

# Van der Waals Equation

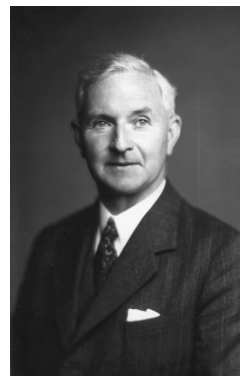
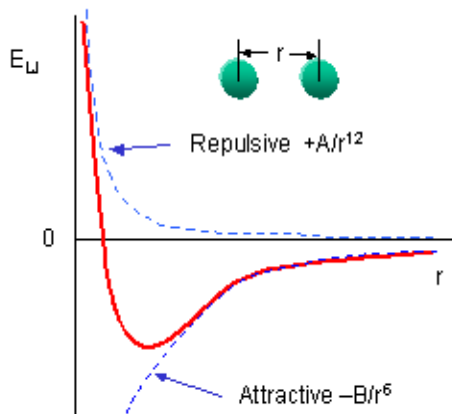
*The Van der Waals equation was a first successful description of thermodynamic phase transitions as originally developed for the liquid-gas transition. Although derived in a somewhat ad-hoc fashion, it is just as valid and consistent as any other mean-field formulation. It succeeded in capturing the main rough qualitative features of first and second order phase transitions, and describes well most experimental features everywhere - except very close to the critical point.*

## Heuristic derivation

Van der Waals had the idea to start with the equation of state for an ideal gas, and then modify it to account for the interactions between molecules. For an ideal gas

$$p = \frac{T}{v},$$

where (as usual) we use energy units such that  $k_B = 1$ , and introduce the inverse density, i.e. volume per particle  $n^{-1} = v = V/N$ .



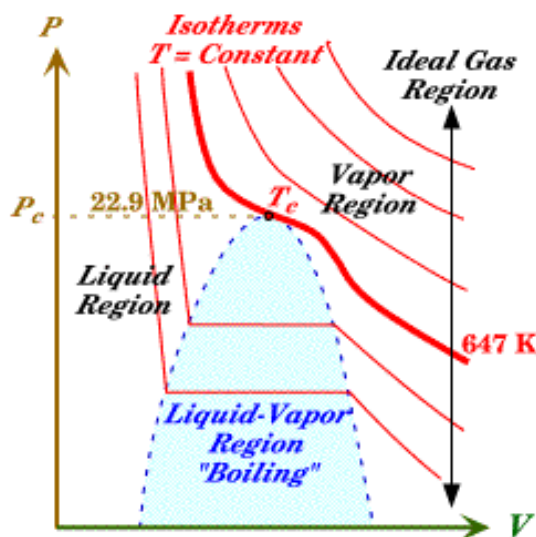
**Sir John Lennard-Jones**

Interaction potentials between particles in the liquid typically have a steep short-range repulsive (core) potential that keeps the atoms apart. This introduces an **excluded volume** per particle which is a constant  $b$  proportional to the volume of the particle itself. Thus, we

may want to replace  $v \rightarrow v - b$ . In addition, in order to get a liquid-gas phase transition, particles must attract each other by a weaker by a longer range attraction (a typical example is the Lennard-Jones potential as shown in the figure) This attraction would lower the energy (and thus the free energy) by an amount inversely proportional to the volume. The pressure  $p = -\frac{\partial F}{\partial V}$  would then be reduced by a factor  $\sim V^{-2}$ , and we can write

$$p = \frac{T}{v - b} - \frac{a}{v^2}.$$

This is the famous Van der Waals equation. As we can see, the entire family of curves  $p = p(V, T)$  has only two adjustable parameters  $a$  and  $b$  that can be fitted to experiments. This important observation is our first encounter of **universality at work**. Here it seems as a result of rather arbitrary assumptions. Later, when we develop the Landau formulation and the renormalization group ideas, we will see that this result is very general and has a simple and robust origin.



**Van der Waals**

We can rewrite it as

$$v^3 - \left(b + \frac{T}{p}\right)v^2 + \frac{a}{p}v - \frac{ab}{p} = 0.$$

As we can see, for given pressure  $p$  this is a cubic equation in  $v$ , hence it has the solutions. Two of these roots correspond to the two stable thermodynamic states at the first order transition - the liquid and the gas. The third root is a thermodynamically unstable solution. This can be seen by observing that at the "middle" solution the  $p(v)$  curve has negative slope, corresponding to negative compressibility  $\kappa_T = -V^{-1}\partial V/\partial p$  (which has to be positive

in equilibrium). Historically, the ambiguities on how to interpret the Van der Waals equation within the coexistence region have been first elucidated using a thermodynamic argument using the so-called Maxwell construction (yes, by the EM guy!). However, this behavior is physically much simpler to understand within the more general Landau formulation that we will explore shortly.

As  $T$  increases, at some critical temperature  $T_c$  the three roots merge into one - we reach the critical point where the liquid and the gas become indistinguishable. The equation then takes the form

$$(v - v_c)^3 = v^3 - 3v^2v_c + 3vv_c^2 - v_c^3 = 0.$$

By comparing this with the above expression, we get expressions determining the critical values  $v_c$ ,  $p_c$ , and  $T_c$

$$3v_c = b + \frac{T_c}{p_c}; \quad 3v_c^2 = \frac{a}{p_c}; \quad v_c^3 = \frac{ab}{p_c},$$

or

$$v_c = 3b; \quad p_c = a/27b^2; \quad T_c = 8a/27b^2.$$

### Law of Corresponding States

Now we introduce our first **scaling expression**, as follows. If we scale  $v$ ,  $p$ , and  $T$  in terms of their critical values, we can write the Van der Waals equation in its **universal form**

$$\left(\frac{p}{p_c} + 3\left(\frac{v_c}{v}\right)^2\right) \left(3\frac{v}{v_c} - 1\right) = 8\frac{T}{T_c}.$$

This means that if we can determine the parameters of the critical point for different liquids, and then plot them in such a scaling form, isotherms corresponding to the given scaled temperature  $T/T_c$  but for many different materials would **collapse** on a single curve! This is the **law of corresponding states**. This predicts, for example, that the quantity

$$\frac{p_c v_c}{T_c} = \frac{3}{8},$$

i.e. is an universal number. Experiments show this ratio to be close to 0.3 for many fluids, in surprising agreement with such a simple theory.

### Critical behavior

Once one knows the equation of state it is easy to calculate all thermodynamic quantities. We will not elaborate this here, as similar computations will be done in more detail when we explore the Weiss mean-field theory for magnetism and the more general Landau formulation. It is possible to show (**Homework # 2**) that within this theory  $C_V$  remains finite (critical exponent  $\alpha = 0$ ) at the critical point, while

$$C_p \sim \kappa_T \sim (T - T_c)^{-1}.$$

Thus the critical exponent  $\gamma = 1$ . Similarly if we define the reduced temperature

$$t = \frac{T - T_c}{T_c}; \delta v = \frac{v - v_c}{v_c},$$

one finds that

$$\delta v \sim t^{1/2},$$

i.e. the critical exponents  $\beta = 1$ . As we will see, identical exponents are found within any mean-field formulation. This is our second example of **universality**.

Finally, a well-known relation in elementary Statistical Mechanics relates the compressibility to the density fluctuations

$$\langle N^2 \rangle - \langle N \rangle^2 = T n^2 V \kappa_T.$$

As we can see, this indicates large density fluctuations near the critical point, in agreement with the phenomenon of critical opalescence.