

Fluid state equation

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A thermodynamic approach based on the analysis of an excluded volume results in a general state equation, including the Planck and van der Waals equations as particular cases, and a new precise state equation.

Let us consider an isotropic uniform molecular system. Since a state equation may be always given by a set of isotherms, we shall deal with an isotherm equation. We deduce it by integrating the trivial relationship

$$vdp = d\mu, \quad (1)$$

where v is the volume, p is the pressure, and μ is the chemical potential given by the standard expression

$$\mu = \mu^0 + kT \ln(c\Lambda^3), \quad (2)$$

where μ^0 is the chemical potential of a molecule with resting center of mass in the system under consideration, k is the Boltzmann constant, T is the temperature, c and Λ are the concentration and the de Broglie wavelength, respectively (Λ is a function of temperature). The traditional term with an activity coefficient has been included in μ^0 whose only difference from μ is that μ^0 refers to molecules at rest. By analogy with (1), we may write for such molecules (as if they were really present in the system as a second component)

$$d\mu^0 = \bar{v}dp \quad (3)$$

with \bar{v} as the partial molecular volume of a resting molecule, i.e., the volume increment needed for restoring the initial pressure after introducing a single resting molecule into the system. Putting now (2) in (1) and accounting for (3), we arrive at the universal differential form of a state equation

$$\frac{dp}{dc} = \frac{kT}{1 - \bar{v}c}. \quad (4)$$

To integrate equation (4), we have to know the concentration dependence of \bar{v} , which is strongly influenced by attraction forces. To avoid this complication, we may integrate (4) as if there were no attraction forces (but with a given molecular structure caused by attractive forces) and then add an attractive term (which is well known) to a final expression. If there are no attraction forces, \bar{v} acquires the physical meaning of an excluded volume v^{ex} . Indeed, among moving molecules, a single resting and not interacting molecule (with a fixed centre of mass) plays the role of a specific ‘wall’, which is evident to create an excluded volume. Thus, we can write the resulting state equation as

$$p = kT \int_0^c \frac{dc}{1 - v^{\text{ex}}c} - ac^2, \quad (5)$$

where a is the molecular attraction constant. Introducing the intrinsic molecular volume v_0 and the exclusion factor $f^{\text{ex}} \equiv v^{\text{ex}}/v_0$, we can rewrite (5) in the dimensionless form

$$\tilde{p} = \int_0^\varphi \frac{d\varphi}{1 - f^{\text{ex}}\varphi} - a'\varphi^2, \quad (6)$$

where $\tilde{p} \equiv pv_0/kT$ is the ratio of the real pressure to the pressure of an ideal gas of the same density, $\varphi \equiv v_0c$ is the volume fraction of matter, and $a' \equiv a/kTv_0$ is the dimensionless image of the constant a .

Although we excluded an attractive contribution from the integral in (6), the problem of the dependence of f^{ex} on φ is maintained. Planck showed that $f^{\text{ex}} = 8$ for a monatomic gas.¹ However, the excluded volume can vary with concentration due

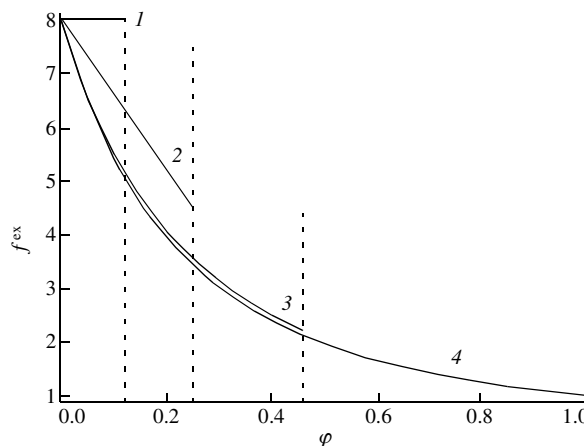


Figure 1 The dependence of the exclusion factor on the volume fraction (solid lines) and the limits of applicability for the corresponding state equations (dashed lines): (1) the Planck equation, (2) the van der Waals equation, (3) equation (17), and (4) the line obtained from equation (6) and the virial expansion for hard spheres with known ten coefficients.

to clustering, which starts already in the gaseous state of matter. Let a system consist of spherical clusters containing n molecules on average and having a dense structure with a minimum volume v_0 per molecule. The cluster volume is nv_0 and the cluster radius is $R = (3nv_0/4\pi)^{1/3} = \lambda n^{1/3}$, where λ is the radius of an equivalent sphere corresponding to the volume v_0 . Depending on packing conditions, the volume of a free molecule can differ from v_0 , but we ignore this for the sake of simplicity. Defining then the excluded volume per molecule in a cluster as

$$v^{\text{ex}} = \frac{4\pi(R + \lambda)^3}{3n} = \frac{v_0(n^{1/3} + 1)^3}{n}, \quad (7)$$

we obtain an expression for the exclusion factor

$$f^{\text{ex}} = 1 + 3n^{-1/3} + 3n^{-2/3} + n^{-1}. \quad (8)$$

According to (8), f^{ex} monotonically decreases from $f^{\text{ex}} = 8$ at $n = 1$ to the limiting value $f^{\text{ex}} = 1$ at $n \rightarrow \infty$. The dependence of f^{ex} on φ should be qualitatively the same since clustering develops with increasing concentration.

Knowing the behaviour and the limits of f^{ex} , we can compute the integral in (6). The roughest approximation (applicable, if any, only to some parts of the isotherm) is that f^{ex} is not a function but a constant. In this zero-order approximation, equation (6) becomes

$$\tilde{p} = \frac{\ln(1 - f^{\text{ex}}\varphi)}{f^{\text{ex}}} - a'\varphi^2. \quad (9)$$

Equation (9) represents the Planck state equation at $f^{\text{ex}} = 8$ (ref. 1) and a state equation typical of the lattice models of fluids at $f^{\text{ex}} = 1.2$ – 4 . According to (8), the value $f^{\text{ex}} = 8$ is attained at a finite slope of the $f^{\text{ex}}(n)$ curve ($df^{\text{ex}}/dn = -4$ at $n = 1$), whereas the exclusion factor approaches unity asymptotically (at $df^{\text{ex}}/dn \rightarrow 0$). Therefore, equation (9) with $f^{\text{ex}} = 1$ can prove to be practical within a sufficiently wide range of state parameters of a condensed phase. As for the Planck gas equation with $f^{\text{ex}} = 8$, it exhibits its particular usefulness by producing a correct value

for not only the first ($b_1 = 1$) but also the second virial coefficient ($b_2 = 4$) in the dimensionless virial expansion

$$\tilde{p} = \sum_i b_i \varphi^i.$$

Proceeding to the first approximation, we assume a linear decrease of f^{ex} as

$$f^{\text{ex}} = 8 - k\varphi, \quad (10)$$

where k is a constant, which restricts the range of possible variation of φ . The whole range from zero to unity is embraced at $k = 7$. This is a minimally possible value for k . As for a maximum value, it can be easily calculated from the virial expansion and is $k = 34$. Putting (10) in (6) yields the state equation in the first approximation

$$\tilde{p} = \int_0^\varphi \frac{d\varphi}{1 - 8\varphi + k\varphi^2} - a'\varphi^2, \quad (11)$$

The result of integration in (11) depends on the value of k . Equation (11) is written for $k > 16$ as

$$\tilde{p} = \frac{1}{\sqrt{k-16}} \left(\arctan \frac{k\varphi - 4}{\sqrt{k-16}} - \arctan \frac{-4}{\sqrt{k-16}} \right) - a'\varphi^2 \quad (12)$$

for $k < 16$ as

$$\tilde{p} = \frac{1}{2\sqrt{16-k}} \left(\ln \left| \frac{k\varphi - 4 - \sqrt{16-k}}{k\varphi - 4 + \sqrt{16-k}} \right| - \ln \left| \frac{4 + \sqrt{16-k}}{4 - \sqrt{16-k}} \right| \right) - a'\varphi^2 \quad (13)$$

and for $k = 16$ as

$$\tilde{p} = \frac{1}{4-16\varphi} - \frac{1}{4} - a'\varphi^2. \quad (14)$$

The smaller the k value, the wider the state interval included, and the lower the accuracy of the state equation. In the gas region at $k = 34$, equation (12) correctly yields not only the first and second but also the third virial coefficient ($b_3 = 10$). At $k < 64/3$, a van der Waals loop appears in the isotherm, indicating the possibility of a first-order phase transition and a critical state. However, at the minimum value $k = 7$, when equation (10) comprises the whole region $0 \leq \varphi \leq 1$, resultant state equation (13) is practical only until $\varphi = 1/7$.

As for equation (14), this is nothing else but the van der Waals equation. This unexpected result supplies the famous equation with a quite new interpretation. Traditionally, the van der Waals equation is regarded as an equation with a constant excluded volume (referring to the zero approximation in our classification), which van der Waals equated, by mistake, not to the eightfold but to fourfold molecule volume (the mistake was corrected by Planck¹). However, the van der Waals equation yields a correct value for the second virial coefficient, and, when belonging to the zero approximation, this could be explained only by an accidental compensation of two mistakes: an incorrect functional dependence and an incorrect value of the excluded volume. In reality, as we now see, the van der Waals equation refers not to the zero approximation but to the first approximation of the theory of excluded volume. The excluded volume is not constant in the van der Waals equation, but it changes according to a certain linear law. As for the functional form of the van der Waals equation, it corresponds to an exact particular solution of the first approximation.

Proceeding to the second approximation, we replace the linear behaviour of f^{ex} expressed in (10) by the ratio of two linear functions chosen so as to satisfy the initial value $f^{\text{ex}} = 8$ and the initial slope $f^{\text{ex}} = -34$:

$$f^{\text{ex}} = \frac{8 - (34 - 8k)\varphi}{1 + k\varphi}. \quad (15)$$

Then, state equation (6) takes the form

$$\tilde{p} = \int_0^\varphi \frac{(1 + k\varphi)d\varphi}{1 - (8 - k)\varphi + (34 - 8k)\varphi^2} - a'\varphi^2. \quad (16)$$

As in the first approximation, the form of the solution depends on the value of k . The simplest solution corresponds to $k = (136)^{1/2} - 8 \approx 3.6619$. For this particular value of k , equation (16) becomes

$$\tilde{p} = 1.239 \left(\frac{1}{1 - 2.169\varphi} - 1 \right) + 0.778 \ln(1 - 2.169\varphi) - a'\varphi^2. \quad (17)$$

We present equation (17) as a new precise fluid state equation. It exhibits a high accuracy both in the gaseous region (yielding correctly first three virial coefficients) and in the critical region (yielding the ratio of the Boyle point temperature to the critical temperature 2.74 against the experimental value 2.75). In contrast to the Planck and van der Waals equations, equation (17) is valid in a much wider range of states up to $\varphi = 0.461$ (cf. the maximally possible value $\varphi = 0.74$ for the packing of hard spheres).

To compare the above three approximations, Figure 1 shows the $f^{\text{ex}}(\varphi)$ functions (solid lines) within the applicability limits of the corresponding state equations (dashed lines). Figure 1 also demonstrates the dependence of f^{ex} on φ calculated from equation (6) for a system of hard spheres ($a' = 0$) using the values of first ten virial coefficients known in the literature⁵ (line 4). It can be seen that line 3 corresponding to equation (17) is very close to line 4.

As a concluding remark, the above relationships formulated for a one-component system may be easily expanded to a system with many chemical species. Equation (6) is easily generalised to a multicomponent system by averaging the excluded and molecular volumes with respect to various chemical species present in the system ($v^{\text{ex}} \equiv \sum_i x_i v_i^{\text{ex}}$ and $v_0 \equiv \sum_i x_i v_{i0}$, where x_i is the mole fraction of the i th species). The resultant equation is

$$\tilde{p} = \int_0^\varphi \frac{d\varphi}{1 - f^{\text{ex}}\varphi} - \sum_{i,k} a'_{ik} \varphi_i \varphi_k, \quad (18)$$

where φ is the aggregate volume fraction of all species and $a'_{ik} \equiv a_{ik} v_{i0} / k T v_{k0}$ is the dimensionless image of the pair attraction constant a_{ik} for molecules of the i th and k th species, f^{ex} visually maintaining its original definition as v^{ex}/v_0 . Since the integrals in (6) and (18) look similarly, only the repulsive term should be replaced, as shown in (18), when passing to a multicomponent system.

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