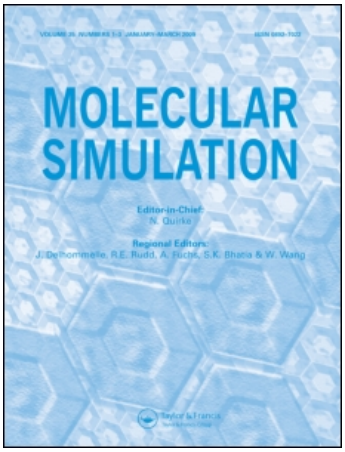

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Can the second virial coefficient be a predictor for the critical temperature?

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A recently proposed 3rd-order thermodynamic perturbation theory (TPT) is employed to calculate critical parameters of several model fluids. It is found that no matter how dis-continuous or continuous attractive perturbation part of whole interaction potential is, the 3rd-order TPT is accurate reliably for prediction of the critical parameters only on condition that the interaction potential is long-ranged or intermediate-ranged. Even when the 2nd-order macroscopic compressibility approximation TPT (2nd-order MCA-TPT) completely fails, the 3rd-order TPT still performs well. The 3rd-order TPT is then used to investiagte in detail validity and range of a recently emerging empirical $B_2(T_c)/v_0 \approx -6$ rule. It is found that the empirical rule only applies for potentials consisting of a hard sphere core and a continuous and attractive perturbation tail, whether the attractive perturbation tail is differentiable with respect to particle separation or not does not matter. But for potentials with dis-continuous perturbation tail and those diaplaying two fluid–fluid critical points, the empirical rule fails completely.

Keywords: Critical temperature; Second virial coefficient; Vapour-liquid transition

A recently proposed 3rd-order thermodynamic perturbation theory (TPT) is employed to calculate critical parameters of several model fluids. It is found that no matter how discontinuous or continuous attractive perturbation part of whole interaction potential is, the 3rd-order TPT is accurate reliably for prediction of the critical parameters only on condition that the interaction potential is long-ranged or intermediate-ranged. Even when the 2nd-order macroscopic compressibility approximation TPT (2nd-order MCA–TPT) completely fails, the 3rd-order TPT still performs well. The 3rd-order TPT is then used to investigate in detail validity and range of a recently emerging empirical $B_2(T_c)/v_0 \approx -6$ rule. It is found that the empirical rule only applies for potentials consisting of a hard sphere core and a continuous and attractive perturbation tail, whether the attractive perturbation tail is differentiable with respect to particle separation or not does not matter. But for potentials with discontinuous perturbation tail and those displaying two fluid–fluid critical points, the empirical rule fails completely.

Second virial coefficient of a fluid is an important quantity for measuring the relative ratio of repulsion interaction and attraction interaction in a total interparticle potential. Recently, it is indicated [1] that whereas critical point is very sensitive to the range of interaction, the second virial coefficient has a relatively constant value at the critical temperature, this enables one to predict the critical temperature with fair accuracy only by the second virial coefficient. This empirical rule is concluded only from several often-employed model potentials such as a hard core attractive Yukawa potential (HCAY), a square well (SW) potential, a Lennard–Jones $2n - n$ potential. It is not known whether the empirical rule is also valid for other interaction potentials. To investigate the validity of the empirical rule for a wide spectrum of potentials, firstly, we establish the excellent performance of a recently proposed 3rd-order TPT for prediction of critical temperature, then we employ the 3rd-order TPT to calculate the second virial coefficient at critical temperature for several new interaction potentials, and specify the application range of the empirical rule.

Calculational detail of the 3rd-order TPT is reported in Reference [2], the critical temperature T_c and critical density ρ_c can be calculated with the 3rd-order TPT by following standard thermodynamic relations, then the second virial coefficient $B_2(T_c)$ at the critical temperature

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T_c is calculated by

$$B_2(T) = 2\pi\int_0^{\infty}\left(1 - \exp\left(-\frac{u(r)}{kT}\right)\right)r^2 dr \qquad (1)$$

here $u(r)$ is the investigated interaction potential, k is Boltzmann constant, and T is absolute temperature. The calculational results from the 3rd-order TPT for the SW fluid and the HCAY fluid are presented in tables 1 and 2 in which the second virial coefficient $B_2(T_c)$ is represented in a reduced form of $B_2(T_c)/v_0$ with $v_0 = (\pi/6)\sigma^3$ and σ a hard sphere diameter. The calculational results for the SW fluid are also presented in figures 1 and 2 for clarity. It should be noted that the predictions from a 2nd-order macroscopic compressibility approximation (MCA) TPT [8] (2nd-order MCA–TPT) are also presented in tables 1 and 2 for comparison, numerical details of the 2nd-order MCA–TPT can be found from Reference [2].

The sample potentials are respectively given by

$$\begin{array}{ll} u(r) = \infty, & r/\sigma \le 1 \\ -\varepsilon & \lambda \ge r/\sigma > 1 \\ 0 & r/\sigma > \lambda \end{array} \qquad (2)$$

for the SW potential and

$$\begin{array}{ll} u(r) = \infty, & r/\sigma \le 1 \\ -\varepsilon\sigma\exp[-\kappa^*(r-\sigma)/\sigma]/r, & r/\sigma > 1 \end{array} \qquad (3)$$

for the HCAY potential.

Tables 1 and 2 show that the 3rd-order TPT can predict the T_c and $B_2(T_c)$ at the critical temperature satisfactorily except for the case where the range of the perturbation tail is very short compared with the hard sphere core diameter σ. It is true for the two sample potentials and all potential parameter cases that the predicted T_c and $B_2(T_c)$ are in unison above the simulated ones.

In table 3, the temperature T_{C_1} and T_{C_2}, pressure P_{C_1} and P_{C_2} and density ρ_{C_1} and ρ_{C_2} for the critical point C_1 and C_2 of a core-softened fluid with an internal repulsive core given by equation (4), respectively, computed by MD simulation method [5], the 3rd-order TPT, and the 2nd-order MCA–TPT, are presented. In table 4, the $B_2(T_c)/v_0$ at the critical temperature for the criticl point C_1 and C_2 of the core-softened fluid specified by equation (4) are presented, also respectively computed by MD simulation method [5], the 3rd-order TPT, and the 2nd-order MCA–TPT. It is clearly shown that for the core-softened fluid denoted by equation (4), $B_2(T_c)/v_0$ is not a constant, and deviates largely from the -6.0. Table 3 also shows that the 3rd-order TPT still performs well even if the 2nd-order MCA–TPT fails completely for the discontinuous core-softened potential fluid with two interrupted points. Figure1(a) shows that for the SW fluid, $B_2(T_c)/v_0$ is also not a constant, and deviates largely from -6.0. The 3rd-order TPT honestly reflects the change tendency for the whole potential range. Table 5 presented the calculated values for B_2/v_0 at T_c of the core-softened fluid with an internal attractive core given by equation (5) from the MD simulation [6], one can conclude that for this core-softened fluid, the $B_2(T_c)/v_0$ is also not a constant, and deviates largely from -6.0.

Table 1. Critical temperature T_c, critical density ρ_c and calculated values for B_2 at T_c for the SW fluid.

λ	kT_c/ε	$\rho_c\sigma^3$	$B_2(T_c)/v_0$
3.00	9.87		−7.0893
	(10.1001)	(0.2634)	(−6.8239)
	[10.2012]	[0.2534]	[−6.7113]
2.75	(7.7767)	(0.2478)	(−6.8663)
2.5	(5.8011)	(0.2614)	(−7.0056)
2.4	5.08		−7.1601
	(5.1411)	(0.2687)	(−7.0141)
	[5.1468]	[0.2556]	[−7.0006]
2.25	(4.132)	(0.2717)	(−7.3803)
2.2	3.80		−7.6174
	(3.8312)	(0.2776)	(−7.5099)
	[3.8478]	[0.2445]	[−7.4535]
2.0	2.764	0.225	−8.21
	(2.8131)	(0.2395)	(−7.9522)
	[2.8502]	(0.2467)	(−7.7678)
1.75	1.811	0.284	−8.85
	(1.9332)	(0.2645)	(−7.8131)
	[1.9678]	[0.2434]	[−7.5482]
1.5	1.219	0.299	−8.08
	(1.3141)	(0.3284)	(−6.8335)
	[1.3411]	[0.3323]	[−6.5243]
1.375	0.974	0.355	−7.46
	(1.0738)	(0.4034)	(−5.8391)
	[1.0923]	[0.3678]	[−5.5850]
1.25	0.764	0.37	−6.30
	(0.8312)	(0.4606)	(−4.8845)
	[0.8552]	[0.4787]	[−4.4629]

Quantities situated at first line, second line with the brackets () and third line with the brackets [], are respectively from the computer simulation results [3], the 3rd-order TPT and the 2nd-order MCA–TPT.

The core-softened potential with an internal repulsive core is given by

$$\begin{array}{ll} u(r) = \infty, & r/\sigma \le 1 \\ W_R, & b/\sigma \ge r/\sigma > 1 \\ -W_A & c/\sigma \ge r/\sigma > b/\sigma \\ 0 & r/\sigma > c/\sigma \end{array} \qquad (4)$$

Table 2. The same as in table 1 but for the HCAY fluid, the computer simulation results are from Reference [4].

$k\sigma$	kT_c/ε	$\rho_c\sigma^3$	$B_2(T_c)/v_0$
1.8	1.17	0.313	−6.23
	(1.2455)	(0.3034)	(−5.5919)
	[1.2711]	[0.2978]	[−5.3694]
3.0	0.715	0.375	−6.12
	(0.7634)	(0.3723)	(−5.2879)
	[0.7911]	[0.3595]	[−4.8607]
4.0	0.576	0.377	−5.90
	(0.6116)	(0.4142)	(−5.0774)
	[0.6431]	[0.4245]	[−4.4394]
7.0	0.412	0.500	−5.45
	(0.4329)	(0.5383)	(−4.6600)
	[0.4691]	[0.5523]	[−3.5128]

Table 3. Temperature T_{C_1} and T_{C_2}, pressure P_{C_1} and P_{C_2} and density ρ_{C_1} and ρ_{C_2} for the criticl point C_1 and C_2 of the core-softened fluid interacting through the potential equation (4), respectively, computed by MD simulation mehod [5] (1st line), 3rd-order TPT (2nd line), 2nd-order MCA–TPT (3rd line).The parameters value of each case can be found in Reference [5].

Set	kT_C/U_A	σ^3P_C/U_A	$\sigma^3\rho_{C_1}$	kT_{C_2}/U_A	$\sigma^3P_{C_2}/U_A$	$\sigma^3\rho_{C_2}$
(ii)	1.3±0.01	0.04±0.01	0.11±0.02	0.58±0.02	0.15±0.02	0.33±0.02
	1.3101	0.03107	0.12245	0.58310	−0.04897	0.31415
	1.1	0.02486	0.08312	1.6342	6.7076	0.8306
(iii)	1.24±0.01	0.03±0.01	0.09±0.02	0.69±0.02	0.11±0.02	0.28±0.02
	1.2401	0.02159	0.09931	0.7423	−0.01692	0.32114
	1.0788	0.01865	0.0489	1.4988	4.6294	0.7406
(iv)	1.18±0.03	0.025±0.003	0.08±0.02	0.75±0.01	0.07±0.01	0.24±0.02
	1.1150	0.0004112	0.1001	0.78423	−0.06531	0.2568
	1.0928	0.01775	0.04654	1.1988	3.5276	0.6854
(xi)	1.52±0.01	0.05±0.01	0.11±0.02	0.69±0.01	−0.11±0.01	0.33±0.02
	1.5015	0.03510	0.1156	0.7801	−0.0506	0.3491
	1.2936	0.02759	0.05793	1.3822	3.8122	0.7812
(xii)	1.82±0.01	0.06±0.02	0.12±0.02	0.96±0.02	−0.21±0.02	0.32±0.03
	1.8045	0.05314	0.1107	1.05121	−0.1627	0.32673
	1.633211	0.04337	0.07615	1.1565	1.6768	0.7112
(xiv)	1.59±0.01	0.043±0.004	0.10±0.02	0.58±0.01	−0.01±0.01	0.35±0.02
	1.5411	0.02889	0.09887	0.6701	0.1471	0.3434
	1.3633	0.01674	0.06123	0.9201	6.0191	0.8193

the core-softened potential with an internal attractive core is given by

$$\begin{array}{ll} u(r) = \propto, & r/\sigma \le 1 \\ -\varepsilon\delta, & b/\sigma \ge r/\sigma > 1 \\ -\varepsilon & c/\sigma \ge r/\sigma > b/\sigma \\ 0 & r/\sigma > /\sigma \end{array}, \tag{5}$$

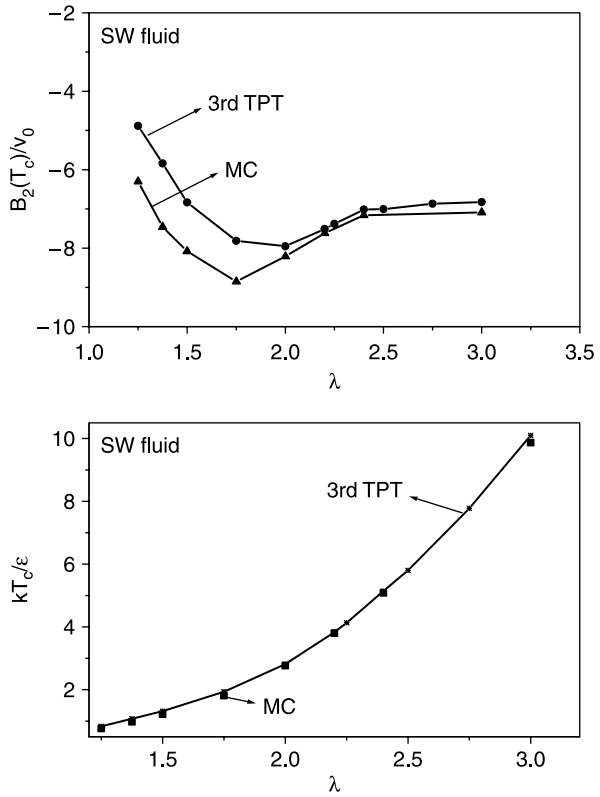

Figure 1. Calculated values for B_2/v_0 at T_c (a) reduced critical temperature kT_c/ε for the SW fluid as a function of potential parameter λ. The MC simulation data are from Reference [3].

To display whether the empirical rule is valid for other continuous potentials, we construct three such potentials. One is a combination of two attractive Yukawa potential with different mixing ratio and screening parameter as given by equation (6)

$$\begin{array}{ll} u(r)=\propto & r<\sigma \\ -\varepsilon\sigma\exp\left[-\kappa_1^*(r-\sigma)/\sigma\right]/r-\tau\varepsilon\sigma\exp\left[-\kappa_2^*(r-\sigma)\sigma\right]/r & r\ge\sigma \end{array} \tag{6}$$

The other is a combination of a van der Waals (vdW) potential (also called Sutherland or generalized Sutherland potential) and Yukawa-like potential with different mixing ratio and potential exponent for the vdW part and the screening parameter for the Yukawa-like part, and is given by

$$\begin{array}{ll} u(r) = \propto & r < \sigma \\ -\tau\varepsilon(\sigma/r)^n - \varepsilon\sigma^2\exp[-\kappa^*(r-\sigma)/\sigma]/r^2 & r \ge \sigma \end{array} \tag{7}$$

The last is a combination of the SW potential and the Yukawa potential with different mixing ratio and screening parameter, and given by

$$\begin{array}{ll} u(r) = \propto & r < \sigma \\ -\varepsilon & \lambda\sigma > r \ge \sigma \\ -\varepsilon\lambda\sigma\ \exp[-\kappa^*(r-\lambda\sigma/\sigma)]/r & r \ge \lambda\sigma \end{array} \tag{8}$$

It should be noted that the attractive perturbation part of the potential denoted by equation (8) is continuous, but not differentiable at $\lambda\sigma$.

The $B_2(T_c)/v_0$ for the above three potentials are presented in tables 6–8. The potential parameters are chosen such that the potential is long-ranged or at least intermediate-ranged, thus the 3rd-order TPT calculational results are accurate and can be used as judging criterion of the empirical rule. From the Tables 6–8 one can conclude

Table 4. Calculated values for B_2/v_0 at T_{C_1} and T_{C_2} of the core-softened fluid interacting through the potential equation (4), respectively, from the MD simulation [5], 3rd-order TPT and 2nd-order MCA–TPT.

Set	$B_2(T_c)/v_0$ MDC_1	$B_2(T_c)/v_0$ MDC_2	$B_2(T_c)/v_0$ $3rd\ TPTC_1$	$B_2(T_c)/v_0$ $3rd\ TPTC_2$	$B_2(T_c)/v_0$ $2rd\ MCA-TPTC_1$	$B_2(T_c)/v_0$ $2rd\ MCA-TPTC_2$
(ii)	−22.2314	−120.8488	−21.8844	−119.3659	−31.1582	−13.8466
(iii)	−26.1146	−89.5450	−26.1102	−76.3494	−34.8470	−17.5071
(iv)	−30.7605	−81.0130	−34.7028	−73.5023	−36.2166	−29.7397
(xi)	−21.7801	−101.6720	−22.2918	−78.7891	−29.5419	−26.0696
(xii)	−20.2730	−64.3340	−20.5857	−54.3325	−24.5949	−45.6230
(xiv)	−24.5365	−179.1366	−26.0330	−111.9923	−32.7914	−68.9888

that for the three continuous potentials the $B_2(T_c)/v_0$is surely near a constant, but a little above -6.0. Taking into account that the computed results by the 3rd-order TPT is itself a little above -6.0, and the deviation increases as the potential range decreases, one therefore concludes that for the potential with a hard sphere core plus a continuous and attractive perturbation tail no matter how indifferentiable the attractive perturbation tail is, the $B_2(T_c)/v_0$ is near -6.0. For the SW case, the $B_2(T_c)/v_0$ is not a constant, but when the SW tail is combined with an attractive perturbation tail so that the whole attractive perturbation tail is continuous, the $B_2(T_c)/v_0$ becomes near a constant -6.0.

To summarize, based on simulation data and accurate 3rd-order TPT results, we find that the empirical rule is only suitable for those potentials consisting of a hard sphere core plus a continuous and attractive perturbation tail, whether the attractive perturbation tail is differentiable with respect to the particle separation or not does not matter. The empirical rule does not apply for those potentials consisting of a hard sphere core plus a discontinuous and repulsive or attractive tail. Especially for the core-softened potential displaying two fluid–fluid critical points, the empirical rule fails completely. The present discoveries can be explained as follows. In the TPT, the 1st-order term depends on the integration of product of the hard sphere radial distribution function and the perturbation part of the potential, if the perturbation part is discontinuous, the resultant 1st-order term will display some artifact due to the sudden truncation, the same situation also happens for higher-order terms. It is the sudden truncation of the perturbation part which results in the violation of the empirical rule. In fact, the artifact due to the sudden truncation of the perturbation part more obviously shows up in solid phase than in fluid phase, this is why the solid phase diagram associated with the discontinuous perturbation tail displays discontinuous changes as the range of the perturbation part changes. Having known the validity range of the empirical rule, one can apply the empirical rule to simplify the calculation, help to choose potential parameters and bulk density as input into computer simulation and complicated theoretical calculation. Especially the $B_2(T_c)/v_0 \approx -6$ empirical rule recently has successfully been employed for making bulk fluid bridge function approximation [7], the present establishment of the $B_2(T_c)/v_0 \approx -6$ empirical rule for potentials consisting of a hard sphere core and continuous, attractive perturbation tail lends support to such practice of bridge functional approximation, specifies the validity

Table 5. Calculated values for B_2/v_0 at T_c of the core-softened fluid interacting through the potential equation (5) from the MD simulation [6].

b, c and δ	kT_c/ε	$B_2(T_c)/v_0$
$b = 1.1$ $c = 1.2$ $\delta = 0.5$	0.545	−6.3494
$b = 1.2$ $c = 1.5$ $\delta = 0.5$	1.025	−8.7194
$b = 1.4$ $c = 2.0$ $\delta = 0.5$	2.237	−9.5975

Table 6. Calculated values for B_2/v_0 at $T_c$of the fluid interacting through the potential equation (6) from the 3rd-order TPT.

κ_1^*, κ_2^* and τ	kT_c/ε	$B_2(T_c)/v_0$
$\kappa_1^* = 1.8$, $\kappa_2^* = 1.5$, $\tau = 1.5$	2.7843	−5.4349
$\kappa_1^* = 1.8$, $\kappa_2^* = 1.0$, $\tau = 1.0$	2.2443	−5.5964
$\kappa_1^* = 1.8$, $\kappa_2^* = 3.0$, $\tau = 1.0$	2.0084	−5.3992
$\kappa_1^* = 1.8$, $\kappa_2^* = 3.0$, $\tau = 2.0$	2.7848	−5.2872
$\kappa_1^* = 2.0$, $\kappa_2^* = 4.0$, $\tau = 2.0$	2.3048	−5.2927
$\kappa_1^* = 3.0$, $\kappa_2^* = 7.0$, $\tau = 0.8$	1.1004	−4.9560
$\kappa_1^* = 4.0$, $\kappa_2^* = 7.0$, $\tau = 0.4$	0.7801	−4.9734

Table 7. Calculated values for B_2/v_0 at $T_c$of the fluid interacting through the potential equation (7) from the 3rd-order TPT.

κ^* n and τ	kT_c/ε	$B_2(T_c)/v_0$
$\kappa^* = 1.8$, $n = 6$, $\tau = 1.0$	1.5133	−5.0822
$\kappa^* = 2.0$, $n = 8$, $\tau = 1.0$	1.2773	−5.0190
$\kappa^* = 1.0$, $n = 12$, $\tau = 1.5$	1.8489	−5.0225
$\kappa^* = 3.0$, $n = 12$, $\tau = 1.5$	1.1387	−4.7748
$\kappa^* = 3.0$, $n = 24$, $\tau = 0.5$	0.7339	−4.8420
$\kappa^* = 1.8$, $n = 36$, $\tau = 1.0$	1.0239	−4.9573
$\kappa^* = 1.8$, $n = 60$, $\tau = 2.0$	1.0987	−4.7578
$\kappa^* = 2.5$, $n = 60$, $\tau = 0.5$	0.7587	−4.9626

Table 8. Calculated values for B_2/v_0 at T_c of the fluid interacting through the potential equation (8) from the 3rd-order TPT.

κ^* and λ	kT_c/ε	$B_2(T_c)/v_0$
$\kappa^* = 1.8$, $\lambda = 3.0$	16.9843	−6.5466
$\kappa^* = 3.0$, $\lambda = 3.0$	13.7832	−6.7760
$\kappa^* = 7.0$, $\lambda = 3.0$	11.5643	−6.8205
$\kappa^* = 1.8$, $\lambda = 2.0$	6.1443	−6.6771
$\kappa^* = 1.8$, $\lambda = 1.5$	3.0943	−6.6858
$\kappa^* = 3.0$, $\lambda = 1.25$	1.4643	−5.9863
$\kappa^* = 7.0$, $\lambda = 1.75$	2.4373	−7.4173
$\kappa^* = 7.0$, $\lambda = 3.5$	18.1373	−6.7157
$\kappa^* = 12.0$, $\lambda = 3.5$	18.4334	−6.5391

range of such practice, and motivates one to apply such practices safely to these fluids.

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