1)^*}} \tag{10}$$

In these equations m, k, ρ, σ, and T are the particle mass, Boltzmann constant, number density, molecular diameter, and absolute temperature. In addition $\Omega^{(1,1)*}$ and $\Omega^{(2,2)*}$ are the reduced collision integrals. As may be seen in these equations, we encounter with the collision integrals, i.e., $\Omega^{(1,1)*}$ and $\Omega^{(2,2)*}$ which have to be calculated. But these quantities have already been computed and tabulated for the SW and ST potentials (see appendices IV and V of Ref. [18]). We have used these values and fitted them into a polynomial; we found that the reported values for the collision integrals are quite well fitted into the following polynomials. For the ST we found that

$$\Omega^{(l,s)^*} = a + b\left(\frac{1}{2T^*}\right) + c\left(\frac{1}{2T^*}\right)^2 + d\left(\frac{1}{2T^*}\right)^3 + e\left(\frac{1}{2T^*}\right)^4 + f\left(\frac{1}{2T^*}\right)^5 + g\left(\frac{1}{2T^*}\right)^6 + h\left(\frac{1}{2T^*}\right)^7 + i\left(\frac{1}{2T^*}\right)^8 + j\left(\frac{1}{2T^*}\right)^9 \tag{11}$$

the reported data are fitted into Eq. (11), which is valid for $T^* > 0.25$, where $T^* = kT/\varepsilon$ is the reduced temperature and values of the coefficients of Eq. (11) with the correlation coefficients (R^2) are given in Table 2. For the SW for which the collisional integrals are given in terms of T^* and $1/\lambda$, are fitted as a function of T^* for different given values of λ Then $\Omega^{(l,s)*}$ are obtained from interpolations for the desired values of λ. Finally, we found that,

$$\Omega^{(l,s)^*} = a + b\left(\frac{1}{T^*}\right) + c\left(\frac{1}{T^*}\right)^2 + d\left(\frac{1}{T^*}\right)^3 + e\left(\frac{1}{T^*}\right)^4 + f\left(\frac{1}{T^*}\right)^5 \tag{12}$$

which is valid for $T^* > 1$. The values for the coefficients of Eq. (12) along with the correlation coefficients are given in Table 3. Now we may compute transport coefficients, i.e., viscosity, thermal conductivity, and self-diffusion coefficients. These calculations have been performed for all gases given in Table 1, using the potential parameters given in Table 1. We have shown in Figs. 4–6 the results of these calculations for Ne as an example, using the SW, ST, MST, MSW, ST–VW, and SW–VW potential models. Fig. 4 shows the calculated viscosity obtained by using the potential parameters of Table 1 along with the viscosity calculated by using the potential parameters obtained from viscosity coefficients (V–ST and V-SW) taken from Ref. [18] for comparison. The reported error bars for some experimental data are also shown. As may be seen, the results obtained from these new modified potentials are in much better agreement with experimental data than those obtained from the non-modified original model, especially at high temperatures. As may be seen in Fig. 4, the agreement between the three calculated viscosities with experimental data is very good at low temperatures, whereas at high temperatures only the modified models give closer result to

Table 2
Values of coefficients of Eq. (11) for $\Omega^{(1,1)^*}$ and $\Omega^{(2,2)^*}$ along with their correlation coefficients, R^2

Coefficients	$\Omega^{(1,1)^*}$	$\Omega^{(2,2)^*}$
a	1.00014	1.00007
b	0.31205	0.33600
c	1.87524	1.58426
d	−5.81541	−2.89715
e	9.99791	2.43445
f	−10.71868	−0.85739
g	7.24213	−0.17984
h	−2.99283	0.28312
i	0.69041	−0.09880
j	−0.06809	0.01213
R^2	1.00000	0.99999

Table 3
Values of coefficients of Eq. (12) for $\Omega^{(1,1)^*}$ and $\Omega^{(2,2)^*}$ along with their correlation coefficients, R^2

	$1/\lambda$		
	0.4	0.6	0.8
Coefficients of $\Omega^{(1,1)^*}$			
a	0.99999	0.99999	0.99999
b	0.55672	0.38962	0.21563
c	1.37396	0.49438	0.29865
d	−2.16354	−0.95208	−0.89896
e	1.52604	0.67188	0.81510
f	−0.42188	−0.17708	−0.26042
R^2	1.00000	1.00000	1.00000
Coefficients of $\Omega^{(2,2)^*}$			
a	0.99999	0.99999	0.99999
b	0.68941	0.31958	0.18096
c	1.25490	1.20073	0.80073
d	−0.48385	−1.75885	−1.59167
e	−0.65365	1.13802	1.20052
f	0.43490	−0.29427	−0.33854
R^2	1.00000	1.00000	1.00000

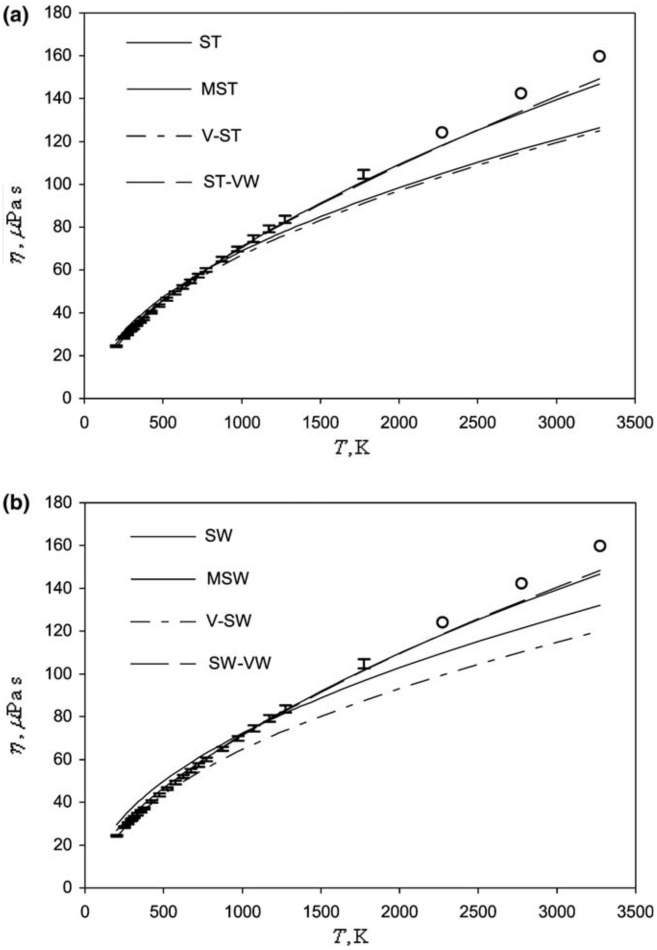

Fig. 4. (a) Comparison of experimental viscosity coefficient of Ne at $\rho \to 0$ with those calculated from the ST, V–ST, MST, and ST–VW potential models (the potential parameters of the two former cases are taken from Ref. [18] and the latter from Table 1). (b) Same as (a) for the SW, V–SW, MSW, and SW–VW Models.

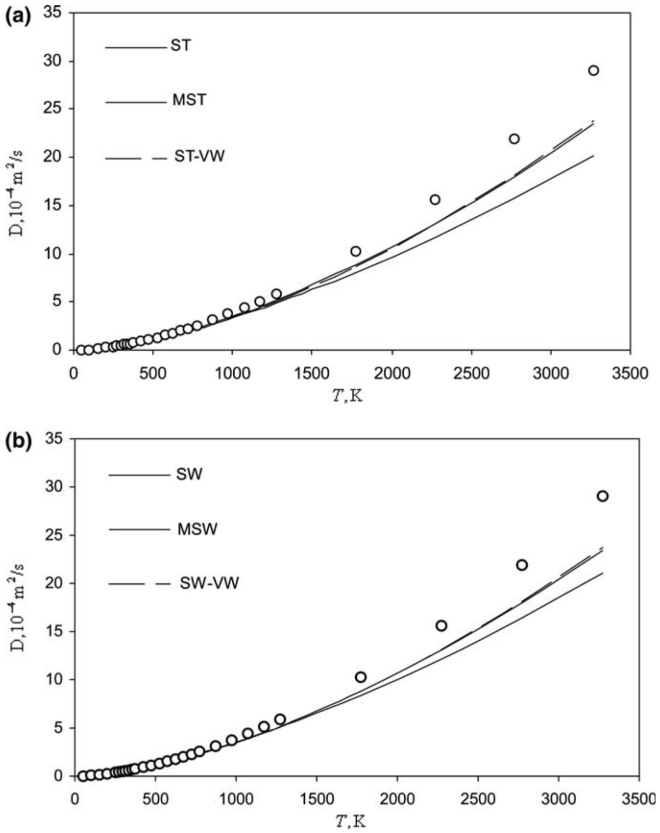

Fig. 5. (a) Same as Fig. 4(a) for self- diffusion coefficient. (b) Same as Fig. 4(b) for self-diffusion coefficient.

experimental values. At low temperatures, the attraction between molecules is more important than the repulsion; hence this branch of potentials plays the main role in the equilibrium and/or transport properties. At high temperatures, the repulsion between molecules is prevalent, hence has more contribution in the equilibrium and/or transport properties. But real molecules are fairly penetrable especially at high temperatures; actually there is no molecule to be completely rigid. Such penetration leads to inversion temperature of the second virial coefficient. Indeed the reason for the superiority of MSW and MST potential models with respect to hard-core ones (especially at high temperatures) is due to the fact that they allow the penetration occurs. For this reason, the modified models give a better agreement with experimental data than the hard-core potential models such as ST/SW in which molecule is assumed to be an impenetrable hard-core. Similar results may be obtained for other transport coefficients of gases whose MST and MSW potential parameters have been given in Table 1. Calculations for the other gases is done, for which we have merely reported the average absolute error percentage for their viscosity, thermal conductivity, and self diffusion coefficients in Table 4, which clearly shows the priority of the MSW and MST potentials with respect to their simple forms. As may be seen, the results of calculations for viscosity are in better agreement with experimental data than those obtained for thermal conductivity, and they are better than those for self-diffusion. We may note that the experimental data of viscosity are more accurate than those of thermal conductivity and also these are more accurate than those of self-diffusion [26]; hence comparison of the calculated viscosity with those of experimental values is more reasonable, for evaluation of a potential model. In addition, it is seen that the agreement with experimental data at low temperatures is better than that at high temperatures. In order to explain such a behavior, we may note that Eqs. (8)–(10) are the first order approximations of the transport properties. In order to obtain the Kihara correction terms, the calculated values must be multiplied in a factor larger than unity. For instance, viscosity may be given as

$$[\eta]_k = [\eta]_1 f_\eta^{(\mathrm{Kihara})} \tag{13}$$

where the multiplier factor, $f_\eta^{(\mathrm{Kihara})}$, is given as

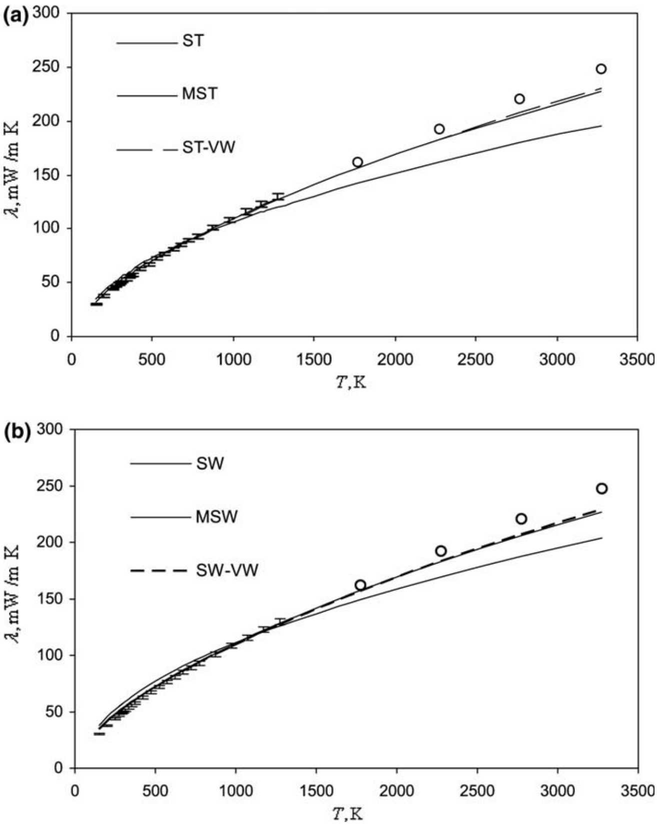

Fig. 6. (a) Same as Fig. 4(a) for thermal-conductivity coefficient. (b) Same as Fig. 4(b) for thermal-conductivity coefficient.

$$f_\eta^{(\text{Kihara})} = 1 + \frac{3}{49}\left[\frac{4\Omega^{(2,3)^*}}{\Omega^{(2,2)^*}} - \frac{7}{2}\right]^2 \tag{14}$$

We have used the values of the collision integrals for ST model, given in Refs. [18,19], to obtain the values of the Kihara approximation multiplier factor for the viscosity at some temperatures. The calculated values are given in Table 5. As shown in this table, $f_\eta^{(\text{Kihara})}$ increases with T. Therefore, we may expect that the significant deviation at high temperatures is mainly due to the correction terms which are not included in this work. Considering all above-mentioned facts, we may conclude that:

(a) There is no need to have two sets of potential parameters to calculate equilibrium (e.g. the second virial coefficient) and non-equilibrium properties (e.g. viscosity coefficient) if temperature dependence of the molecular diameter is taken into account; i.e. using the MSW and MST models instead of the SW and ST models.

(b) The fact that the calculated results based on the modified models of the SW and ST are in much better agreement with experimental data especially at high temperatures, indicates the superiority of the modified models for computation of equilibrium and non-equilibrium properties.

Table 4
Average absolute deviation of viscosity, thermal conductivity, and self-diffusion coefficients for some given gases

Gas	Temperature range (K)	ST	MST	SW	MSW
Average absolute deviation of viscosity (μPa s)					
He	150–523	0.95	0.67	0.88	0.59
	523–1273	5.84	1.57	4.81	1.61
	1273–2273	18.83	5.53	16.96	5.01
	2273–3273	33.22	12.21	30.72	10.88
Ne	150–523	2.83	0.91	5.21	2.06
	523–1273	2.11	0.47	2.73	0.87
	1273–2273	12.34	3.47	8.12	3.01
	2273–3273	26.27	9.46	21.09	9.39
O_2	150–523	0.27	0.98	3.49	0.81
	523–1273	0.67	1.26	2.64	0.66
	1273–2273	4.97	0.87	2.32	0.79
	2273–3273	11.57	1.69	7.85	1.17
N_2	150–523	0.14	0.71	2.78	0.50
	523–1273	0.96	0.69	2.00	0.64
	1273–2273	5.92	0.97	2.60	0.78
	2273–3273	13.69	3.54	9.11	3.33
CO	150–523	0.47	1.53	2.30	0.14
	523–1273	1.80	1.34	1.30	0.22
	1273–2273	6.95	1.37	3.55	0.61
	2273–3273	14.90	4.07	11.03	3.47
NO	150–523	0.12	1.13	3.12	0.56
	523–1273	0.89	1.47	2.31	0.45
	1273–2273	4.97	0.92	2.28	0.78
	2273–3273	11.61	1.74	8.03	1.21
System					
Average absolute deviation of thermal conductivity (mW/m K)					
He	150–523	7.15	5.98	6.56	5.22
	523–1273	46.67	13.40	38.68	13.77
	1273–2273	148.37	44.89	133.80	40.82
	2273–3273	260.93	97.40	241.46	87.07
Ne	150–523	4.14	1.24	7.82	3.10
	523–1273	3.34	0.76	4.05	1.17
	1273–2273	19.60	5.91	3.09	5.20
	2273–3273	41.27	15.29	33.27	15.19
Average absolute deviation of self-diffusion ($10^{-4} m^2/s$)					
He	150–523	0.41	0.48	0.35	0.48
	523–1273	3.56	2.53	3.27	2.54
	1273–2273	16.63	10.49	15.67	10.24
	2273–3273	40.09	25.51	38.24	24.58
Ne	150–523	0.02	0.05	0.02	0.04
	523–1273	0.42	0.36	0.29	0.33
	1273–2273	2.42	1.58	2.06	1.56
	2273–3273	6.34	4.00	5.65	4.02
O_2	150–523	0.02	0.04	0.01	0.02
	523–1273	0.16	0.17	0.08	0.12
	1273–2273	0.87	0.62	0.70	0.54
	2273–3273	2.42	1.54	2.12	1.49
N_2	150–523	0.02	0.04	0.01	0.02
	523–1273	0.17	0.16	0.08	0.12
	1273–2273	0.94	0.60	0.71	0.55
	2273–3273	2.58	1.57	2.15	1.56
CO	150–523	0.03	0.04	0.01	0.02
	523–1273	0.20	0.17	0.11	0.13
	1273–2273	1.01	0.63	0.80	0.57
	2273–3273	2.70	1.62	2.43	1.58

(*continued on next page*)

Table 4 (*continued*)

Gas	Temperature range (K)	ST	MST	SW	MSW
NO	150–523	0.03	0.04	0.01	0.02
	523–1273	0.16	0.17	0.08	0.13
	1273–2273	0.90	0.63	0.72	0.54
	2273–3273	2.56	1.63	2.26	1.58

Table 5
The multiplier factor for the Kihara second order approximation of viscosity coefficient

T^*	$f_\eta^{(\text{Kihara})}$
0.25	1.0023
0.50	1.0025
1.00	1.0035
2.00	1.0072
4.00	1.0112
10.00	1.0139
16.67	1.0145
25.00	1.0148
50.00	1.0151
∞	1.0153

5. Conclusion

We have presented in this paper a new method of modifying hard-core potentials in such a way that one can use them to predict correctly the equilibrium and non-equilibrium properties of real fluids by only *one* set of potential parameters. By the fact that the molecule diameter becomes smaller when temperature increases, we introduce a new expression for the variation of diameter with temperature that incorporates this effect. Then we show that the second virial coefficient of the modified –ST and –SW, also ST–VW, and SW–VW can correctly represent the experimental data of real fluids in an extremely wide temperature range, including the inversion temperature. By obtaining the parameters of the modified potential models by fitting the experimental data of the second virial coefficient into the new purposed expressions, we have calculated the non-equilibrium properties of real fluids, i.e., viscosity, thermal conductivity, and self-diffusion coefficients. When these calculations were performed we found that the obtained results were in a closer agreement with experimental data, that is, there is no need to have two sets of potential parameters for the equilibrium and non-equilibrium properties of real fluids when the temperature dependence of the molecular parameter are taken into account, correctly. Also, using the Verlet–Weis equation, along with ST and SW models gives the transport coefficients as accurately as those obtained from the MST and MSW (see Figs. 4–6). Such a conclusion is reasonable, because of the fact that an accurate potential, like the Aziz and Slaman [27,28] for the noble gases, is expected to give accurate results for both the equilibrium and transport properties. We expect also that this method of modifying the ST/SW potential models can equally well applied to other hard-core potential models such as triangular-well and trapezoidal-well potentials. As shown in Fig. 4, the set of potential parameters obtained and reported for the non-equilibrium properties are appropriate for low temperatures only. Using such a set for high temperatures may lead to a significant error.

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References

[1] M. Khanpour, G.A. Parsafar, B. Najafi, J. Phys. Soc. Jpn. 73 (5) (2004) 1197.
[2] M. Khanpour, G.A. Parsafar, B. Najafi, Fluid Phase Equilibria, submitted for publication.
[3] S.B. Yuste, A. Santos, J. Chem. Phys. 101 (3) (1994) 2355.
[4] L. Verlet, J.J. Weis, Phys. Rev. A5 (1972) 939.
[5] J. Largo, J.R. Solana, Int. J. Thermophys. 21 (4) (2000) 899.
[6] N. Kern, D. Frenkel, J. Chem. Phys. 118 (21) (2003) 9882.
[7] J. Largo, J.R. Solana, Phys. Rev. E 67 (2003) 066112.
[8] A. Tiwari, K.N. Khanna, Mol. Phys. 103 (5) (2005) 621.
[9] J. Largo, J.R. Solana, S.B. Yuste, A. Santos, J. Chem. Phys. 122 (2005).
[10] H.L. Vörtler, W.R. Smith, J. Chem. Phys. 112 (2000) 5168.
[11] D.M. Heyes, P.J. Aston, J. Chem. Phys. 97 (8) (1992) 5738.
[12] G. Orkoulas, A.Z. Panagiotopoulos, J. Chem. Phys. 110 (1999) 1581.
[13] J. Largo, J.R. Solana, Mol. Simul. 29 (6–7) (2003) 363.
[14] L.A. del Pino, A.L. Benavides, A. Gil-Villegas, Mol. Simul. 29 (6–7) (2003) 345.
[15] S. Labik, V. Jirasek, A. Malijevsky, M. Lisal, Mol. Phys. 98 (2000) 2033.
[16] S.K. Ma, Statistical Mechanics, World Scientific, Singapore, 1985.
[17] B. Roulet, J.-O. Goussard, Am. J. Phys. 61 (1993) 845.
[18] J.O. Hirschfelder, C.F. Curtiss, R.B. Bird, Molecular Theory of Gases and Liquids, John Wiley & Sons, 1964.
[19] D.A. McQuarrie, Statistical Mechanics, Harper and Row, 1976.
[20] J.J. Hurly, M.R. Moldover, J. Res. NIST 105 (5) (2000) 667.
[21] P. Nowak, R. Kleinrahm, W. Wagner, J. Chem. Thermodyn. 29 (1997) 1137.
[22] J. Klimeck, R. Kleinrahm, W. Wagner, J. Chem. Thermodyn. 30 (1998) 1571.
[23] C. Evers, H.W. LÖsch, W. Wagner, Int. J. Thermophys. 23 (6) (2002) 1411.
[24] J. Kestin, K. Knierim, E.A. Mason, B. Najafi, S.T. Ro, M. Waldman, J. Phys. Chem. Ref. Data 13 (1) (1984) 229.
[25] A. Boushehri, J. Bzowski, E.A. Kestin, J. Phys. Chem. Ref. Data 16 (3) (1987) 445.
[26] B. Najafi, E.A. Mason, J. Kestin, Physica 119A (1983) 387.
[27] R.A. Aziz, M.J. Slaman, J. Chem. Phys. 92 (2) (1990) 1030.
[28] R.A. Aziz, M.J. Slaman, J. Chem. Phys. 94 (12) (1991) 8047.