

**On the van der Waals equation**

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**Abstract**

The status of the van der Waals equation is re-analyzed. The renormalized mass is introduced for interacting atoms in a real classical gas. It is shown that the van der Waals equation is not warranted by the virial treatment of interaction. The equation is derived by assuming explicitly the excluded volume.

The van der Waals equation is one of the most revered achievements in statistical physics. It is based on a picture which is perceived as an interpolation scheme. Accordingly, the equation of state of an ideal classical gas reads

$$p = nT \quad , \quad (1)$$

where  $p$  is the pressure,  $n = N/V$  is the gas concentration,  $N$  is the number of molecules in gas,  $V$  is the volume and  $T$  is temperature. As it is well-known, it holds for rarefied gases at high temperature. On the other side, at high densities, the volume of the gas is limited by introducing an excluded volume  $b$ , according to the scheme  $V \rightarrow V - Nb$ . Consequently, the equation of state reads

$$p = NT/(V - Nb) = nT/(1 - nb) \quad . \quad (2)$$

It is usually thought that the van der Waals equation is an interpolation between equations (1) and (2). However, the only natural interpolation between the two equations is precisely equation (2), which is not exactly the van der Waals equation. On the other hand, equation (2) captures much of the desired "high pressure at small volumes", thought to be specific to liquids, *i.e.* to high-density ensembles of particles. It is seldom noticed however, that liquids have actually a low pressure, because the high values of the pressure at high concentrations are compensated in fact by internal cohesion. Cohesion is not brought, unfortunately, in discussion. It is the compressibility  $(\partial V/\partial p)/V$  of the liquids which is low, which is indeed supported by equation (2).

Cohesion is not brought into discussing liquids, but interaction forces between gas molecules are introduced, so that it is thought that the van der Waals equation can be derived from the theory of real classical gases, taking into account the interaction.

The "derivation" of the van der Waals equation proceeds as follows. The free energy of an interacting gas reads

$$F = F_{id} - T \ln \left( \frac{1}{V^N} \int d\mathbf{r}_1 \dots d\mathbf{r}_N e^{-U/T} \right) \quad , \quad (3)$$

where

$$F_{id} = -NT \ln[eV(T/T_0)^{3/2}/d^3N] , \quad (4)$$

is the free energy of the ideal gas,  $T_0 = 2\pi\hbar^2/md^2$  is the characteristic temperature of the gas ( $T \gg T_0$ ),  $d = (V/N)^{1/3}$  is the mean inter-particle spacing, and

$$U = (1/2) \sum_{i \neq j} U(\mathbf{r}_i - \mathbf{r}_j) \quad (5)$$

is the interaction between the gas molecules. A very useful trick is used in expressing the argument of the logarithm in (3) as

$$\frac{1}{V^N} \int d\mathbf{r}_1 \dots d\mathbf{r}_N (e^{-U/T} - 1) + 1 . \quad (6)$$

Now,  $e^{-U/T} - 1$  vanishes at infinite, so the main contribution to the integral in (6) comes from particles close to each other. Now, let us assume that the gas is sufficiently rarefied that only pairs of particles are sufficiently close to each other. Under this assumption the integral in (6) becomes

$$\frac{N^2}{2V^2} \int d\mathbf{r}_1 d\mathbf{r}_2 [e^{-U(\mathbf{r}_1 - \mathbf{r}_2)/T} - 1] = \frac{N^2}{2V} \int d\mathbf{r} [e^{-U(\mathbf{r})/T} - 1] = -N^2 B(T)/V , \quad (7)$$

where

$$B(T) = \frac{1}{2} \int d\mathbf{r} [1 - e^{-U(\mathbf{r})/T}] \quad (8)$$

stands for the pair integral. It is called the (first) virial coefficient.

The pair approximation given by (7) has a serious drawback: in the thermodynamic limit it is not a finite quantity. It is thought that higher-order contributions to the integral in (6) (Mayer cluster expansion) allows the correcting free energy in (3) to be read as

$$\Delta F = -T \ln(1 - N^2 B/V) = -T \ln(1 - NB/V)^N = -NT \ln(1 - NB/V) \simeq N^2 TB/V , \quad (9)$$

under the "weak-interaction" assumption

$$NB(T)/V \ll 1 , \quad (10)$$

which provides a good thermodynamic description of the interaction effects. Another argument consists in writing  $N'^2 B/V'$  as for small sub-ensembles, so that it is then permissible to write  $\Delta F' = N'^2 TB/V'$ , then juxtapose the sub-ensembles at equilibrium such that  $\Delta F = N(N'/V')TB = N^2 TB/V$ .

A different derivation leads to the same result. It consists in assuming that the effect of the interaction shows itself in the renormalization of the particle mass in the free energy of the ideal gas. The correction to the free energy reads then

$$\Delta F = -(3/2)NT(\Delta m/m) . \quad (11)$$

Now, the mean equation of motion reads

$$\langle m^*(d\mathbf{v}/dt) \rangle = -(N/V') \int d\mathbf{r} \cdot (\partial U / \partial \mathbf{r}) , \quad (12)$$

where  $V' \sim d^3$ , for instance; then, since  $\Delta t = d/2v$ ,<sup>1</sup>

$$(m^*/m)\Delta(mv^2) = -(N/V')d^3\Delta U = -(N/V) \int d\mathbf{r} \cdot \mathbf{U} . \quad (13)$$

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<sup>1</sup>Two particles move toward each other, in a relative motion.

Further,  $(m^*/m)\Delta(mv^2) = -(\Delta m^*/m)(mv^2) = (\Delta m/m)(mv^2) = 3(\Delta m/m)T$ , so that<sup>2</sup>

$$\Delta m/m = -(N/3TV) \int d\mathbf{r} \cdot U = -2NB(T)/3V , \quad (14)$$

and the correction to the free energy given by (11) becomes  $\Delta F = -(3/2)NT(\Delta m/m) = N^2BT/V$ , which coincides with (9). We can see that mass renormalization amounts to the first-order approximation in the virial expansion ( $2BT = \int d\mathbf{r} \cdot U$ ). The effect of higher-order virial expansion cannot be included in mass renormalization, because the former are statistical effects, while the latter is a classical-motion effect. In this sense, we can view the mass renormalization as the mechanical limit of the statistical physics. This shows again, that statistical motion is not fully reducible to mechanical motion. The latter is only the most-probable limit of the former.

Turning back to equation (9), we get the correction to entropy

$$\Delta S = -N^2(B + TB')/V , \quad (15)$$

and the correction to energy

$$\Delta E = -N^2T^2B'/V , \quad (16)$$

as due to the interaction. The pressure becomes

$$p = nT + \frac{n^2TB}{1 - nB} = \frac{nT}{1 - nB} = nT + n^2TB , \quad (17)$$

and none of the equations (17) is the van der Waals equation. They are simply, virial expansions in powers of density for a real gas. In particular, none of the above equations exhibit the van der Waals isotherms.

As it is well-known, according to (8), the first virial coefficient can be written as

$$B = b - a/T , \quad (18)$$

where  $b$  is the excluded volume of the highly-repulsive interaction at short distances and  $a$  is the integral of the attractive part of the interaction. Then, (17), can be written as

$$p = nT + n^2Tb - n^2a , \quad (19)$$

or

$$p + n^2a = nT(1 + nb) . \quad (20)$$

It is the extrapolation from  $1 + nb$  to  $1/(1 - nb)$  in the *rhs* of equation (20) which leads to van der Waals equation  $(p + n^2a)(1 - nb) = nT$ , but this extrapolation is not warranted.

It is tempting to estimate the interaction integral in (3) by

$$\int d\mathbf{r}_1 \dots d\mathbf{r}_N e^{-U/T} = N!(V/N - b)^N e^{-\langle U \rangle/T} , \quad (21)$$

as if each atom would be enclosed in a cell, and their motion would be replaced by permutations among the cells. The result can also be written as

$$\int d\mathbf{r}_1 \dots d\mathbf{r}_N e^{-U/T} = [(V - Nb)/e]^N e^{-\langle U \rangle/T} , \quad (22)$$

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<sup>2</sup>For close collisions, at small distances, the motion proceeds until the mean interaction becomes of the order of magnitude of the temperature.

and the correction to the free energy would be

$$\Delta F = -NT \ln[(1 - nb)/e] + \langle U \rangle . \quad (23)$$

The pressure is then given by

$$p + \partial \langle U \rangle / \partial V = NT / (V - Nb) , \quad (24)$$

and it would appear that we have a derivation for the van der Waals equation, because  $\langle U \rangle = (N^2/2V) \int' dr \cdot U = -N^2 a/V$  (prime on the integral means the integration over the allowed volume). The trick lies in our replacing of the motion by permutations of the atoms among the cells, which is not permissible, as we can see from the fact that in the limit of vanishing interaction the correction (23) to the free energy does not go to zero, but instead it goes to  $\Delta F \rightarrow NT$ .

All the difficulties described above arise from the assumption that the gas is weakly interacting. In fact, the partition function of the interacting gas reads

$$Z = \frac{(2\pi mT/\hbar^2)^{3N/2}}{N!} \cdot \int d\mathbf{r}_1 \dots d\mathbf{r}_N e^{-U/T} \quad (25)$$

and we may write

$$Z = \frac{(2\pi mT/\hbar^2)^{3N/2}}{N!} \cdot e^{-\langle U \rangle / T} (V - Nb)^N , \quad (26)$$

where  $b$  is the excluded volume. It is worth noting that it is not related directly to the interaction. It is this parameter that makes the gas strongly interacting, as if the gas particles would have a "hard core". Now, it follows directly the free energy

$$\begin{aligned} F &= -NT - (3NT/2) \ln(2\pi mT/\hbar^2) - NT \ln(V/N - b) + \langle U \rangle = \\ &= F_{id} - NT \ln(1 - Nb/V) + \langle U \rangle \end{aligned} \quad (27)$$

and, by making use of  $\langle U \rangle = (N^2/2V) \int' dr \cdot U = -N^2 a/V$ , we get straightforwardly the van der Waals equation

$$(p + aN^2/V^2)(V - Nb) = NT . \quad (28)$$

We see that the free energy (27) can be obtained from (9) by expanding  $1 - NB/V = 1 - Nb/V + Na/VT$  in powers of  $a$ . It is worth noting that the derivation given above introduces two distinct assumptions: the excluded volume and the effect of the interaction. It is difficult to relate these assumptions to each other, so, the derivation presented here for the van der Waals equation, though reasonable, does not make use exclusively of the effects of the interaction. The two distinct assumptions cause also the unphysical behaviour in-between the van der Waals isotherms, related to metastable states. The isotherms for a realistic gas exhibit in fact horizontal plateaux, according to the discontinuities in the volume for the gas-liquid transition.