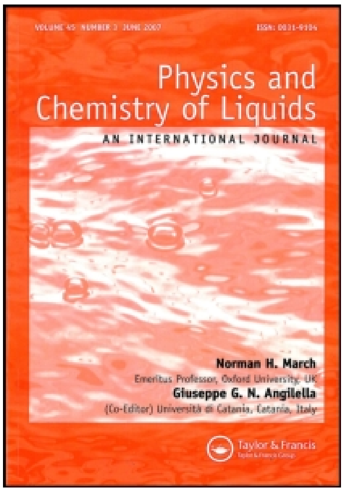

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Hard and Soft - Core Equations of State for Simple Fluids: VI. General Theory of Termination Temperatures, and a Validity Criterion for the Second Virial Coefficient

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Hard and Soft-Core Equations of State for Simple Fluids

VI. General Theory of Termination Temperatures, and a Validity Criterion for the Second Virial Coefficient†

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A general proof is given that the classical second virial coefficient satisfies the requirement for the non-existence of a termination point of any locus of C_v extrema. This validity criterion is applied to some proposed forms for the second virial coefficient. The order of the termination temperatures is verified for a fairly general intermolecular potential. In particular a proof is given that T_F lies between T_C and T_A. Also the hard-core limit of the ratio T_D/T_A (~ 2) is examined briefly.

1 INTRODUCTION

Once the intermolecular potential is known, it is straightforward to calculate the classical second virial coefficient and its temperature derivatives, and hence to extract numerical values for the six termination temperatures associated with the characteristic curves of a simple fluid. For the model systems and the Lennard-Jones *m*, *n* potential, which have been analyzed in the two preceding papers IV and V,[1] we find that the termination temperatures occur in the order

$$T_B < T_C < T_F < T_A < T_D < T_E. \tag{1}$$

One would expect to be able to construct a proof of this sequence of inequalities under fairly general conditions. Except for the inequality $T_F < T_A$, this sequence can be verified quite easily from the defining relations IV (12)

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provided the graph of the second virial coefficient has the usual shape, with B large and negative at low temperatures, and small and positive at high temperatures, with one zero at T_B and one maximum at T_A.

The features that deserve detailed proof concern

i) the general shape of the B versus T graph,
ii) the finiteness of T_E,
iii) the inequality $T_F < T_A$.

In Section 4 we examine briefly the rather general occurrence of a limiting value of 2 for the ratio T_D/T_A in the hard-core limit, and obtain the asymptotic forms of T_A, T_D and T_E for a generalized model based on the Lennard-Jones second virial coefficient.

In IV we argued that it is impossible for a single locus of extrema of the constant volume specific heat C_v to terminate on the temperature axis at zero density. We showed that as a consequence the strict inequality

$$2T\dot{B} + T^2\ddot{B} < 0 \tag{2}$$

must hold. We now verify in Section 5 when the second virial coefficient is obtained from the classical integral formulae, that the desired inequality (2) is satisfied at all temperatures for any "reasonable" intermolecular potential ϕ. This inequality acts as a validity criterion for any temperature dependent expression representing a second virial coefficient, whether obtained from an approximate theory, or proposed for fitting experimental data. We will give some examples of its application.

2 SHAPE OF THE SECOND VIRIAL COEFFICIENT AND THE ORDER OF TERMINATION TEMPERATURES

The classical formulae for the second virial coefficient are

$$B = (b/\sigma^3)\int_0^\infty d(r^3)\,(1 - e^{-\phi/kT}), \tag{3a}$$

$$= (-b/\sigma^3 kT)\int_0^\infty dr r^3 \phi' e^{-\phi/kT}, \tag{3b}$$

where $\phi(r)$ is the intermolecular potential, assumed to be spherically symmetric.[2] In (3),

$$b = \frac{2\pi}{3} L\sigma^3 \tag{4}$$

is four times the volume of the L(Avogadro number) molecules in a mole, and σ is an effective molecular diameter chosen so the potential ϕ has a minimum depth ε at a radial distance σ.

It appears one should be able to verify the general temperature dependence of the second virial coefficient, at least when the intermolecular potential is spherically symmetric and not too singular or oscillatory. We shall need to calculate the first and second temperature derivatives of B, which are obtained by differentiating (3) under the integral sign. With the abbreviation

$$\psi = \phi/kT, \tag{5}$$

we have from (3b)

$$B = (-b/\sigma^3)\int_0^\infty dr r^3 \psi' e^{-\psi}, \tag{6a}$$

$$T\dot{B} = (-b/\sigma^3)\int_0^\infty dr r^3 \psi'(\psi - 1)e^{-\psi}, \tag{6b}$$

$$T^2\ddot{B} = (-b/\sigma^3)\int_0^\infty dr r^3 \psi'(\psi^2 - 4\psi + 2)e^{-\psi}. \tag{6c}$$

Integration by parts, or differentiation under the integral sign in (3a), then yields

$$T\dot{B} = (-b/\sigma^3)\int_0^\infty dr 3r^2 \psi e^{-\psi}, \tag{7a}$$

$$T^2\ddot{B} = (-b/\sigma^3)\int_0^\infty dr 3r^2 (\psi^2 - 2\psi)e^{-\psi}. \tag{7b}$$

To ensure the existence of the thermodynamic limit and the convergence of the integrals in (3), we assume that ϕ is large and positive at small radial distances, and small and negative at large radial distances, with

$$\phi = O(1/r^{3+\delta}),\ \delta > 0 \text{ as } r \to 0 \text{ or } \infty. \tag{8}$$

To simplify matters we further assume that ϕ has one zero at a point σ_0, and one minimum at σ.

Inspection of (3b) shows that at very low temperatures the contribution to the integral from the exponential is important when ϕ is negative, which is the case when $r > \sigma_0$. If the temperature is *sufficiently* low, only the contribution to the integral from the range $r > \sigma$, where ϕ is negative and ϕ' is positive, need be considered. Consequently B is large and negative at low temperatures.

At the opposite extreme at very high temperatures, make a variable transformation of the form

$$x = (Tr^{3+\delta})^{-1}, \tag{9}$$

so that the effects of the attractive term in the argument of the exponent in (3b) can be neglected at sufficiently high temperatures, as in the Lennard–Jones case, with repulsive exponent $n = 3+\delta$. The repulsive small r portion of the potential below σ_0, where $\phi > 0$ and $\phi' < 0$, determines the asymptotic behaviour. So B is positive at high temperatures, and has a tail of the form

$$B \sim \Gamma(1 - 3/n)/T^{3/n}, \tag{10}$$

up to a multiplicative constant.

To see that B has just one maximum, where $\dot{B}$ vanishes, observe that the range of integration in (7a) can be divided into two parts at $r = \sigma_0$ where ψ vanishes. The positive and negative contributions to $\dot{B}$ are then separated, and by analyzing the behaviour of the exponential factor in these contributions as the temperature changes, one deduces that $\dot{B}$ has exactly one zero, at T_A. From (7a) one observes that if the positive part of the potential is an infinite hard-wall barrier, then it does not contribute to the integral for $\dot{B}$, which then comes entirely from the negative portion of the potential. $\dot{B}$ is then positive at all temperatures, so in this hard-core case B is a monotonic increasing function of temperature, as it is for the Sutherland potential and for the square-well potential, approaching the value $b\sigma_0^3$ as $T \rightarrow \infty$. A proof that $\ddot{B}$ has only one zero, without invoking extra conditions on the potential, has eluded us, although it seems one could try starting from (6c), using the information that ψ' has just one zero.

The existence of T_E is established by first noting that at T_D, $\ddot{B}$ vanishes and $T\dot{B} < 0$, so the defining expression $T\dot{B} + T^2\ddot{B}$ for T_E is negative at T_D, IV(12*f*). Then at very high temperatures one uses the asymptotic form for B, derived above, to show that $T\dot{B} + T^2\ddot{B}$ is positive. Consequently T_E is finite.

3 PROOF OF $T_C < T_F < T_A$

T_F is determined by the vanishing of $B - T\dot{B} + T^2\ddot{B}$, so if we wish to prove that T_F lies between T_C and T_D, we note that at T_C $B - T\dot{B}$ vanishes and $\ddot{B} < 0$, whereas at T_D $\ddot{B} = 0$ and $B - T\dot{B} > 0$. Consequently the defining expression for T_F changes sign between T_C and T_D, so $T_C < T_F < T_D$.

The difficulty is to prove that $T_C < T_F < T_A$. First we observe again that at T_C the defining expression $\dot{B} - T\dot{B} + T^2\ddot{B}$ is negative. Then at T_A, $\dot{B}$ vanishes, so from (7a) and (6b)

$$\int_0^\infty dr r^2 \psi e^{-\psi} = 0. \tag{11}$$

and

$$\int_0^\infty dr r^3 \psi' e^{-\psi} = \int_0^\infty dr r^3 \psi\psi' e^{-\psi}. \tag{12}$$

Now at T_A, using (6a) for B and (7b) for $T^2\ddot{B}$, we have with the help of (11) and then (12),

$$B - T\dot{B} + T^2\ddot{B} = (-b/\sigma^3)\int_0^\infty dr(r^3\psi' + 3r^2\psi^2)e^{-\psi}, \tag{13a}$$

$$= (-b/\sigma^3)\int_0^\infty dr r^2\psi(3\psi + r\psi')e^{-\psi}. \tag{13b}$$

We now show that this expression is positive at T_A, and hence verify that T_F lies between T_C and T_A.

As an aid to following the proof that the expressions in (13) are positive, we have sketched the various factors in the integrand in Figure 1 for the case of the Lennard-Jones 6, 12 potential. We observe that, because of the asymptotic forms of ψ and ϕ in (8), the factor $(3\psi + r\psi')$ is negative at small r, positive at large r, and moreover has just *one* zero in between. This last property follows since the combination $f = r^3\psi$ has the same shape as ψ

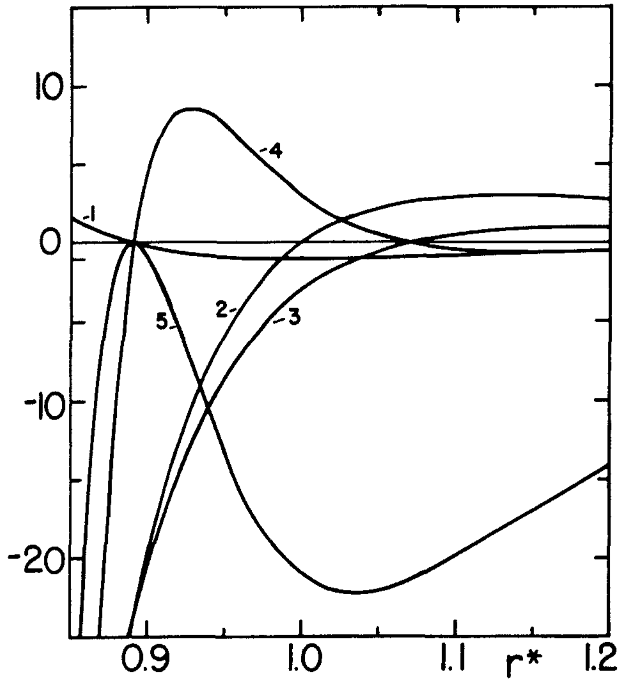

FIGURE 1 Factors in the integrands used in proving $T_F < T_A$ graphed versus the scaled radial distance $r^* = r/\sigma$. The potential is scaled so $\psi(\sigma) = -1$. The graphs are numbered as follows: 1, ψ; 2, $r\psi'$; 3, $3\psi + r\psi'$; 4, $\psi(3\psi + r\psi')$; 5, $\psi(3\psi + r\psi' + \alpha)$. For purposes of illustration we have used the Lennard-Jones 6, 12 potential at a temperature $T^* \equiv kT/\varepsilon = 1$ so $\psi \equiv \phi/kT = \phi^*/T^*$ and $\phi^*(r^*) = \phi(r)/\varepsilon = (r^{*-12} - 2r^{*-6})$.

and ϕ as described above, so its derivative f' changes sign once, and $(3\psi + r\psi') = f'/r^3$. Further, this zero lies to the right of σ. We can shift this zero towards σ_0 by adding a positive constant α, which is to be chosen in such a way that $(3\psi + r\psi' + \alpha)$ is zero exactly at σ_0. The appropriate choice of α is obviously $(-)\sigma_0\psi'(\sigma_0)$. Next we add zero to (13b) in the form of α times the LHS of (11) obtaining

$$(-b/\sigma^3)\int_0^\infty dr r^2 \psi(3\psi + r\psi' + \alpha)e^{-\psi}.$$

The zeros of ψ and $(3\psi + r\psi' + \alpha)$ now coincide at σ_0, so the product of these factors is always negative. Consequently the integral is negative, and we have shown that $B - T\dot{B} + T^2\ddot{B}$ is positive at T_A, *QED*.

4 THE RATIO T_D/T_A IN THE HARD-CORE LIMIT

We remark briefly in this section on the rather general occurrence of a limiting value of 2 for the ratio T_D/T_A, and obtain the asymptotic forms of T_A, T_D and T_E, as one approaches the hard-core limit. We consider the situation in which the second virial coefficient admits an expansion in inverse fractional powers of temperature, of a form based on the Lennard–Jones model:

$$B \sim b'/T^N - a'/T^{N+1-p} + \text{higher order negative terms}, \qquad (14)$$

where a' and b' are positive constants depending on N. In the Lennard–Jones case we would have $N = 3/n$ where n is the repulsive exponent, and $p = m/n$ where m is the attractive exponent. More generally we shall assume that the hard-core limit is taken by letting N and p tend to zero, and that the asymptotic values of the diverging termination temperatures T_A, T_D and T_E are determined by only the first two terms in (14), which have opposite signs. From the defining expressions for T_A, T_D and T_E:

$$T_A: \quad \dot{B} = 0, \qquad (15a)$$

$$T_D: \quad \ddot{B} = 0, \qquad (15b)$$

$$T_E: \quad \dot{B} + T\ddot{B} = 0, \qquad (15c)$$

one immediately obtains from (14), as N and p tend to zero,

$$T_A \sim (a'/b')(1/N), \qquad (16a)$$

$$T_D \sim (a'/b')(2/N), \qquad (16b)$$

$$T_E \sim (a'/b')(1/N^2). \qquad (16c)$$

These forms are equivalent to the corresponding asymptotic expressions obtained for the M-N model in IV with $M = 1$, except that (a'/b') may now depend on N. In the present more general situation, we now see that

$$T_D/T_A \sim 2, \qquad (17)$$

and

$$T_E/T_A \sim 1/N = n/3, \qquad (18)$$

independent of the ratio of coefficients (a'/b'), whereas the relation

$$T_E \sim (b'/a')T_A{}^2 \qquad (19)$$

involves the knowledge of this coefficient ratio. In the Lennard–Jones case the ratio (a'/b') tends to a constant involving only m in the hard-core limit.

5 NON-EXISTENCE OF C_V LOCUS TERMINATION TEMPERATURE

In order to verify the inequality (2) when the second virial coefficient is given by the classical formulae (3) for a general intermolecular potential ϕ, we substitute the expressions (7a) and (7b) for the required temperature derivatives of B. One immediately obtains

$$2T\dot{B} + T^2\ddot{B} = (-b/\sigma^3)\int_0^\infty dr 3r^2\psi^2 e^{-\psi} < 0, \qquad QED. \qquad (20)$$

As an example of the use of this result, we point out the danger of keeping just the first two terms of the series expansion form V (11) of the Lennard–Jones second virial coefficient as an approximate form for B:[3]

$$B_{m,n} \sim b'/T^{3/n} - a'/T^{1+3/n-m/n}. \qquad (21)$$

This two-term approximation is an M-N model with

$$M = 1 - (m - 3)/n, \quad \text{and} \quad N = 3/n, \qquad (22)$$

so

$$M + N = 1 - (m - 6)/n. \qquad (23)$$

When $m = 6$ the sum $M + N = 1$ for all values of n. Referring to IV (14g) we see that the seventh termination temperature T_G of the undesired C_v locus termination point now exists when $m > 3$, and coincides with the Boyle point T_B when $m = 6$, for all values of n. The above danger does not exist in Section 4, since $N \to 0$ there.

As a second example of the utility of the validity criterion (2) we examine the second virial coefficient of argon, as obtained by Gosman, McCarty and Hust[4]. Their expression for B yields a temperature $T_G = 84.60\ K$ where $2\dot{B} + T\ddot{B}$ vanishes, which is slightly above the triple point $T_t = 83.80\ K$. By comparison the critical point is at $150.86\ K$. Thus, the fitted second virial coefficient expression becomes theoretically unsatisfactory just above the triple point, which is at the lower end of the temperature range employed by Gosman et al.

CONCLUDING REMARKS

The validity criterion (2) has been especially useful in constructing model expressions for the second virial coefficient in IV, and in checking the range of validity of various expressions used to fit experimental data. We have shown that the classical second virial coefficient satisfies the requirement (2) that no locus of C_v extrema may terminate on the temperature axis at zero density.

Our proof that the termination temperatures occur in the expected order (1) has depended on the graph of the second virial coefficient versus temperature having its usual shape, which can be verified for especially simple intermolecular potentials. The complication which arose in proving that $T_C < T_F < T_A$ was to be expected, since a similar difficulty occurred in proving the same inequality for the M-N model in IV. However, it is to be hoped that a simpler and more general proof can be found.

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