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Influence of quantum effect on deviation from linear isotherm regularity

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Hard sphere model.

Abstract A general regularity was found based on an effective pair potential of Lennard-Jones LJ (12, 6), for both dense, nonmetallic and nonionic fluids and solids according to which $(Z - 1)v^2$ linearly varies with respect to ρ^2 for each isotherm, and this equation of state (EoS I) is known as LIR. However, despite the fact that Ne is a simple spherical species, unexpectedly, its solid and liquid phases both show a significant deviation from EoS I. In this work, we have investigated the accuracy of the EoS I for other systems, including quantum light molecules, such as D_2 , H_2 and He, in both fluid and solid states at different temperatures. Like Ne, we have noticed that these systems do not well obey the EoS I. Then, using a simple van der Waals equation, it is shown that significant deviations in dense systems of light molecules are because of the unbalance between repulsive and attractive interactions, due to the importance of the quantum effect. Also, we notice that at higher temperatures and for heavier species, LIR is valid due to a decrease in the quantum effect. We have shown that the hard-sphere fluid remarkably deviates from LIR. Two other EoSs have also been examined.

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1. Introduction

Linear Isotherm Regularity (LIR) was reported based on the effective pair potential of Lennard-Jones LJ (12, 6), for a variety of pure dense fluids and fluid mixtures [1–6], for densities greater than Boyle density and temperatures lower than twice that of the Boyle temperature; the temperature at which the second virial coefficient is zero. Also, the LIR Equation of State (EoS) holds for solids including nonmetallic and nonionic compounds [7]. The regularity states that isotherms of $(Z - 1)v^2$ are linear with ρ^2 where $Z = \rho/pRT$ is the compressibility factor and $\rho = 1/v$ is the molar density.

Although this EoS gives a good description for a wide range of fluids and solids, it has recently been found that isotherms of $(Z - 1)v^2$, with respect to ρ^2 , show significant deviations from

linearity for some types of compound. Because of the fact that the LJ (12, 6) is suitable for spherical molecules, nonspherical molecules, such as long-chain organic compounds, show a deviation from the linear behavior of the LIR, in such a way that the deviation becomes more significant when the chain becomes longer. For this reason, a new method, called the group contribution, via the Modified Linear Isotherm Regularity (MLIR), was introduced to predict the volumetric properties of long-range compounds [8,9]. Another type is liquid metals, for which a remarkable deviation has been observed when the metal–nonmetal transition takes place [3,10]. Ghatee and Bahadori [10] especially showed deviation from LIR for liquid Cs. They derived another EoS, on the basis of an effective pair potential of LJ (6, 3), according to which the isotherm $(Z - 1)v^2$ is linear in terms of $1/\rho$. Then, Shokouhi et al. indicated that this EoS gives an excellent fit to experimental pvT data of metallic and ionic solids, while LIR is not appropriate for this class of solids [7]. Also, Alavi reported that experimental pvT data of water show a systematic deviation from the linear prediction of LIR [11]. Even though Ne is a simple spherical molecule that belongs to normal compounds, unexpectedly, solid and liquid Ne indicates a significant deviation from LIR [12]. Recently, however, a general EoS based on an effective near-neighbor pair interaction of the extended LJ (12, 6, 3) type, has been introduced for a wide variety of fluids and solids with different

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properties, ranging from Ne to long-chain hydrocarbons and to ionic and metallic solids.

The purpose of this research is to give answers to the following questions:

1. Why does the fluid and solid Ne show noticeable deviations from LIR?
2. Do other quantum light species, like D_2 , H_2 and He, show large deviations from this regularity?
3. How is the magnitude of deviation from the LIR related to molecular weight and temperature?
4. Does hard sphere fluid deviate from the mentioned linearity?
5. Which of the mentioned equations of state has the best agreement with experimental data of quantum light molecules?

2. Linear isotherm regularity equation of state (LIR EoS)

The LIR EoS was derived on the basis of the assumption that the Average Effective Pair Potential (AEPP) is a Lennard-Jones (12, 6) function. Using such AEPP, the configuration potential energy may be given as:

$$U = \frac{N}{2} z \left(\frac{C_{12}}{\bar{r}^{12}} - \frac{C_6}{\bar{r}^6} \right), \quad (1)$$

where N is the number of molecules, z is the mean coordination number, \bar{r} is the average distance between the nearest neighbors, and C_6 and C_{12} are constants, depending on the molecular identity. For dense systems that are complicated at the molecular level, due to the significance of many-body interactions, such a potential function (AEPP) is considered to be the interaction of the nearest neighboring molecules, to which all long range interactions and also the influence of the medium on the charge distributions of two neighboring molecules are added [2]. The Lennard-Jones (12, 6) potential function applies to fluids with short range interactions, undergoing dispersive interactions as a dominating contribution. The interest in the Lennard-Jones (12, 6) function is due to its simple form that facilitates its integration and differentiation for derivation of an analytical form for thermodynamic functions. With this assumption and on the basis of an exact thermodynamic expression, known as the exact thermodynamic equation of state, the LIR EoS was obtained as [1]:

$$(Z - 1)v^2 = A + B\rho^2. \quad (2)$$

We will refer to it as EoS I, hereafter, where A and B are the LIR parameters, which depend on temperature as:

$$A = A_2 + \frac{A_1}{T}, \quad (3)$$

$$B = \frac{B_1}{T}, \quad (4)$$

where A_1 and B_1 are related to the attractive and repulsive terms of the average effective pair potential and A_2 is related to the nonideal thermal pressure.

The LIR is able to explain many experimentally known regularities for a variety of dense fluids; both compressed liquids ($T < T_C$) and dense supercritical fluids. The temperature range at which the linear relation holds is $T < 2T_B$, where T_B is the Boyle temperature; the temperature at which the second virial coefficient is zero. Also, it has been found that the linearity holds when $\rho > \rho_B \approx 1.8\rho_C$, where ρ_C is the critical density. The upper density limit for linearity in the liquid region is the freezing line, and is at least almost twice the Boyle density for supercritical fluids. It was recently shown that EoS I is valid for nonmetallic and nonionic solids [7] as well.

2.1. Comparison with van der Waals EOS

Although the van der Waals equation does not apply to dense fluids and solids, it can be checked for compatibility with the linearity of $(Z - 1)v^2$ versus ρ^2 . Then, its success or failure can indicate what features of an EoS are crucial for the explanation of a phenomenon. The van der Waals EoS can be written as [1]:

$$(Z - 1)(v/b)^2 = \frac{1}{bp} \left(\frac{1}{1 - b\rho} - \frac{a}{bRT} \right), \quad (5)$$

where b and a are associated with repulsive and attractive interactions, respectively, and a/bR is equal to T_B . At low densities, where $b\rho \rightarrow 0$, the term $(a/bRT)(b\rho)^{-1}$ makes Eq. (5) approach negative infinity, which can be related to the attraction forces. At high densities, where $b\rho \rightarrow 1$, the intermolecular repulsion is dominant, so the term $(1 - b\rho)^{-1}$ causes the expression to diverge. However, within intermediate densities ($b\rho \approx 0.5$), the linear region results in a balance between attraction and repulsion. Actually, the linear portion does not depend on any special features of molecular interaction, but only on the existence of long-range attraction and short-range repulsion.

2.2. Experimental test of EoS I for quantum light molecules

Owing to the fact that Ne is in the group of ordinary pure compounds, we would expect that $(Z - 1)v^2$ versus ρ^2 for its isotherms would become linear for both fluid and solid states. However, Parsafar et al. [12] have recently shown that EoS I unexpectedly shows a significant deviation from LIR linearity at 298 K, if a wide density range is considered. Since Boyle temperature and density [13,14] for Ne are about 120.32 K and 12.8 mol/L, respectively, we have examined the accuracy of EoS I for the fluid Ne at 200 K, which is lower than twice that of the Boyle temperature and in a density range of 15–62 mol/L. The pressure range of the experimental data [14] used for the examination is 30–400 MPa. As shown in Figure 1(a), it is obvious that EoS I cannot be fitted into the data.

Due to the fact that Ne is a relatively light atom with weak dispersion interaction, we have attempted to investigate the accuracy of the LIR EoS for the other systems including quantum light molecules, such as D_2 , H_2 and He, in the fluid and solid states at different temperatures. First, we have used experimental pVT data [14] to check the accuracy of the EoS I for the fluid D_2 at 200 K, the Boyle temperature and density [13,14] for D_2 are 227.4 K and 31.18 mol/L. The data are plotted in the density range of 31–43 mol/L and pressure range of 101–206 MPa (see Figure 1(b)).

As D_2 is classified in the group of normal fluids, it is expected to obey the LIR EoS, but as shown in Figure 1(b), the fluid D_2 , like Ne, shows a remarkable concave deviation with the coefficient of determination $R^2 = 0.9491$. Of course the deviation for D_2 is smaller than that of Ne, which may be due to the smaller density range of data. Similar investigations have been done for H_2 and He in both fluid and solid states as well. The results of such investigations are summarized in Table 1.

As may be seen in Table 1, it is obvious that dense systems of light molecules do not obey the LIR regularity. As mentioned in Section 2.1, the van der Waals equation can offer some explanations for the deviation of Ne and other quantum light molecules, like D_2 , H_2 and He. On the basis of the van der Waals EoS, $(Z - 1)v^2$ can be written as [12]:

$$(Z - 1)v^2 = b^2 + (b - a/RT)\frac{1}{\rho} + b^3\rho + b^4\rho^2 + \dots, \quad (6)$$

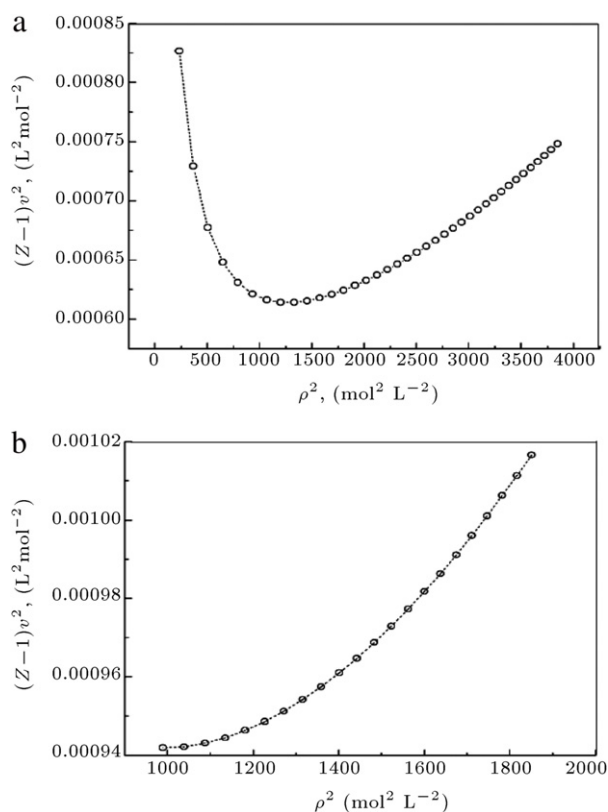


Figure 1: The 200 K isotherm $(Z - 1)v^2$ versus ρ^2 for (a) fluid Ne, and (b) fluid D_2 . Note that EoS I deviates significantly from the linearity.

Table 1: Examining the accuracy of the LIR EoS for quantum light molecules over the given pressure range (Δp) and density range ($\Delta \rho$) along with the coefficient of determination (R^2) associated with each fit.

	Fluid			
	T (K)	Δp (MPa)	$\Delta \rho$ (mol/L)	R^2
D_2	200	101–206	31–43	0.9491
He^a	40	20–100	35–68	0.9848
H_2^b	50	12–220	28–57	0.9944
	Solid			
	T (K)	Δp (kg/cm ³)	$\Delta \rho$ (mol/L)	R^2
D_2^c	4	0–20000	51–105	0.9516
He^c	4	0–20000	58–156	0.9339
H_2^c	4	0–20000	44–99	0.9569

^a [14].

^b [14,15].

^c [16].

where b and a are the van der Waals parameters that are attributed to repulsive and attractive interactions, respectively. In Eq. (6), the $1/\rho$ term depends on both b and a . Therefore, if the terms b and a/RT largely cancel each other, the $1/\rho$ term will be insignificant, and the EoS I works well. But, probably for quantum light molecules, due to the existence of a significant quantum effect in addition to a weak dispersion interaction, the term $b - a/RT$ does not vanish and, therefore, the $1/\rho$ contribution becomes important. As an example, the quantum effect in H_2 as a fermion particle appears as a repulsion that causes a higher pressure for Fermi–Dirac ideal gas than that of classical ideal gas under the same circumstances [17]. In general, this means that the quantum effect might weaken

Table 2: Fitting EoS I in experimental data for H_2 and CH_4 at some given temperatures.

Substance	T (K)	Δp (MPa)	$\Delta \rho$ (mol/L)	R^2
H_2	4 ^a	0–1961	44–99	0.9560
	50 ^b	12–220	28–57	0.9944
	100 ^b	40–300	29–57	0.9978
	150 ^b	65–1000	29–74	0.9998
	200 ^b	90–1000	29–67	0.9930
	210 ^b	100–1000	29–71	0.9910
	250 ^b	120–1000	30–70	0.9620
CH_4	300 ^b	140–800	29–62	0.5830
	100 ^c	0.1–12	27.41–27.90	1.000
	120 ^c	0.2–20	25.56–26.71	1.000
	150 ^c	1.2–200	22.36–30.21	1.000
	200 ^c	16–200	18.74–28.38	1.000

^a [16].

^b [14].

^c [18].

Table 3: Fitting EoS I in experimental data for given isotherms of some species.

	T (K)	Δp (kg/cm ²)	$\Delta \rho$ (mol/L)	R^2
Diatomic molecules				
H_2	4	0–20000	44–99	0.9569
D_2	4	0–20000	51–105	0.9516
N_2^a	65	0–19000	34–51	0.9841
Monoatomic molecules				
He	4	0–20000	58–156	0.9339
Ne	4	0–20000	71–106	0.9974
Ar ^a	77	0–19000	41–57	0.9992

^a [16].

the balance between repulsion and attraction interactions that consequently leads to the deviation from LIR EoS.

2.3. Effect of molecular weight and temperature on the magnitude of deviation from the LIR

The magnitude of the quantum effect depends on the molecular weight and temperature in such a way that this effect is more important at lower temperatures and for lighter species, such as D_2 , H_2 and He. Therefore, it is expected that the deviation from the linearity behavior of EoS I is more at lower temperatures due to the quantum effect. As an example, the value of the coefficient of determination for the fit to the EoS I for some isotherms of H_2 and CH_4 [18] is given in Table 2.

From the value of R^2 given in Table 2, we may notice that H_2 at 4 K shows a noticeable deviation from EoS I, while it behaves more according to EoS I when temperature increases. However, for temperatures higher than 200 K, its consistency with EoS I decreases, so that the deviation from linearity at 300 K is quite significant; such a temperature is larger than twice that of the Boyle temperature. A similar situation was observed for D_2 and Ne. The validity of LIR is examined for methane, as well. The result for some isotherms is given in Table 2. From such a result ($R^2 = 1.000$), we may conclude that the quantum effect for methane is insignificant at least at the given temperatures. Considering the fits to EoS I for monoatomic and diatomic molecules, it is interesting to check the predictive power of EoS I for some other species (the results are given in Table 3). One can see that EoS I is more appropriate for heavier molecules.

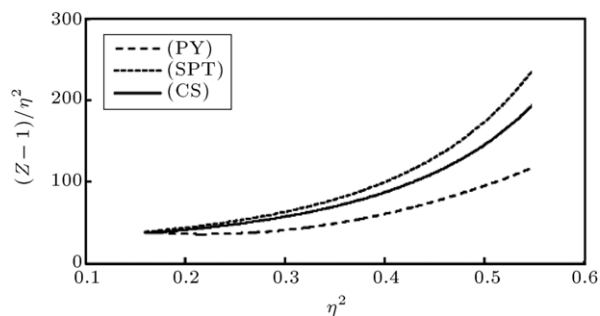


Figure 2: Significant deviations of the PY, SPT and CS EoSs from the LIR linearity.

3. Validity of the LIR for systems with significant unbalance forces

To verify the reason mentioned in part 2b, regarding deviation of quantum light molecules from the LIR EoS, we may use the hard sphere fluid that plays a central role in almost all theories of liquid state chemical physics, for example, in perturbation theories, in statistical associating fluid theories, etc. [19]. The hard sphere model is simply defined as impenetrable spheres that cannot overlap in space. They mimic an extremely strong repulsion that atoms and spherical molecules experience at very close distances. On the other hand, there is no contribution of attraction in the potential function of the hard sphere model, and the behavior of repulsion in this model is roughly similar to real molecules. The hard sphere potential function is:

$$\begin{aligned} U(r) &= \infty, & r < \sigma, \\ U(r) &= 0, & r \geq \sigma, \end{aligned} \quad (7)$$

where r is the intermolecular separation and σ is the molecular diameter. Therefore, the hard sphere fluid is a simple model in which the forces are quite unbalanced.

Using the first several exact virial coefficients of hard sphere fluid along with the asymptotic expansion method of Percus–Yevick (PY), Scaled Particle Theory (SPT) and Carnahan–Starling (CS), the following EoSs have been derived [19,20]:

SPT EoS:

$$Z = \frac{1 + \eta + \eta^2}{(1 - \eta)^3}. \quad (8)$$

PY EoS:

$$Z = \frac{1 + 2\eta + 3\eta^3}{(1 - \eta)^2}. \quad (9)$$

CS EoS:

$$Z = \frac{\eta^3 - \eta^2 - \eta - 1}{(\eta - 1)^3}, \quad (10)$$

where $Z = p/\rho kT$ is the compressibility factor, $\eta = \pi/6\rho\sigma^3$ is the packing fraction, ρ is the number density, p is the pressure, T is the absolute temperature, σ is the diameter of the hard sphere, and k is the Boltzmann constant. As shown in Figure 2, all mentioned equations of state (SPT, PY and CS) deviate significantly from the linearity of EoS I, within $\eta \approx 0.5$ – 0.74 for normal liquid density (Note that the hard sphere has only one fluid phase [11]). Since the hard sphere model only assumes repulsive forces among molecules, it is a good example with unbalanced forces for which the deviation from the LIR is expected.

Table 4: The coefficients of determination for the fits of EoS II and EoS III to experimental data of the light species at the given temperature.

Substance	Physical state	T (K)	R ² for EoS II	R ² for EoS III
D ₂	Fluid	200	0.8799	0.9996
He	Fluid	40	0.8509	1.000
H ₂	Fluid	50	0.9456	0.9999
D ₂	Solid	4	0.9948 ^a	0.9985
He	Solid	4	0.9824	0.9965
H ₂	Solid	4	0.9896	0.9962

^a For solid D₂; experimental data are shown systematic deviation of EoS II.

4. Predictive power of some other equations of state

For some ionic and metallic dense fluids and solids, especially within the metal–nonmetal transition range, the thermodynamic properties and derived equation of state, based on Lennard–Jones (12, 6), lose their applications, because they introduce an unrealistic hard repulsion that is suitable for fluids with short-range interactions, while ionic and metallic fluids highly interact with an appreciable Coulombic feature. Hence, the long-range dispersive interaction potential is underestimated if treated by only a simple sixth power of the inverse of interatomic distance [10]. To consider this effect, and because of the electrostatic interaction energies between two molecules with non-symmetrical charge distribution, we see the interaction between dipole moments of these two molecules; we may take this effect into account using the \bar{r}^{-3} term. On the other hand, it is found that the interionic dipole–dipole interaction has an effect on softening the repulsive part of the pair potential [21,22]. From the discussion mentioned above, eventually, Lennard–Jones (6, 3) is supposed for ionic and metallic dense fluids and solids [7,10].

$$u(r) = A\epsilon \left[\left(\frac{\sigma}{\bar{r}} \right)^6 - \left(\frac{\sigma}{\bar{r}} \right)^3 \right], \quad (11)$$

where A is a constant, ϵ is the potential well depth and σ is the diameter of the molecule [10]. The final form of the equation of state derived on the basis of LJ (6, 3) for these kinds of dense system is as (which is hereafter referred to as EoS II) [10]:

$$(Z - 1)v^2 = c + \frac{d}{\rho}, \quad (12)$$

where c and d are temperature-dependent parameters, as $c = c_2 + c_1/T$ and $d = d_1/T$, with d_1 and c_1 related to the attractive and repulsive parts of the effective potential, respectively. Since there are no obvious long-range interactions or correlations in dense systems with light molecules, and because they are normal fluids with dispersion interaction, we may expect that EoS II cannot justify the behavior of these systems. We have used experimental data of light molecules to examine the accuracy of this EoS. The results of such examinations are presented in Table 4.

In a real fluid, there are dipole–dipole interactions including permanent and/or induced dipoles, London dispersion interactions and some other interactions, so that in different fluids, the contributions of these interactions are different. For example, in a fluid like Ar, there are only London dispersion interactions, while in some fluids, like CO, there are dipole–dipole interactions in addition to London interactions. As a result, recently, a general equation of state was suggested on the basis of an effective near-neighbor pair potential of an extended Lennard–Jones

(ELJ) (12, 6, 3), which includes both the ρ^2 dependence of EoS I and the $1/\rho$ dependence of EoS II. It also appears to work well for all types of solid and fluid, even for those that do not work with EoS I and EoS II. The ELJ (12, 6, 3) potential function is given by [12]:

$$U = \frac{N}{2}z \left(\frac{C_{12}(T)}{\bar{r}^{12}} + \frac{C_6(T)}{\bar{r}^6} + \frac{C_3(T)}{\bar{r}^3} \right), \quad (13)$$

where \bar{r} , which is given by $v^{1/3}$, is a mean near-neighbor distance and z is the average number of nearest neighbors, which is not dependent on density, and the $C_i(T)$ are temperature-dependent parameters. The \bar{r}^{-12} and \bar{r}^{-3} terms are related to the short-range repulsive and long-range attractive interactions, respectively. On the basis of ELJ (12, 6, 3), a general equation of state has been obtained as follows [12] (which will, hereafter, be referred to as EoS III):

$$(Z - 1)v^2 = e + \frac{f}{\rho} + g\rho^2, \quad (14)$$

where e, f and g are temperature dependent parameters. The EoS III is a universal equation of state that gives a good description of all types of fluid and solid, including nonpolar, polar, hydrogen-bonded, metallic compounds and ionic systems. This EoS works well in a wide density range, and there are no upper and lower density limitations for this EoS. For solids, there appear to be no pressure and temperature limitations as well. Since experimental data of the quantum light molecules do not well obey either EoS I or EoS II, we have examined the validity of this new equation of state for them. The results for Ne and D₂ fluids are plotted in Figure 3(a) and (b), respectively. We see that EoS III gives excellent agreement with experimental data of fluid Ne and fluid D₂ at 200 K. Similar investigations have been made for He and D₂, as well. The fitting results are summarized in Table 4.

As shown in Table 4, EoS II, like EoS I, is not accurate for quantum light molecules, but it is evident that EoS III has very good agreement with isotherms considered for these systems (the value of coefficient of determination verifies this point). In regard to the van der Waals expression, given in Section 2.2, the terms b and a/RT do not omit each other, and both $1/\rho$ and ρ^2 contributions must be taken into account. Therefore, EoS III, which includes both terms, gives a good description of the behavior of these systems (see Table 4).

5. Discussion and conclusion

In this paper, we have investigated the accuracy of LIR (EoS I) for some types of normal spherical molecule called quantum light systems including Ne, He, H₂ and D₂ in both fluid and solid states. Although LIR has been derived on the basis of the effective pair potential of Lennard-Jones (12, 6), which is appropriate for simple spherical nonmetallic and nonionic compounds, unexpectedly, we noticed that the dense systems of light molecules show remarkable deviations from EoS I (see Figure 1 and Table 1). As seen in Eq. (2), LIR only includes the term ρ^2 . Recently, however, a general equation of state (EoS III), based on an effective near-neighbor pair interaction of the ELJ (12, 6, 3) type, has been introduced for a wide variety of fluids and solids, as we have shown in Figure 3 and Table 4, which gives an excellent fit to experimental pVT data of dense systems with light molecules. The EoS III includes both $1/\rho$ and ρ^2 contributions, where ρ^2 is related to short-range interaction, and the $1/\rho$ term is particularly important

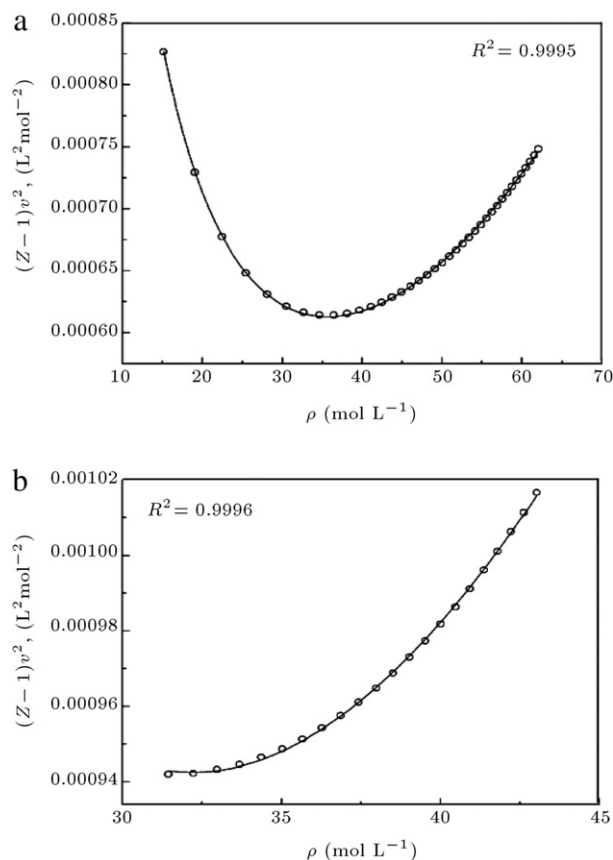


Figure 3: The excellent fits of EoS III to experimental data of (a) fluid Ne and (b) fluid D₂ at 200 K. (compared to Figure 1).

in systems where long-rang correlations are expected, such as ionic and metallic fluids and solids. This term is related to the \bar{r}^{-3} contribution in the effective pair potential. However, we have found that the $1/\rho$ term is essential to fit experimental data for quantum light molecules. Since there are no obvious long-rang interactions or correlations in these systems, the results suggest that the above explanation is not complete. Looking for a possible reason as to why the $1/\rho$ contribution is crucially important for some substances but not at all for others, we expand the van der Waals equation for $(Z - 1)v^2$, and we noted that the coefficient of the $1/\rho$ term contains two opposing contributions from the repulsive and attractive parts of the intermolecular force. If these contributions exactly cancel each other out, the term of $1/\rho$ will be unimportant, and EoS I works well for instance for Ar. But, for Ne and other quantum light molecules, there is not a balance between repulsion and attraction, and the $1/\rho$ term will be significant in addition to ρ^2 ; therefore, EoS III gives a good description for these systems. For some materials, such as ionic and metallic fluids and solids, the $1/\rho$ term even dominates the ρ^2 term, so that EoS II, given in Eq. (12), works well. As we can see in Tables 2 and 3, at higher temperatures and for heavier species, EoS I becomes valid due to a decrease in the quantum effect. To verify such a conclusion, related to a deviation of the light molecules from EoS I we have shown that the hard-sphere fluid remarkably deviates from EoS I for which only repulsive forces exist among molecules, and therefore it is obvious that there is no balance between repulsion and attraction in this model at all (see Figure 2). As shown in Figure 2, the Percus–Yevick, Scaled Particle Theory, and Carnahan Starling (CS) EoSs based on the hard sphere model, all indicate significant deviations from EoS I.

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