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van der Waals revisited

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ABSTRACT

The van-der-Waals version of the second virial coefficient is not far from being exact if the model parameters are appropriately chosen. It is shown how the van-der-Waals resemblance originates from the interplay of thermal averaging and superposition of scattering phase shift contributions. The derivation of the two parameters from the quantum virial coefficient reveals a fermion-boson symmetry in non-ideal quantum gases. Numerical details are worked out for the Helium quantum gases.

1. Occupation number statistics and the van-der-Waals model

Occupation number statistics for $N = n\Omega$ non-interacting distinguishable quantum particles (Boltzmann statistics) in a volume Ω yields the entropy density functional

$$s = \frac{k_B}{\Omega} \int \mathrm{d}^3 p \rho(\vec{p}) \nu_{\vec{p}} (1 - \ln \nu_{\vec{p}}), \tag{1}$$

where $\nu_{\vec{p}}$ is the average occupation number of a single-particle energy eigenstate. These eigenstates are enumerated by corresponding points $\vec{p}$ in momentum space, the density of which is $\rho(\vec{p})$. k_B denotes Boltzmann's constant. For the more general case of indistinguishable quasi-particles, one may consider Eq. 22 of Ref. [1], where the Fermi–Bose functional is stated. Nevertheless, this simplifies to our Eq. (1) or (5) if $\nu_{\vec{p}} \ll 1$, which is the case that we discuss in this article.

A hard-core like repulsive interaction is taken into account by the van-der-Waals ansatz

$$\rho(\vec{p}) = (\Omega - Nb)/(2\pi\hbar)^3. \tag{2}$$

Here the "single-particle volume" b is our first van-der-Waals parameter. We consider elementary cells of volume

$$v_{e\ell} = \frac{\Omega}{\rho(\vec{p})} = \frac{(2\pi\hbar)^3}{1 - nb} \tag{3}$$

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in six-dimensional phase space (μ-space) and the one-particle distribution function

$$f(\vec{p}) = \nu_{\vec{p}}/v_{e\ell}. \tag{4}$$

The entropy density

$$s = k_B \int \mathrm{d}^3p f(\vec{p})(1 - \ln(f(\vec{p})v_{e\ell})) \tag{5}$$

is then to be maximized as a functional of f subject to the constraints of fixed particle density

$$n = \int \mathrm{d}^3p f(\vec{p}) \tag{6}$$

and fixed energy density

$$u = \int \mathrm{d}^3p f(\vec{p})\epsilon_{\vec{p}}. \tag{7}$$

According to the second van-der-Waals ansatz, each particle has its classical kinetic energy and is in the potential field of interaction with the other particles, i.e.

$$\epsilon_{\vec{p}} = \frac{p^2}{2m} - an, \tag{8}$$

where a is the second van-der-Waals parameter. Clearly, the treatment of correlations is incomplete in this model.

The energy density now becomes

$$u = \int \mathrm{d}^3p \frac{p^2}{2m} f(\vec{p}) - an^2. \tag{9}$$

From the principle of maximum entropy s and using the temperature definition

$$T = [(\partial s/\partial u)_n]^{-1} \tag{10}$$

one finds f to be the Maxwellian

$$f(\vec{p}) = n(2\pi m k_B T)^{3/2} \exp\left\{-\frac{p^2}{2mk_BT}\right\}. \tag{11}$$

This leads to

$$s = nk_B\left(\frac{5}{2} - \ln\left(\frac{n\lambda^3}{1-nb}\right)\right) \tag{12}$$

with the thermal wavelength

$$\lambda = (2\pi\hbar)/\sqrt{2\pi m k_B T} \tag{13}$$

and to

$$u = \frac{3}{2}nk_BT - an^2. \tag{14}$$

Then the pressure formula

$$P_{eq} = -\frac{1}{n^2}\left(\frac{\partial u}{\partial n}\right)_s \tag{15}$$

results in the van-der-Waals equation of state:

$$P_{eq} = \frac{nk_BT}{1-nb} - an^2. \tag{16}$$

Because of the insufficient treatment of two-particle correlations, this formula will allow a quantitatively satisfying fit for real systems only if $n\lambda^3$ is sufficiently small. Consequently, the van-der-Waals version of the second virial coefficient $B(T)$ is a good approximation if the temperature is not too low:

$$B(T) \approx B_{\mathrm{vdW}}(T) = b - \frac{a}{k_BT}. \tag{17}$$

The appropriate choice of the parameters a and b is dealt with in the following sections. In particular, it could very well be that both parameters depend on the fermionic or bosonic nature of the interacting particles. It will turn out that this is not the case.