

Ratio between two- and three-dimensional critical temperatures from new equations of state

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10.1070/MC2003v013n06ABEH001853

New two- and three-dimensional equations of state are used to deduce the ratio between the two- and three-dimensional critical temperatures as 0.455 against the known value 0.5.

Among numerous equations of state, the van der Waals equation is best known to be equally well developed for both three-dimensional (3D) and two-dimensional (2D) systems. Using a dimensionless notation, the 3D van der Waals equation can be written as

$$\tilde{p} = \frac{\varphi}{1-4\varphi} - \tilde{\alpha}^{(3)}\varphi^2, \quad (1)$$

where $\tilde{p} \equiv pv_0/kT$ (p is the pressure, v_0 is the molecular volume, and kT is of the ordinary meaning), $\varphi = v_0c$ is the packing fraction of matter (c is the molecular concentration), and $\tilde{\alpha}^{(3)} \equiv \alpha^{(3)}/kTv_0$ is the dimensionless form for the 3D attraction constant $\alpha^{(3)}$. Correspondingly, the 2D van der Waals equation is

$$\tilde{\Pi} = \frac{\theta}{1-2\theta} - \tilde{\alpha}^{(2)}\theta^2, \quad (2)$$

where $\tilde{\Pi} \equiv \Pi a_0/kT$ (Π is the 2D pressure, and a_0 is the molecular parking area), $\theta = a_0\Gamma$ is the 2D packing fraction (Γ is the number of molecules per unit surface), and $\tilde{\alpha}^{(2)} \equiv \alpha^{(2)}/kTa_0$ is the dimensionless form for the 2D attraction constant $\alpha^{(2)}$. As de Boer¹ showed for spherical molecules, the 2D and 3D attraction constants are related to each other as

$$\alpha^{(2)}/\alpha^{(3)} = \frac{3}{8d}, \quad (3)$$

where d is the molecular diameter. He also established a simple rule relating 2D and 3D critical temperatures:

$$T_c^{(2)}/T_c^{(3)} = 1/2. \quad (4)$$

Indeed, from the above definition of the attraction constants $\tilde{\alpha}^{(3)}$ and $\tilde{\alpha}^{(2)}$ and from equation (3), it follows that

$$\frac{T_c^{(2)}}{T_c^{(3)}} = \frac{\tilde{\alpha}_c^{(3)}\alpha^{(2)}v_0}{\tilde{\alpha}_c^{(2)}\alpha^{(3)}a_0} = \frac{\tilde{\alpha}_c^{(3)}}{4\tilde{\alpha}_c^{(2)}}, \quad (5)$$

where $v_0 = \pi d^3/6$ and $a_0 = \pi d^2/4$. By equating the first and second derivatives of the 3D and 2D pressures to zero according to equations (1) and (2), we obtain the critical values of the attraction constants $\tilde{\alpha}_c^{(3)} = 13.5$ and $\tilde{\alpha}_c^{(2)} = 6.75$, so that $\tilde{\alpha}_c^{(3)}/\tilde{\alpha}_c^{(2)} = 2$. Putting these values in (5) just leads to equation (4).

Recently,^{2,3} we formulated a new approach to an equation of state and derived both 3D and 2D equations of state. Written in the numerical form, they are

$$\tilde{p} = \frac{2.687\varphi}{1-2.169\varphi} + 0.778\ln(1-2.169\varphi) - \tilde{\alpha}^{(3)}\varphi^2, \quad (6)$$

$$\tilde{\Pi} = \frac{1.801\theta}{1-1.428\theta} + 0.561\ln(1-1.428\theta) - \tilde{\alpha}^{(2)}\theta^2. \quad (7)$$

Within the frames of the same formalism, van der Waals equations (1) and (2) were also obtained in the course of derivation but as belonging to a lower degree of approximation. A direct comparison of equations (1) and (2) with equations (6) and (7) was carried out earlier.^{2,3} It gave additional evidence for a higher accuracy of equations (6) and (7) as compared with equations (1) and (2), respectively. It is due time to compare equations (6) and (7) with each other. Critical parameters are of especial interest as characterising 3D and 2D phase transitions in a given matter.

By equating to zero the first and second derivatives of the right-hand sides of equations (6) and (7), we obtain two sets of critical parameters: $\tilde{p}_c = 0.0436$, $\varphi_c = 0.1190$, and $\tilde{\alpha}_c^{(3)} = 10.96$; $\Pi_c = 0.0748$, $\theta_c = 0.2022$, and $\tilde{\alpha}_c^{(2)} = 6.019$, respectively. Using equation (5), we immediately obtain

$$T_c^{(2)}/T_c^{(3)} \approx 0.455. \quad (8)$$

Condition (8) is close to (4), but the critical temperature ratio is smaller. Other 3D and 2D critical parameters also differ by almost two times. In particular, the 2D critical point occurs at an almost twofold packing fraction as compared with the 3D critical point.

Another important characteristic to be compared for 3D and 2D systems is the Boyle point, *i.e.*, the temperature at which the second virial coefficient changes its sign and passes through zero. The van der Waals equations, written correctly as indicated in (1) and (2), yield true values for the second virial coefficient: $4 - \tilde{\alpha}^{(3)}$ and $2 - \tilde{\alpha}^{(2)}$ for 3D and 2D systems, respectively. This yields the attraction constants for the Boyle point $\tilde{\alpha}_B^{(3)} = 4$ and $\tilde{\alpha}_B^{(2)} = 2$. Using these values and remembering the definition of the dimensionless attraction constants, we obtain, similarly to (5), the ratio between the 2D and 3D Boyle temperatures

$$\frac{T_B^{(2)}}{T_B^{(3)}} = \frac{\tilde{\alpha}_B^{(3)}}{4\tilde{\alpha}_B^{(2)}} = \frac{1}{2}. \quad (9)$$

Since equations (6) and (7) reproduce the same exact values of the second virial coefficient, they lead again to the condition expressed in (9). Thus, equation (9) is a common relationship for the van der Waals and new equations of state and shows that the Boyle temperature for a 2D system is twice as low as that in the case of a 3D system.

The ratio of the Boyle temperature to the critical one is also an important characteristic of an equation of state, and it can be calculated as

$$\frac{T_B}{T_c} = \frac{\tilde{\alpha}_c}{\tilde{\alpha}_B} \quad (10)$$

from both 3D and 2D equations. Both the van der Waals equations (1) and (2) yield $T_B/T_c = 3.75$. For a 3D system, the experimental value of this ratio is 2.75, whereas equation (6) gives $T_B^{(3)}/T_c^{(3)} = 2.74$. Equation (7) yields the value $T_B^{(2)}/T_c^{(2)} = 3.01$ whose accuracy will be estimated when some experimental data in this field appear in the literature.

This work was supported by the Russian Foundation for Basic Research (grant no. 04-03-32134), the Presidential programme for supporting leading Russian scientific schools (grant no. 789.2003.3), and the programme 'Scientific Research of the Higher School on Priority Trends in Science and Engineering' (grant no. 203.06.06.035).

References

- 1 J. H. de Boer, *The Dynamical Character of Adsorption*, Clarendon Press, Oxford, 1953.
- 2 A. I. Rusanov, *Mendeleev Commun.*, 2003, 11.
- 3 A. I. Rusanov, *Mendeleev Commun.*, 2003, 62.

Received: 8th September 2003; Com. 03/2179