
Course: Statistical Mechanics / Mean field theories / Mean field theories for fluids

Ideal gases are exceedingly idealised systems and are not suited to describe the behaviour of real systems: they always obey the same state equation and never undergo phase transitions (for example they never condense). We must therefore step a little further: using the “philosophy” of mean field theories we can make the description of fluids a little bit more realistic. As we will see this will also lead to the derivation of the *Van der Waals equation*, which better describes the behaviour of real fluids (even if, as we will shortly see, it still has some problems).

In general, in a real gas all the atoms or molecules interact through a certain potential $\Phi(\{\vec{r}_i\})$ that will depend on the positions of all the particles. For a system of N particles the configurational contribution to the partition function will therefore be:

$$Q_N = \int \prod_{i=1}^N d\vec{r}_i e^{-\beta(\sum_{i=1}^N \varphi_{\text{ext}}(\{\vec{r}_i\}) + \Phi(\{\vec{r}_i\}))}$$

where φ_{ext} is an external potential and in general:

$$\Phi(\{\vec{r}_i\}) = \sum_{i \neq j} U_2(\vec{r}_i, \vec{r}_j) + \sum_{i \neq j \neq k} U_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \dots$$

(where U_n can be a generic n -body interaction potential). Generally φ_{ext} does not pose great problems while it is Φ that makes Q_N impossible to compute exactly, forcing us to resort to approximations. In the framework of mean field theories we substitute the interaction potential Φ with an *effective single-particle potential* $\varphi(\vec{r}_i)$ that acts on every particle in the same way: $\Phi(\{\vec{r}_i\}) \approx \sum_i \varphi(\vec{r}_i)$. Therefore, neglecting the external term for the sake of simplicity, mean field theories allow us to compute Q_N as:

$$Q_N = \left(\int d\vec{r} e^{-\beta\varphi(\vec{r})} \right)^N$$

Of course, every particular mean field theory will provide a different form of φ , which will lead to different results.



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1.1 Text

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