

● "DERIVATION" OF THE COMPLETE VAN DER WAALS' EQUATION FROM STATISTICAL MECHANICS

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THE usual discussion of van der Waals' equation from the point of view of statistical mechanics (1-3) proceeds as follows: (a) the van der Waals' equation

$$\left(P + \frac{N^2a}{V^2}\right)(V - Nb) = NkT \quad (1)$$

is expanded in the form

$$P = \frac{NkT}{V} \left[1 + \frac{N}{V} \left(b - \frac{a}{kT} \right) + \dots \right]; \quad (2)$$

(b) taking for the potential energy of interaction of a pair of molecules a distance r from each other

$$u(r) = \infty \quad r \leq r^* \\ = -\epsilon (r^*/r)^m \quad r > r^* \quad (3)$$

where ϵ and r^* are parameters ($m = 6$ usually), and neglecting the simultaneous interaction of any molecule with more than one other molecule (dilute gas), a straightforward evaluation of the configuration integral leads again to equation (2), with

$$a \cong \frac{2\pi\epsilon r^{*3}}{m-3} \quad (4) \\ b = \frac{2\pi r^{*3}}{3}$$

That is, the statistical derivation using equation (3) agrees with van der Waals' equation as far as the second virial coefficient.

It may be of some pedagogical interest to note that the complete van der Waals' equation (1) (rather than just the leading terms as in equation (2)) can be obtained from a simple statistical argument that is, as might be expected, rather analogous to the qualitative argument (3) used by van der Waals in "deriving" his equation. The argument to be given is of course incorrect but it exhibits the statistical foundation (or lack of foundation) of the complete van der Waals' equation.

For a perfect gas of N molecules in a volume V the partition function Q for the system is (omitting the internal partition function)

$$Q = \frac{1}{N!} q^N \quad (5)$$

where

$$q = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \quad (6)$$

In the "smoothed potential model" (2) of a gas or liquid we picture a given molecule as moving through the free volume V_f (not excluded by other molecules) in

which there is a uniform potential $-\chi$ due to all other molecules. For this model

$$q = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V_f e^{\chi/kT} \quad (7)$$

What sort of an argument, using equation (3) and based on a smoothed potential model, will lead to van der Waals' equation? In the first place we have to write $V_f = V - Nb$. In order to agree with equation (4) (there is no reason to insist on this) we must assume that the volume excluded to a given molecule is

$$N \cdot \frac{1}{2} \cdot \frac{4}{3} \pi r^{*3}$$

This amounts to stating that the excluded volumes associated with the other $N-1$ molecules do not overlap—in other words we assume that b can be calculated from the second virial coefficient treatment mentioned above, and then used regardless of whether the gas is only slightly imperfect or very imperfect or even liquefied. The factor of $1/2$ above is to avoid counting each excluded volume twice over.

In order to obtain $-\chi$ we imagine that the N molecules are smeared out *uniformly* over the volume V . The potential energy of interaction between a given molecule and those smeared out molecules at distances between r and $r + dr$ is

$$u(r) \cdot \frac{N}{V} \cdot 4\pi r^2 dr$$

In order to calculate the total interaction potential, $-\chi$ in which the given molecule moves we must first integrate over r from $r = r^*$ to $r = \infty$ (no other molecules can be nearer than $r = r^*$), and then divide the result by two, because we would otherwise be attributing the complete interaction energy to our specified molecule whereas, since two molecules are involved in each interaction, only half "belongs" to a given molecule. Then we have

$$-\chi = \frac{1}{2} \cdot 4\pi \frac{N}{V} \int_{r^*}^{\infty} \left[-\epsilon \left(\frac{r^*}{r} \right)^m \right] r^2 dr \quad (8)$$

$$= \frac{-aN}{V} \quad (9)$$

where a is given by equation (4). So

$$q = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} (V - Nb) e^{aN/VkT} \quad (10)$$

From equations (5) and (10), and

$$P = kT \left(\frac{\partial \ln Q}{\partial V} \right)_T$$

one obtains van der Waals' equation, equation (1).

A further discussion of van der Waals' equation as a free volume model but from a somewhat different point of view has been given elsewhere (4).

Finally, it might be worth comparing the function χ of equation (7) associated with several different empirical equations of state ($v = V/N$):

Van der Waals

$$(P + a/v^2)(v - b) = kT \quad (11)$$

$$\chi = a/v \quad (12)$$

Berthelot

$$(P + a/Tv^2)(v - b) = kT \quad (13)$$

$$\chi = a/Tv \quad (14)$$

Dieterici

$$P(v - b) = kTe^{-a/kTv} \quad (15)$$

$$\chi = kT \int_v^\infty \frac{1 - e^{-a/kTv}}{v - b} dv \quad (16)$$

For large v , equation (16) reduces to equation (12). These expressions for χ follow from the equation of state and equation (804, 1) of Fowler and Guggenheim (2). For all of these equations of state, $v_f = V_f/N = v - b$.

LITERATURE CITED

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