

The Dieterici alternative to the van der Waals approach for equations of state: second virial coefficients

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Historically, the development of equations of state for fluids has almost invariably followed the lead of the van der Waals equation by simply adding together contributions from intermolecular repulsion and attraction. Recently an alternative approach, first suggested by Dieterici (*Ann. Phys. Chem. Wiedemanns Ann.*, 1899, **69**, 685), has been revised (R. J. Sadus, *J. Chem. Phys.*, 2001, **115**, 1460) with the benefit of modern developments in equations of state. In contrast to the traditional van der Waals-type equations of state, the Dieterici approach results in an equation of state that is the product of a repulsive term with an exponential attractive term. This formulation significantly enhances the accuracy of the prediction of vapour–liquid equilibria, particularly in the vicinity of the critical point. In this work, the ability of the equation to predict second virial coefficients is investigated. A comparison is also reported with traditional van der Waals-type equations of state. The results indicate that the Dieterici approach yields superior prediction of the second virial coefficients.

Introduction

An equation of state for fluids provides a relationship between pressure (p), temperature (T) and volume (V). In the spirit of the van der Waals equation,¹ equations of state in the literature^{2–5} almost invariably follow the “repulsion + attraction” formula, *i.e.*,

$$p = p_{\text{rep}} + p_{\text{attr}} \quad (1)$$

where the subscripts identify the contributions to pressure of intermolecular repulsion and attraction. Despite the enormous amount of work reported^{2–5} using this conceptual framework, the goal of a universally accurate equation of state has proved elusive. In contrast to this additive approach, Dieterici⁶ proposed an equation in which the pressure is calculated by multiplying the van der Waals repulsive term with an exponential attractive term. The advantages of the original Dieterici equation, such as a more realistic critical compressibility factor, are documented.^{6–9} However, in contrast to the important role of van der Waals-type equations, the Dieterici approach has not contributed significantly to the development of modern equations of state.

Recently,¹⁰ Dieterici’s approach was generalized to provide an alternative framework for the development of new equations of state:

$$p = p_{\text{rep}} e^{-\text{attractive term}/RTV} \quad (2)$$

Sadus¹⁰ observed that a potentially useful equation of state could be obtained if the Carnahan–Starling¹¹ and van der Waals terms (a) for repulsion and attraction, respectively, were combined in accordance with eqn. (2):

$$p = \frac{RT(1 + y + y^2 - y^3)}{V(1 - y)^3} e^{-a/RTV} \quad (3)$$

where $y = b/4V$, b is the co-volume parameter and R is the molar universal gas constant. This, “Dieterici–Carnahan–Starling (DCS)” equation yields significantly improved predic-

tion¹⁰ of the vapour–liquid coexistence of pure fluids ranging from the noble gases, small polyatomic molecules and small n-alkanes. In particular, good agreement between theory and experiment was obtained in the vicinity of the critical point.

The virial coefficient is an important property of a fluid because it is both a simple means of describing gas imperfection and it can be related directly to the intermolecular potential. The aim of this work is to examine whether the DCS equation can be used to accurately predict second virial coefficients. It is of particular interest if the prediction of the second virial coefficients is better than can be obtained from other van der Waals-type equations of state. Therefore, calculations are also presented for the van der Waals¹ (vdW), original Dieterici⁶ and Carnahan–Starling–van der Waals¹² (CSvdW) equations of state.

Results and discussion

In general, the n th-virial coefficient (B_n) can be obtained from any equation of state *via* the following relationship:

$$B_n = \frac{1}{(n-1)!} \left(\frac{\partial^{n-1} Z}{\partial \rho^{n-1}} \right)_{\rho=0} \quad (4)$$

where Z is the compressibility factor ($Z = pV/RT$) and ρ is the number density ($\rho = N/V$, N is the number of particles). For all Dieterici-type and van der Waals-type equations of state, application of eqn. (4) yields the following general relationship for the second virial coefficient:

$$B_2 = b - \frac{a}{RT} \quad (5)$$

The a and b parameters for the vdW¹ ($a = 0.4219R^2T_c^2/p_c$, $b = V_c/3$), Dieterici⁶ ($a = 0.5411R^2T_c^2/p_c$, $b = V_c/2$), CSvdW¹² ($a = 0.4963R^2T_c^2/p_c$, $b = 0.5218V_c$) and DCS¹⁰ ($a = 0.8143R^2T_c^2/p_c$, $b = 1.5285V_c$) equations can be obtained by solving the critical conditions of a pure fluid.

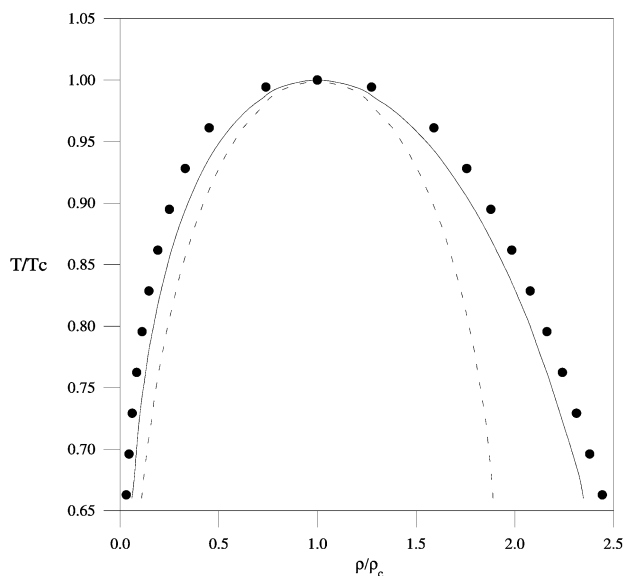


Fig. 1 The coexisting vapour–liquid phase densities of argon predicted using the DCS equation with $a = a_c$ and either $b = b_c$ (—) or $b = b_c(T_c/T)^{1/3}$ (- - -). The experimental data (●) were obtained from the literature.¹⁴

However, it is well known⁵ that it is unrealistic to expect parameters obtained at one state point to be valid over a wide range of temperatures. In the calculations presented here, we have assumed $a = a_c$ and allowed the covolume parameter to have the temperature-dependence suggested by Christoforakos and Franck,¹³ namely $b = b_c(T_c/T)^{1/3}$ where the subscript identifies a critical property. This temperature-dependent relationship was used for all the equations of state studied here. Most of the experimental second virial coefficient data examined here occur at temperatures greater than the critical temperature. This temperature-dependence relationship is an expedient way of extending the equation of state parameters beyond the critical temperature. However, it should be noted that this temperature-dependence is not suitable for vapour–liquid equilibria calculations. For example, calculations with the DCS equation for the vapour–liquid equilibria of argon

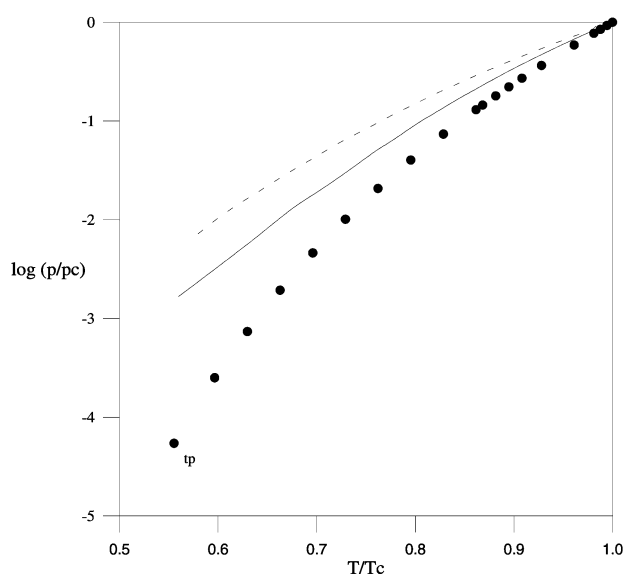


Fig. 2 The vapour pressure of argon from the triple point (tp) to the critical point predicted using the DCS equation with $a = a_c$ and either $b = b_c$ (—) or $b = b_c(T_c/T)^{1/3}$ (- - -). The experimental data (●) were obtained from the literature.¹⁴

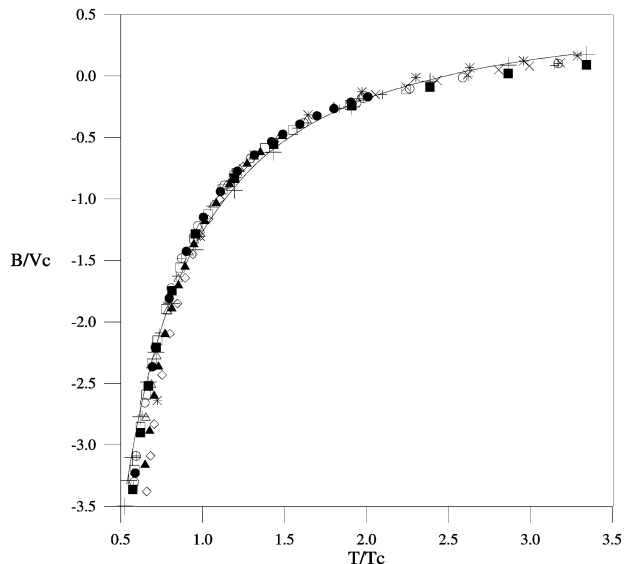


Fig. 3 Comparison of experimental data with the predictions (—) of the Dieterici–Carnahan–Starling (DCS) equation of state for the reduced second virial coefficient as a function of reduced temperature. Illustrated are experimental data¹⁶ for fluorine (●), oxygen (○), nitrogen (⊕), krypton (■), xenon (□), carbon monoxide (×), carbon dioxide (*), methane (+), ethane (△), propane (▲) and n-butane (◇).

indicate that the accuracy of the predicted coexistence density (Fig. 1) and vapour pressure (Fig. 2) declines when the temperature-dependence is used at sub-critical temperatures.

The ability of the DCS equation to predict the second virial coefficient for simple gases is illustrated in Fig. 3. Experimental data for the critical volume, temperature and pressure used to evaluate the equation of state parameters in eqn. (5) were obtained from the literature.¹⁵ The experimental virial coefficient data used for the comparison with theory are the recommended values reported in the compilation by Dymond and Smith.¹⁶ It is apparent from Fig. 3, that the DCS equations can predict the second virial coefficients of noble gases and small diatomic molecules with a reasonable degree of accuracy. It should be emphasized that the calculations presented here are genuine predictions and no attempt has been made to arbitrarily optimize the agreement of theory with experiment.

It is of interest to compare the accuracy of the DCS with other equations of state. In Fig. 4, experimental second virial coefficient data for argon at different temperatures are compared with calculations using the DCS, CSvdW, vdW and Dieterici equations of state. The difference between the second virial coefficients calculated for the different equations of state arises entirely from the numerical difference of the equation of state parameters. It is clearly apparent from Fig. 4 that the DCS equation of state provides the best prediction of the second virial coefficients. Good overall agreement with experiment is obtained and the DCS equation of state also predicts the temperature at which the second virial coefficient is zero (Boyle temperature) more accurately than the other equations of state. In contrast, the CSvdW, vdW and Dieterici equations are inaccurate over the entire temperature range. The CSvdW equation is only slightly more accurate than the vdW equation and the original Dieterici equation is the least accurate.

It is of interest to briefly consider the prediction of higher virial coefficients. Experimentally,¹⁶ a distinct maximum is observed for the third virial coefficient as a function of temperature. All van der Waals-type equations predict that the third virial coefficient is solely dependent on the covolume:

$$B_3 = b^2 \quad (6)$$

It should be noted that a different multiplier would also appear

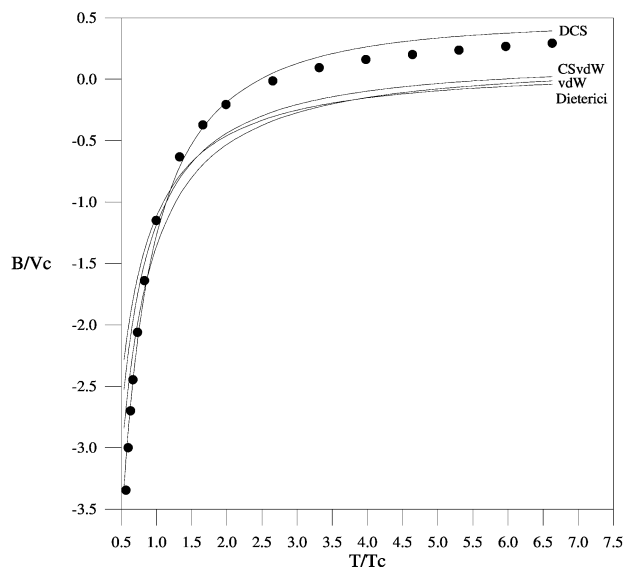


Fig. 4 Comparison of the experimental¹⁶ reduced second virial coefficients of argon (●) as a function of reduced temperature with predictions (—) obtained from the Dieterici–Carnahan–Starling (DCS), Carnahan–Starling–van der Waals (CSvdW), van der Waals (vdW) and Dieterici equations of state.

on the right hand side of eqn. (6) that depends on the nature of the equation of state. In contrast, the following temperature-dependent relationship is obtained for Dieterici-type equations:

$$B_3 = b^2 - \frac{ab}{RT} + \frac{a^2}{2R^2T^2} \quad (7)$$

The temperature-dependence of the third virial coefficient predicted by Dieterici-type equations means that it is reasonable to expect that they will be more accurate than van der Waals-type equations. However, neither the van der Waals-type nor Dieterici-type of equations predicts the experimentally observed maximum in the third virial coefficient. Therefore, both approaches are qualitatively inaccurate at temperatures in the vicinity of the third virial coefficient maximum.

Conclusions

The Dieterici–Carnahan–Starling equation of state yields good predictions of the second virial coefficients of small molecules over a wide range of temperature. The results obtained are superior to those obtained from the original Dieterici equation, the van der Waals equation and the Carnahan–Starling–van der Waals equations of state. These results in conjunction with the improved prediction of phase equilibria obtained previously¹⁰ indicate that the generalized Dieterici approach (eqn. (3)) can provide a useful alternative method for the development of equations of state for fluids.

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