

Contribution of Dispersive Second Virial Coefficient of Liquid Cesium Metal

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This study demonstrates that the slope B' of the linear isotherm of $(Z - 1)V^{8.5/3}$ versus $(1/\rho)^{4.5/3}$ for liquid cesium metal has a contribution from the noncentral part of interaction potential energy function, where Z is the liquid compressibility and $V = 1/\rho$ (where ρ is the molar liquid density). First, it is shown macroscopically that B' conforms to the second virial coefficient B_2 . However, it is exceedingly smaller at low temperatures and approaches close agreement at high temperatures. The substitution of B' for B_2 in the Ihm–Song–Mason statistical mechanical equation of state has led to a prediction of the liquid density of cesium metal within $\pm 5\%$ in the temperature range of 300–1400 K. The fact that the Ihm–Song–Mason equation of state has been derived for nonpolar and slightly polar fluids, with the dispersive interaction potentials as their major intermolecular interaction, has led us to propose that B' is related to the interaction potential that is contributed from dispersive interaction between the Cs atoms. Although a microscopic approach, we have used the perturbation method in the second part and calculated the noncentral second virial coefficient (B_2^{angular}). Angular distribution of the electron density is approximated by the usual multipoles of the electrostatic nature. The Gaussian 98W program at the LanL2DZ and LanL2MB levels of theory has been used to assign and determine components of the multipoles moment required for the calculation of B_2^{angular} . The Boltzmann factor, which comprises the pair potential function used to derive the isotherm, is applied as the energy distribution required for the calculation of B_2^{angular} . The results of the first and second parts of the calculations show that dispersive interaction, which can be described and approximated by the multipole expansion of the noncentral electron density of the Cs atom, contributes to B' .

1. Introduction

Since the time when the linear regularity isotherm was devised to describe the thermodynamic properties of normal liquids,¹ the role and the meaning of its two parameters have been brought into question. In cases where it was applied to simple atomic and molecular liquids in which their intermolecular interactions originate from dispersion forces, the intercept (of the original linear regularity isotherm) was known to conform to the second virial coefficient (B_2).¹ Application of the same theory, with some modification, and using a characteristic potential function for alkali metals, in particular for liquid cesium metal, has led us to the characteristic linear isotherm from which the thermodynamic properties of the compressed liquid cesium can be specified. This method permits the molecular parameters of the pair potential function to be obtained (e.g., the Lennard-Jones (LJ) (6–3) potential function used to derive the isotherm) in close agreement with the molecular parameters of the interaction potential obtained by the corresponding spectroscopic method.^{2,3} In particular, the slope (B) of this linear isotherm mimics the corresponding theoretical B_2 value, although its absolute value is smaller (by up to 4 orders of magnitude at the melting temperature and by a factor of $1/2$ at the critical temperature). Interestingly, both B_2 and B span in the negative region,⁴ so much so that the Boyle temperature (T_B) is never reached. For liquid cesium, we have

shown that the LJ (8.5–4) potential function also leads to a promising linear isotherm over the entire liquid range. Again, the slope of this isotherm (B') conforms to the theoretical B_2 value.

This study proposes and demonstrates that B' conforms and contributes to the B_2 value, proportional to the nonspherical dispersion interaction of fluid particles, in particular in liquid cesium. This proposal primarily is supported by the fact that B' values deviate markedly from the $\langle B_2 \rangle$ value of cesium, which is calculated using the experimental diatom fraction,⁵ and from the B_2 value, which is calculated using the quantum mechanical *ab initio* pair potential function.^{6,7} The absolute value of B' is smaller than that of $\langle B_2 \rangle$ by 3–4 orders of magnitude at low temperatures; however, it comes into close agreement with $\langle B_2 \rangle$ at high temperatures.

The primary test of the proposal is achieved by the fact that B' is applicable to the statistical mechanical equation of state in which B_2 is the central quantity for nonpolar and slightly polar dense liquids. In the second part of this investigation, the magnitude of B' is used as the contribution to B_2 from the noncentral part of the Cs–Cs interaction potential and the calculation of B_2^{angular} is formulated. This formulation actually involves the average value of the 2^n -pole moments interaction potential, where n is related to the degree of a particular multipole. The Boltzmann factor, which comprises the potential function used to derive the linear isotherm, is applied as the energy distribution function.

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2. The Isotherm for Liquid Cesium

We have previously demonstrated that the thermodynamic properties of liquid cesium can be described by the isotherm, using the LJ (6–3) potential function.² In the same way, we have applied the two-parameter LJ (8.5–4) potential function, which has been reported by fitting to an experimental internal pressure of dense liquid cesium, including data at the proximity of absolute zero temperature, and derived the following isotherm:^{8,9}

$$(Z - 1)V^{8.5/3} = C' + B'\left(\frac{1}{\rho}\right)^{4.5/3} \quad (1)$$

where Z is the compression factor, V the molar volume, and ρ the molar density. C' and B' respectively are the intercept and the slope of $(Z - 1)V^{8.5/3}$ versus $(1/\rho)^{4.5/3}$. Both parameters C' and B' are linear functions of the inverse of temperature. Based on the fact that the repulsive branch of the potential function of cesium, with an open shell $6s^1$ electronic structure, is softer than that of the closed-shell atoms, such as argon,¹⁰ the two-parameter LJ (8.5–4) potential function⁹ has been used to derive eq 1 by solving the thermodynamic equation of state.⁸ Relations for the molecular parameters of the potential function (e.g., the potential well depth (ϵ) and the hard sphere diameter (σ)) have been derived, in terms of C' , B' , and the cell parameter that has been approximated for the liquid lattice. These parameters are in close agreement with the molecular parameters derived by accurate experimental atomic spectroscopic data.^{2,3} Furthermore, the isotherm defined by eq 1 is quite applicable to the metal–nonmetal transition range, which occurs because of the transition from a metallic electronic structure to a nonmetallic-type structure.^{11–13} For metal in the liquid state, the valence electron of Cs is delocalized, whereas in the nonmetal state, the valence electron occupies a spatially localized atomic or molecular orbital. Because the variation of the interatomic interaction near the metal–nonmetal transition has an important consequence on the equation of state, the transition state can rarely be treated analytically.

It is worth mentioning that, in regard to predicting the thermophysical properties of cesium vapor (e.g., viscosity and thermal conductivity), the LJ (8.5–4) potential function is more accurate than the LJ (6–3) potential function,² and it is similar to the former, in regard to being advantageous for modeling the interaction potential as an effective pair potential.⁸

3. Dispersive Contribution

3.1. Macroscopic Analysis of B' . The role of B' is verified, in the first place, by applying its values to the Ihm–Song–Mason equation of state.^{14–16} In this equation of state, the second virial coefficient is well-established by a strong statistical mechanical basis. On the other hand, it is applicable to nonpolar and slightly polar fluids, of which their interparticle interaction potential is governed by a dispersive-type interaction as the major interaction. On the basis of these specifications, the Ihm–Song–Mason equation of state is selected for analysis of the properties that we are proposing for B' .

Combining the isotherm defined by eq 1 with the original form of the Ihm–Song–Mason equation of state, we have obtained

$$(Z - 1)V^{8.5/3} = \frac{1}{\rho^{8.5/3}} \left(\frac{(B_2 - \alpha)\rho}{1 + 0.22\Gamma\rho b} + \frac{\alpha\rho}{1 - \Gamma\rho b} \right) \quad (2)$$

where α is the contribution of the repulsive side of the potential function to the second virial coefficient B_2 , b is the van der Waals co-volume, and Γ is a substance-dependent free parameter, which is usually determined by iteration at a reference state such as the triple point. While Γ is expected to be a constant, it does increase slightly with temperature. This equation of state has been applied widely to nonpolar and slightly polar molecular fluids. The free parameter Γ has been known to compensate for any inaccuracy in the value of the second virial coefficient, as well as for covering the shape effect of the fluid molecules on the thermodynamic properties.^{14–16}

B_2 is the central quantity from which α and b can be determined; these are three temperature-dependent parameters of the equation of state defined by eq 2. These parameters can be calculated by integration if a promising pair potential function is known.

In this work, for a pure theoretical treatment, we have calculated temperature-dependent parameters α and b , in terms of the effective pair potential function $u(r)$ by integration, i.e.,

$$\alpha = -2\pi \int_0^{r_m} (\exp(-\beta u_o(r)) - 1)r^2 dr \quad (3)$$

$$b = -2\pi \int_0^{r_m} [(1 + \beta u_o(r)) \exp(-\beta u_o(r)) - 1]r^2 dr \quad (4)$$

where r is the intermolecular distance, $\beta = 1/(k_B T)$ (where k_B is the Boltzmann constant), r_m is the position of the potential minimum, and $u_o(r)$ is the potential function specified by the perturbation scheme of the Weeks–Chandler–Anderson for statistical mechanical treatment of a dense fluid:¹⁷

$$\begin{aligned} u_o(r) &= u(r) + \epsilon & (\text{for } r < r_m) \\ &= 0 & (\text{for } r > r_m) \end{aligned} \quad (5)$$

ϵ is the potential well depth, and, wherever applicable, we have also calculated B_2 in terms of $u(r)$ by integration:

$$B_2 = -2\pi \int_0^\infty (\exp(-\beta u(r)) - 1)r^2 dr \quad (6)$$

To estimate the role and properties of B' , we have substituted its values in eq 2 for B_2 (see section 4 for the dimension applied to B'). This has been achieved by applying the LJ (8.5–4) potential function to calculate α and b by integration, using eqs 3 and 4. Following the calculation of Γ at the boiling temperature, we have predicted the density of compressed liquid cesium metal from the melting temperature to the critical temperature. The validity of our proposal at this preliminary stage is evaluated by comparing the calculated density with the experimental values.¹⁸ Deviation plots for density at saturation pressure and in the pressure range of 50–600 bar are shown in Figure 1.

We have also calculated values of B_2 , α , and b by integration, using the LJ (8.5–4) potential function that has been applied to derive the isotherm defined by eq 1. Values of ϵ and r_m have been used from the previous work.⁸ Following the calculation of Γ , we have calculated the density of liquid cesium; the deviation of calculated density, with respect to experimental values, are depicted in Figure 2. It can be observed that the general trend and the extent of accuracy of the predicted density is a function of both temperature and pressure.

3.2. Microscopic Analysis of B' . The method we have used to support the proposal of this study in the second part is as follows. Rearrangement of eq 1 leads to a characteristic virial equation of state up to the third virial coefficient, where B' and

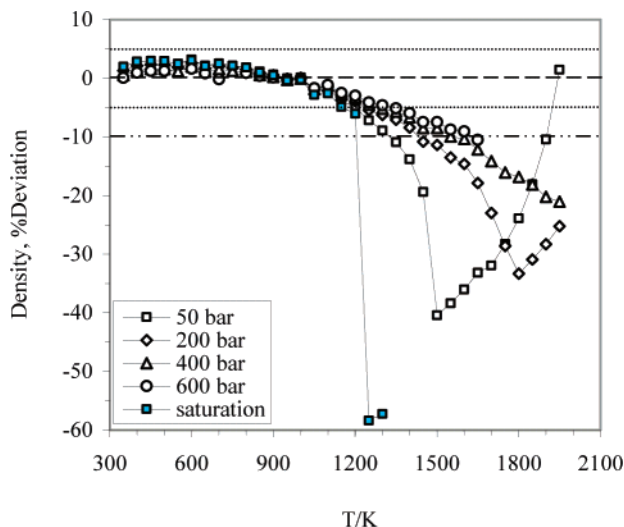


Figure 1. Deviation plots of density versus temperature for the case of substituting B_2 by B' , determined using the isotherm defined by eq 1.

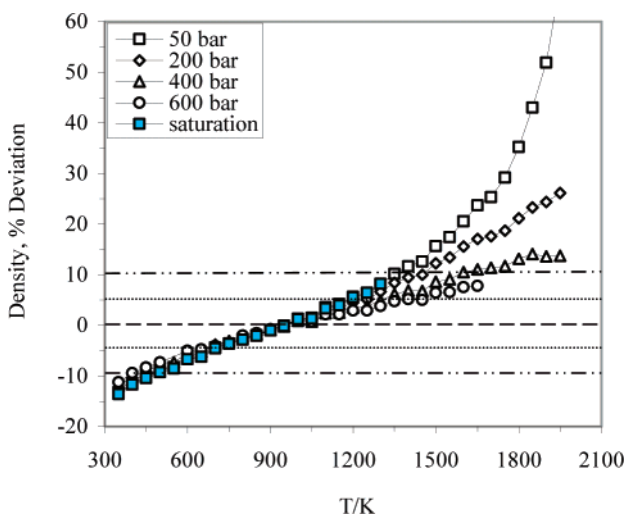


Figure 2. Deviation plots of density versus temperature for the case of applying B_2 (to eq 2), determined by integration using the LJ (8.5-4) potential function.

C' have the role of the second and third virial coefficient, respectively.

$$Z = 1 + B'\rho^{4/3} + C'\rho^{8.5/3} \quad (7)$$

In the liquid state, effective many-body interactions that are due to the special structure of liquid result in a high density, which, in turn, account for the small compressibility Z . The compressibility of a liquid at high pressure is related to the extent that liquid atoms repel each other. However, there exists a small attraction energy holding atoms together, which is normally treated as the perturbation energy in the statistical mechanical treatment of liquids by perturbation theories. The essential reason given to account for the linear behavior of the isotherm of eq 1 is that, at the thermodynamic equilibrium, attraction and repulsion are balanced so much that the interaction potential energy corresponds to states around the potential minimum.^{1,2,19}

One can consider the liquid structure in terms of related intermolecular distances. Considering the theory of liquid state and the linearity of the isotherm defined in eq 1, and considering that eq 7 is essentially a virial equation of state equivalent to the isotherm defined in eq 1, it can be observed that the terms

in eq 1 are the net effect for the compressibility behavior of liquid cesium designated by eq 7. Therefore, the second and third terms on the right-hand side of eq 7 are responsible for the net effect. Here, we can assume that the second term represents the effective interaction between pairs of atoms and the third term represents three-body interactions including the rest of the many-body interactions such that eq 7 describes the compressibility of the liquid cesium.

We have calculated B' on the basis of atomic electronic structure, which is responsible for the thermodynamic properties of liquid cesium. In this regard, we have assumed that the attraction between neutral Cs atoms in the liquid state all result from dispersion interaction. This assumption is justified by the fact that liquid cesium comprises ion matrixes involving nucleus and core electrons with the single valance electrons moving freely all over the entire liquid metal lattice, screening the ions. Therefore, on average, each atom experiences a net zero charge. The Cs atom has a spherical symmetry; therefore, any non-spherical interaction is a contribution from the distribution of electron density that is caused by the superposition of all of the electron atomic orbitals. The distribution of charge density can be well-approximated by a multipole expansion of the charge density. If this technique could be applied accurately, the final results must be in very good agreement with the desired experimental properties.

In this liquid metal system, the total interaction potential energy U has contributions from ion-ion, ion- e , and e - e interactions, as well as dispersion-dispersion interactions. Generally, the interaction potential is composed of a radial contribution, which is dependent on the interparticle distance (involving ion-ion, ion- e , and e - e interactions), and an angular contribution. The former can be approximated by the sum of pair interactions using the pair potential function $u(r_{pq})$, where r_{pq} is the distance between the p th and q th atoms, whereas the latter one can be represented by the sum of the potentials of charge distribution oriented in space by the superposition of occupied atomic orbitals $v_{ij}(r_{pq}, \omega_p, \omega_q)$, where ω_p and ω_q are functions that determine the orientation of charge distribution of p th and q th atoms in a mixture containing i -type and j -type atoms:

$$U = \sum_{i>j=1}^N u_{ij}(r_{pq}) + v_{ij}(r_{pq}, \omega_p, \omega_q) \quad (8)$$

According to the foregoing analysis, the second virial coefficient of the system can be represented by the sum of radial and angular contributions.

$$[B_2]_{ij} = [B_2^{\text{radial}}]_{ij} + [B_2^{\text{angular}}]_{ij} \quad (9)$$

The potential energy $v_{ij}(r_{pq}, \omega_p, \omega_q)$ forms a small fraction of the total potential energy and thus $[B_2^{\text{angular}}]_{ij}$ can be evaluated by perturbation methods. Because the evaluation of eq 1 is made possible by application of experimental PVT data,¹⁸ it is not possible to estimate eq 9 by separation of the interaction potential into potential terms of different natures. However, it is obvious that $[B_2^{\text{angular}}]_{ij}$ is substantially smaller than $[B_2^{\text{radial}}]_{ij}$. Thus, we can write $[B_2]_{ij} \approx [B_2^{\text{radial}}]_{ij}$ and treat $[B_2^{\text{angular}}]_{ij}$ as the perturbation. Therefore, in this study, we calculate $[B_2^{\text{angular}}]_{ij}$ via the perturbation method, using the LJ (8.5-4) potential.

The radial part can be evaluated by numerical integration of eq 6, using the pair potential function, in which the only variable is the interatomic distance. We do not discuss this here further, and we will continue to evaluate the angular contribution, which is the center of our attention.

TABLE 1: Components of Multipoles and Their Numerical Values Determined at Different Levels of Theory

moments ^a	value					
	HF/ SDD	B3LYP/ SDD	HF/ LanL2DZ	B3LYP/ LanL2DZ	HF/ LanL2MB	B3LYP/ LanL2MB
q	0	0	0	0	0	0
μ_x, μ_y, μ_z	0	0	0	0	0	0
$\Theta_{xx}, \Theta_{yy}, \Theta_{zz}$	-35.58	-32.59	-36.26	-35.78	-36.20	-36.21
$\Theta_{xy}, \Theta_{yz}, \Theta_{xz}$	0	0	0	0	0	0
$\Omega_{xxx}, \Omega_{yyy}, \Omega_{zzz}, \Omega_{xxy}, \Omega_{xxz}, \Omega_{yyz}, \Omega_{xzz}, \Omega_{yzz}, \Omega_{xyz}$	0	0	0	0	0	0
$\Phi_{xxxx}, \Phi_{yyyy}, \Phi_{zzzz}$	-234.44	-168.81	-245.61	-245.44	-245.66	-245.75
$\Phi_{xxxz}, \Phi_{xxxy}, \Phi_{yyyz}, \Phi_{yyxz}, \Phi_{zzxz}, \Phi_{zzzy}$	0	0	0	0	0	0
$\Phi_{xxyy}, \Phi_{xxzz}, \Phi_{yyzz}$	-78.14	-56.27	-81.87	-78.14	-81.88	-81.91
$\Phi_{xxyz}, \Phi_{yyxz}, \Phi_{zzxy}$	0	0	0	0	0	0

^a Legend of moments: q , coulomb; μ , Deby; Θ , Deby – Ang; Ω , Deby – Ang²; and Φ , Deby – Ang³.

To calculate $[B_2^{\text{angular}}]_{ij}$, we closely follow the formulation given by Kielich.²⁰ For the i th atom with permanent 2^n -pole moments $M_i^{(n)}$ interacting with the j th atom having permanent 2^m -pole moments $M_j^{(m)}$, the angular contribution to the second virial coefficient at temperature T can be calculated by

$$[B_2^{\text{angular}}]_{ij} = -\frac{N}{2\Omega^2} \sum_{n=1}^{\infty} \frac{1}{n!} \left(\frac{-1}{k_B T} \right)^n \int \int \int \{v_{ij}(r_{pq}, \omega_p, \omega_q)\}^n \times \exp\left(-\frac{u_{ij}}{k_B T}\right) dr_{pq} d\omega_p d\omega_q \quad (10)$$

where N is the Avogadro's number, indexes p and q run over all atoms of the type i and j , and $\Omega = \int d\omega_p = \int d\omega_q$. After determining functions for the angular dependence of the orientation of multipole and performing the integration over the angular part of the integrand, the following relation is finally obtained:

$$[B_2^{\text{angular}}]_{ij} = -\frac{N}{6k_B^2 T^2} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{2^{n+m} (2n+2m)! (n!m!)^2}{(2n)!(2m)!(2n+1)!(2m+1)!} \times (M_i^{(n)}[n]M_i^{(n)})(M_j^{(m)}[m]M_j^{(m)}) \langle r_{ij}^{-2(n+m+1)} \rangle \quad (11)$$

where

$$\langle r_{ij}^{-s} \rangle = \int r_{pq}^{-s} \exp\left(-\frac{u_{ij}(r_{pq})}{k_B T}\right) r_{pq}^2 dr_{pq} \quad (12)$$

The aforementioned formulation considers a system made of a mixture of two different species i and j . For the system that consists of pure liquid cesium metal, i and j are the same and, therefore, the indexes i and j will be dropped in the subsequent derivation. We then must consider all effective interactions between moments available in the multipole expansion series, which are used to approximate nonspherical charge distribution of the Cs atom. The multipole moments of cesium are determined using the Gaussian 98W program²¹ at the B3LYP/SDD, B3LYP/LanL2DZ, and B3LYP/LanL2MB levels of theory.^{22,23} The Gaussian program is essentially the reference for assigning moments and their components and for determination of their corresponding values. The multipoles of the Cs atom and the values of all components determined by the basis sets are shown in Table 1.

We have considered three types of interactions contributing to B_2^{angular} (see Table 1):

$$B_2^{\text{angular}} = B_2^{(\Theta-\Theta)} + 2B_2^{(\Theta-\Phi)} + B_2^{(\Phi-\Phi)} \quad (13)$$

where Θ and Φ represent quadrupole and hexadecapole, respectively. Note that the formulations given here are basically for a mixture of two components with any possible moment. Therefore, we have adopted eq 11 for a single component with two possible quadrupole and hexadecapole moments, as in the case of cesium, and, thus,

$$B_2^{\text{angular}} = -\frac{N}{4k_B^2 T^2} \left[\frac{28}{10} \Theta^2 \Theta^2 \langle r^{-10} \rangle + 22 \Theta^2 \Phi^2 \langle r^{-14} \rangle + \frac{3972}{25} \Phi^2 \Phi^2 \langle r^{-18} \rangle \right] \quad (14)$$

where the three contributing terms in the bracketed portion of eq 14 have been obtained by performing operations on the tensors involved in eq 11 in the following form:

For $(\Theta-\Theta)$ interaction:

$$n = 2 \quad (15a)$$

$$m = 2 \quad (15b)$$

$$B_2^{(\Theta-\Theta)} = -\frac{7N}{10k_B^2 T^2} \Theta^2 \Theta^2 \int_0^\infty \frac{1}{r^{10}} \exp\left(-\frac{u}{k_B T}\right) r^2 dr \quad (16)$$

For $(\Theta-\Phi)$ interaction:

$$n = 2 \quad (17a)$$

$$m = 4 \quad (17b)$$

$$B_2^{(\Theta-\Phi)} = -\frac{22N}{4k_B^2 T^2} \Theta^2 \Phi^2 \int_0^\infty \frac{1}{r^{14}} \exp\left(-\frac{u}{k_B T}\right) r^2 dr \quad (18)$$

For $(\Phi-\Phi)$ interaction:

$$n = 4 \quad (19a)$$

$$m = 4 \quad (19b)$$

$$B_2^{(\Phi-\Phi)} = -\frac{3972N}{100k_B^2 T^2} \Phi^2 \Phi^2 \int_0^\infty \frac{1}{r^{18}} \exp\left(-\frac{u}{k_B T}\right) r^2 dr \quad (20)$$

4. Results and Discussion

In the previous sections, we have justified that the value of B' is equivalent to the second virial coefficient, which receives a contribution from a small attraction. (Actually, in all cases, we have applied values of $B'^{3/4}$ to be consistent with the dimension of B_2 (see eq 7); the numerical values are given in the Appendix in Table A-1.) In terms of the statistical mechanical perturbation theory of dense fluids, this attraction is treated as the perturbation to the repulsion responsible mainly for the structure of the liquid state.^{2,8} We then have assumed, in the case of liquid cesium, that this attraction is mainly

contributed from the noncentral distribution of the electron density, and the technique of the multipole approximation of the atomic charge density allows for the determination of its extent, provided that the components of angular orientation of the electron density in space are known.

In Figure 1, the predicted density is compared with the experimental values. The figure shows that, as the pressure increases, deviations in the calculated density decrease, in agreement with the fact that the Ihm–Song–Mason is essentially applicable to compressed liquid. Furthermore, because B' spans into the negative region only, this gives an account of attractive interaction character, because of dispersive interaction.

The accuracy of the predicted density, as compared to the experimental values, is quite reasonable. Predicted densities in the temperature range of 300–1050 K are in agreement, within approximately $\pm 0.21\%$ to $\pm 1.7\%$ of the experimental values, and those in the temperature range of 1050–1400 K are in agreement, within $\pm 1.7\%$ to $\pm 5\%$ of the experimental values.

In addition, we have made predictions, using the LJ (8.5–4) potential function, to calculate three temperature-dependent parameters (B_2 , α , and b) by integrations (see eqs 3–6). Examination of deviations of the predicted densities, shown in Figure 2, reveal that the LJ (8.5–4) potential function is reasonably accurate, and the method of integration for three temperature-dependent parameters leads to a less-accurate equation of state (e.g., eq 2). Therefore, all conclusions can be specifically based on the isotherm derived by application of the LJ (8.5–4) potential function. Two reasons may be given here. First, the LJ (8.5–4) potential has been determined using the cohesive energy density data of liquid cesium over a relatively large temperature range, including data close to absolute zero temperature.⁹ It has been shown that the LJ (8.5–4) potential function can be used to determine thermodynamic properties as well as transport properties quite accurately.⁸ The second reason lies probably in the fact that, at long range, the real cut-off distance at which a pair of atoms still interact effectively is accounted for, quite accurately, by the LJ (8.5–4) potential, recalling that, for the calculation of the total interaction potential energy used to derive the isotherm defined by eq 1, the effective pair interaction has been considered up to the nearest-neighbor distance only.

From the foregoing discussion in the first step of investigation and examination of Figures 1 and 2, it can be concluded that B' has the similar role as B_2 for nonpolar fluids with induced-dipole interaction as their major intermolecular interaction. The essential reason for treating B' proportional to the dispersive interaction in the liquid cesium is that the Ihm–Song–Mason equation of state has been formulated for nonpolar and slightly polar dense fluids. Furthermore, recent applications of B_2 to the Ihm–Song–Mason equation of state, determined using (i) a diatomic fraction of cesium vapor,⁵ and (ii) an *ab initio* pair potential function,^{6,7} have completely failed to predict⁵ the thermodynamic properties. This failure is evidenced by the fact that predicted density by these two methods are unreasonably high, i.e., within $10^3\%$ to $10^4\%$ of the experimental values. Note that, in method (i) above, the experimental diatom fraction at a pressure of 10^{-5} bar has been used to calculate the average value of the second virial coefficient $\langle B_2 \rangle$.⁵ On the other hand, in method (ii), the pair potential for an isolated pair of Cs atoms has been determined using *ab initio* quantum mechanical methods.^{6,7} The numerical values of $\langle B_2 \rangle$ obtained by these two methods are shown in the Appendix in Table A-2. In these two methods, the interaction between a pair of atoms is actually the result of forces of a rather strong chemical nature.

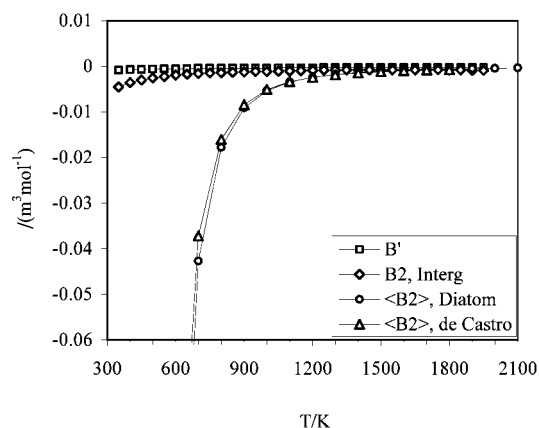


Figure 3. Comparison of B' and B_2 (this work) with $\langle B_2 \rangle$ by different methods.

It is important to compare B' (i) with B_2 values calculated by integration using the LJ (8.5–4) potential function, (ii) with $\langle B_2 \rangle$ calculated from the experimental diatom fraction,⁵ and (iii) with $\langle B_2 \rangle$ calculated by integration using the *ab initio* pair potential function.^{6,7} These comparisons have been made in Figure 3. Although there are good agreements between $\langle B_2 \rangle$ determined from the diatom fraction data and $\langle B_2 \rangle$ determined by the integration of the *ab initio* potential function at all temperatures, both disagree with B' and its corresponding B_2 values by 3–4 orders of magnitude at low temperatures. The large differences between B' and $\langle B_2 \rangle$ values are the essential reason for the Ihm–Song–Mason equation of state to fail to predict the density within a reasonable range of accuracy.

The values of B' varies smoothly in the range of freezing temperature to critical temperature. On the other hand, there is an excellent agreement with B_2 at high temperatures, whereas a fair agreement exists at low temperatures.

It worth mentioning that the value of Γ related to Figure 1 is quite independent of temperature (as it is expected to be). In this case, the Γ value is exactly the same as the Γ value of argon (e.g., 0.454)^{14–16} obtained using the original Ihm–Song–Mason equation of state and application of the LJ (12–6) potential function to calculate the values of B_2 , α , and b by integration^{14–16}.

As a final remarks to the first part, the large deviation at $T > 1300$ K is characteristic of metal–nonmetal transition. This transition is strictly dependent on density. (See Figure 1.) Large deviations are observed at saturation pressures, whereas it diminishes as the pressure increases. The discussion of the metal–nonmetal transition is beyond the scope of the present study and the readers are referred to refs 9–12.

Equation 10, in a sense, involves the average value of the interaction potential energy of the angle-dependent portion of electron density, using the Boltzmann factor as the distribution function of potential energy defined, in this work, by applying the LJ (8.5–4) potential function. Normalizing with respect to thermal energy and averaging over all angles and the relative coordinates, then the value of the angular contribution to the second virial coefficient is determined in the form represented by eq 10.

In regard to the calculation of B_2^{angular} , one can note a logic that converts eq 10 to a functional: the value of B_2^{angular} is determined by a two-parameter pair potential function $u(r) = f(\sigma, \epsilon)$, which, by our method,^{2,5} has been used to determine the isotherms defined by eq 1, and, in turn, to determine the molecular potential parameters ϵ and σ . Expressions for ϵ and σ involve B' and C' . If the approximations on the calculation

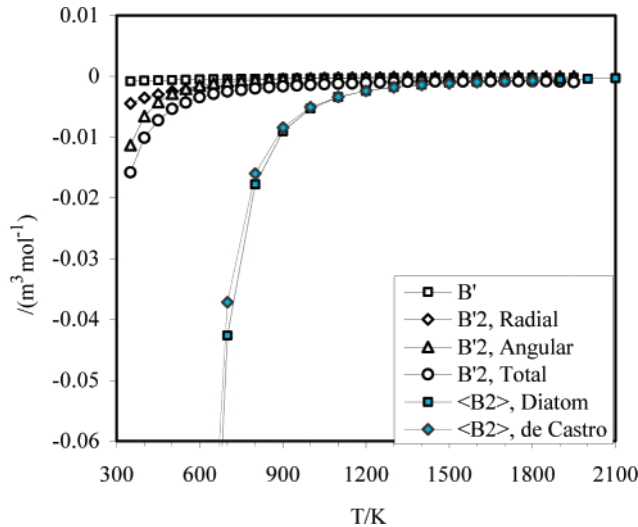


Figure 4. Comparison of B' with B_2^{angular} , B_2^{radial} , and other methods.

of radial and angular portions of the second virial coefficient made in this work, in previous studies,² and in the literature²⁰ could be ignored, then this logic may be responsible for a self-consistent of $B' \cong B_2^{\text{angular}}$.

To calculate the value of B_2^{angular} , we have performed the tensor calculations, which involve the moments and the corresponding orders of the multipoles. For cesium, n -pole moments have been determined by reference to the Gaussian 98W output of the total energy and full calculation using different basis sets. As a result of these calculations, $n = 2$ for the quadrupole and $n = 4$ for the hexadecapole. In Table 1, we have summarized the tensors of 2^n -pole moments of cesium for the three basis sets: SDD, LanL2DZ, and LanL2MB.²⁴ The reason for selecting these basis sets is their ability to incorporate the pseudo-wave functions that are used to develop pseudopotentials suitable for most metal calculations. From Table 1, clearly one can see that LanL2DZ and LanL2MB basis sets give the components of the multipoles, in agreement with each other. For some cases (in particular, for the case of alkali metals), special care has been taken by LanL2DZ and LanL2MB sets to resolve the ambiguity between core electrons and the valence electrons,^{22,23} which occurs because of the finite probabilities of the core electrons where the valence electrons are most probable.

In Figure 4, B_2^{angular} and B_2^{radial} are compared with B' . We cannot explain why $|B_2^{\text{angular}}| > |B_2^{\text{radial}}|$ at very low temperatures. However, the trend is reversed (as expected) rapidly as the temperature is increased. This indicates that, first, the LJ (8.5–4) potential is quite accurate, second, B' is equivalent to the second virial coefficient (which receives a contribution from the angular distribution of atomic electron density), and, third, the perturbation method is quite applicable. An enhancement might be due to the fact that this potential function is used as the interaction potential energy to determine the energy distribution in eq 10. The corresponding values are shown in Table 2.

To our knowledge, it is reported here for the first time that the application of the second virial (like) coefficient B' , characterized by the experimental macroscopic properties of the compressed liquid cesium, is a relevant quantity in statistical thermodynamics.

Previously, we reported a linear isotherm that is defined by application of the LJ (6–3) potential function.² This isotherm is only slightly more accurate for prediction of equilibrium thermodynamic properties than the LJ (8.5–4) potential function. Conversely, in regard to predicting the transport properties

TABLE 2: Results of Calculation of the Second Part^a

temperature, T (K)	LJ (8.5–4) potential ($\times 10^3$ m ³ /mol)		LJ (6–3) potential ($\times 10^3$ m ³ /mol)	
	B_2^{radial}	B_2^{angular}	B_2^{radial}	B_2^{angular}
350	–4.491	–11.317	–52.590	–126.99
400	–3.566	–6.543	–38.372	–88.740
450	–3.009	–4.228	–31.156	–66.823
500	–2.517	–2.833	–25.569	–52.755
550	–2.248	–2.069	–22.541	–43.303
600	–1.930	–1.516	–19.424	–36.159
650	–1.714	–1.165	–17.209	–30.932
700	–1.576	–0.931	–15.790	–26.909
750	–1.481	–0.761	–14.884	–23.795
800	–1.383	–0.629	–13.944	–21.187
850	–1.284	–0.525	–12.959	–19.088
900	–1.207	–0.445	–12.108	–17.356
950	–1.142	–0.381	–11.447	–15.900
1000	–1.101	–0.329	–11.041	–14.668
1050	–1.042	–0.281	–10.435	–13.624
1100	–0.981	–0.251	–9.7959	–12.715
1150	–0.939	–0.217	–9.2994	–11.935
1200	–0.901	–0.193	–8.8733	–11.194
1250	–0.863	–0.172	–8.4546	–10.603
1300	–0.832	–0.154	–8.1439	–10.086
1350	–0.806	–0.138	–7.8557	–9.6291
1400	–0.790	–0.125	–7.5885	–9.2249
1450	–0.784	–0.111	–7.4848	–8.8647
1500	–0.773	–0.101	–7.2837	–8.4996
1550	–0.774	–0.090	–7.1780	–8.2650
1600	–0.771	–0.082	–7.1228	–8.0207
1650	–0.771	–0.073	–6.9062	–7.7740
1700	–0.737	–0.068	–6.6389	–7.4705
1750	–0.752	–0.061	–6.5993	–7.3189
1800	–0.769	–0.055	–6.5973	–7.1943
1850	–0.795	–0.049	–6.6369	–7.1384
1900	–0.837	–0.043	–6.6915	–7.0647
1950	–0.913	–0.036	–6.9173	–7.1158

^a The result for application of the LJ (6–3) potential is shown for comparison.

(e.g., viscosity and thermal conductivity) of cesium metal vapor, the latter potential function is more accurate. In particular, the slope B of this isotherm² has the same properties as B' , which has been reported in detail in this work. However, by the detail given in this work, B' is more accurate for the proposal of this investigation and is attributed to the more inaccuracies gained by the LJ (8.5–4) potential function than the LJ (6–3) potential function (see the fourth paragraph of this section for details).

In short, we have found that the compressibility behavior of liquid cesium metal can be explained by the virial (like) equation of state, where B' and C' are the parameters that correspond to the attraction and repulsion components of the LJ (8.5–4) potential function. We have attempted to prove the proposal that B' has a contribution from the dispersive interaction potential at the macroscopic level, using the Ihm–Song–Mason statistical mechanical equation of state, and at microscopic level, by treating the angular second virial coefficient using the perturbation method. The angular second virial coefficients obtained in this way are in reasonable agreement with B' , from the melting temperature to the critical temperature. The magnitude of n -pole moments required for perturbation calculation of angular second virial coefficient are obtained by Gaussian 98W at the B3LYP/LanL2DZ and B3LPY/LanL2MB levels of theory, where only the quadrupole and hexadecapole have nonzero components.

In conclusion, if one considers the compressibility behavior, using a virial equation of state up to third virial coefficient, this article confirm that the second virial coefficient is equivalent to the angular second virial coefficient that has a contribution from the angular distribution of electron density. This has been proven at the macroscopic level, using a statistical mechanical

equation of state, and at microscopic level, using perturbation theory.

5. Conclusion

The linear isotherm derived by the application of the Lennard-Jones LJ (8.5–4) potential has been investigated for its role in the slope B' . The parameter B' conforms to the second virial coefficient B_2 ; however, its values are exceedingly larger at low temperatures and come into close agreement with B_2 at high temperatures. At the macroscopic level, it has been shown that, by substitution of B' for B_2 in the Ihm–Song–Mason equation of state, the density of liquid cesium metal can be predicted within $\pm 5\%$ of the experimental value over a rather large temperature range. Evidence has shown that B' conforms to B_2 ; however, quantitatively, they are different. Because of this quantitative difference in the second part of the investigation, the role of parameter B' has been studied at the microscopic level. This formulation has been used to calculate the noncentral second virial coefficient B_2^{angular} , obtained using the Boltzmann factor that comprises the LJ (8.5–4) potential as the energy distribution function of the cesium metal liquid system. The noncentral second virial coefficient calculated by the perturbation scheme, prove the proposal that B' is (in close agreement with) the contribution from the noncentral interaction to B_2 . The LJ (8.5–4) potential function is superior in that it maintained self-consistency in the form $B' \cong B_2^{\text{angular}}$.

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Appendix

TABLE A1: Values of B' and C' at Different Temperatures

temperature, T (K)	B'		C'	
	($\times 10^5$ ($\text{m}^3/\text{mol})^{4/3}$)	($\times 10^3$ m^3/mol)	($\times 10^{11}$ ($\text{m}^3/\text{mol})^{8.5/3}$)	($\times 10^7$ m^6/mol^2)
350	−7.7419	−0.8253	4.6869	1.3005
400	−6.7299	−0.7430	4.1404	1.1967
450	−6.0110	−0.6826	3.7590	1.1223
500	−5.2989	−0.6210	3.3672	1.0433
550	−4.8473	−0.5809	3.1341	0.9931
600	−4.3226	−0.5331	2.8393	0.9308
650	−3.9247	−0.4958	2.6173	0.8821
700	−3.6527	−0.4698	2.4758	0.8504
750	−3.4476	−0.4499	2.3769	0.8274
800	−3.2493	−0.4303	2.2788	0.8040
850	−3.0374	−0.4091	2.1629	0.7756
900	−2.8657	−0.3916	2.0744	0.7539
950	−2.7151	−0.3761	1.9977	0.7368
1000	−2.6121	−0.3653	1.9568	0.7269
1050	−2.4643	−0.3497	1.8767	0.7070
1100	−2.3316	−0.3355	1.8030	0.6868
1150	−2.2146	−0.3228	1.7409	0.6714
1200	−2.1166	−0.3120	1.6914	0.6585
1250	−2.0174	−0.3010	1.6380	0.6455
1300	−1.9329	−0.2915	1.5956	0.6349
1350	−1.8578	−0.2829	1.5589	0.6243
1400	−1.8038	−0.2767	1.5413	0.6189
1450	−1.7631	−0.2720	1.5357	0.6189
1500	−1.7188	−0.2669	1.5241	0.6136
1550	−1.6908	−0.2636	1.5310	0.6163
1600	−1.6622	−0.2603	1.5366	0.6189
1650	−1.6288	−0.2563	1.5360	0.6189
1700	−1.5568	−0.2478	1.4841	0.6028
1750	−1.5465	−0.2466	1.5112	0.6109
1800	−1.5473	−0.2467	1.5547	0.6216
1850	−1.5567	−0.2478	1.6131	0.6376
1900	−1.5870	−0.2514	1.7041	0.6611
1950	−1.6654	−0.2607	1.8845	0.7070

TABLE A2: Values of Calculated B_2 at Different Temperatures^a

temperature, T (K)	$\langle B_2 \rangle_{\text{de Castro}}$ ($\times 10^3 \text{ m}^3/\text{mol}$)	$\langle B_2 \rangle_{\text{diatom}}$ ($\times 10^3 \text{ m}^3/\text{mol}$)
600	−139.03	−117.05
700	−42.67	−37.17
800	−17.78	−16.01
900	−9.08	−8.43
1000	−5.33	−5.09
1100	−3.45	−3.39
1200	−2.41	−2.43
1300	−1.78	−1.83
1400	−1.36	−1.43
1500	−1.09	−1.16
1600	−0.90	−0.96
1700	−0.68	−0.82
1800	−0.61	−0.71
1900	−0.52	
2000	−0.43	
2100	−0.35	
2200	−0.27	
2300	−0.19	
2400	−0.12	
2500	−0.06	

^a Data taken from refs 6, 7, and 19.

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