

Van der Waals theory of order - disorder transitions

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys.: Condens. Matter 8 9633

(<http://iopscience.iop.org/0953-8984/8/47/075>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 23:01

Please note that [terms and conditions apply](#).

Van der Waals theory of order–disorder transitions

M Baus and R Achrayah

Faculté des Sciences, CP 231, Université Libre de Bruxelles, B-1050 Brussels, Belgium

Received 15 July 1996

Abstract. In analogy with the well-known Van der Waals theory for disordered fluid phases we propose a simple analytic expression for the Helmholtz free energy of an ordered crystalline phase. It is based on a free-volume approximation to the entropic contribution due to the hard-core repulsions and a static lattice energy approximation to the contribution of the attractions. In this way we are able to describe in a simple way phase transitions between two disordered phases, between two ordered phases and between an ordered and a disordered phase in systems of any spatial dimensionality.

1. The basic ideas of the Van der Waals theory

A system of N non-interacting particles enclosed in a volume V at temperature T can be described by the ideal- (id) gas (Helmholtz) free energy, $F_{id}(N, V, T)$. When the interactions are switched on, the system's free energy, $F(N, V, T)$, acquires an excess (ex) contribution, $F_{ex}(N, V, T) \equiv F(N, V, T) - F_{id}(N, V, T)$. These interactions, which one imagines to be well described by a pair potential $V(r)$, can always be written as the sum of repulsions and attractions. In the Van der Waals (VdW) theory one considers that the excess free energy can likewise be written, $F_{ex}(N, V, T) = F_{ex}^R(N, V, T) + F_{ex}^A(N, V, T)$, as the sum of a contribution due to the repulsions (R) and the attractions (A). The main characteristic of the repulsions is their hard-core character which provides the particles with a proper volume and a hard-sphere behaviour. This reduces the freely accessible volume from the total volume, V , to the free volume, αV , with $\alpha < 1$ and $(1 - \alpha)V$ being the so-called excluded volume. If the repulsions are sufficiently harsh to be viewed as hard-sphere (HS) repulsions, $F_{ex}^R(N, V, T) \equiv F_{ex}^{HS}(N, V, T)$, then their contribution will be purely entropic, $F_{ex}^{HS}(N, V, T) = -TS_{ex}^{HS}(N, V)$, with the excess entropy $S_{ex}^{HS}(N, V)$ entirely due to the reduction of accessible volume, $F_{ex}^{HS}(N, V, T) = F_{id}(N, \alpha V, T) - F_{id}(N, V, T) = -Nk_B T \ln \alpha$, or $S_{ex}^{HS}(N, V) = -Nk_B \ln \alpha$, k_B being Boltzmann's constant. If the pair potential $V(r)$ is written, consequently, as the sum of a HS potential and some attraction, say $V_A(r)$, then the main effect of $V_A(r)$ will be to provide the HS system with some mean cohesion energy, $F_{ex}^A(N, V, T) = E_{ex}^A$. This mean cohesion energy, E_{ex}^A , can be written as N times the mean potential energy due to the attractions

$$E_{ex}^A = \frac{N}{2} \int d\mathbf{r} \bar{\rho}(\mathbf{r}) V_A(r)$$

as seen by a particle placed at the origin. Here $\bar{\rho}(\mathbf{r})$ is the distribution of particles around the particle placed at the origin. In the VdW approximation the total excess free energy per particle, $F_{ex}(N, V, T)/N = f_{ex}(\rho, T)$, can thus be written as

$$f_{ex}(\rho, T) = -k_B T \ln \alpha(\rho) + \frac{1}{2} \int d\mathbf{r} \bar{\rho}(\mathbf{r}) V_A(r) \quad (1)$$

Table 1. The hard-sphere packing fractions, $\phi = v\rho$, for d -dimensional hard spheres of diameter σ and volume v (with $v = \sigma$ for $d = 1$, $v = (\pi/4)\sigma^2$ for $d = 2$ and $v = (\pi/6)\sigma^3$ for $d = 3$) at the order–disorder transition between a fluid phase (F) and a compact crystalline solid phase (S) as obtained from equations (2) and (3) with $V_A(r) \equiv 0$. Between brackets we quote the simulation results [1] whereas $\phi_0 = v\rho_0$ and $\phi_{cp} = v\rho_{cp}$ with ρ_0, ρ_{cp} defined as in equations (2) and (3). Equations (2) and (3) predict a hard-sphere transition to occur for any spatial dimension $d > 1$.

d	ϕ_0	ϕ_{cp}	ϕ_F	ϕ_S
2	0.70	0.91	0.66(0.65)	0.78(0.72)
3	0.495	0.74	0.475(0.494)	0.625(0.545)

where $\rho = N/V$ is the average number density.

2. Ordered and disordered phases

If, as we will assume, the interaction potential is given, then the HS diameter σ and the attractions $V_A(r)$ are known. To use (1) there remains then to be known the free-volume fraction, $\alpha = \alpha(\rho)$, and the site distribution, $\bar{\rho} = \bar{\rho}(\mathbf{r})$. In a disordered fluid-like phase the distribution of sites is uniform and hence, $\bar{\rho}(\mathbf{r}) = \rho$, whereas the dimensionless quantity $\alpha(\rho)$ will be a function of some dimensionless density ρ/ρ_0 which decreases with increasing ρ/ρ_0 from $\alpha = 1$ for $\rho/\rho_0 = 0$ to $\alpha = 0$ for $\rho/\rho_0 = 1$, so that ρ_0 is in fact the maximum value of ρ for which the disordered phase can exist ($\alpha > 0$). In view of the isotropy of the fluid phase we simply put, $\alpha(\rho) = 1 - \rho/\rho_0$, and equation (1) yields then

$$f_{ex}(\rho, T) = -k_B T \ln\left(1 - \frac{\rho}{\rho_0}\right) + 2\pi\rho \int_{\sigma}^{\infty} dr r^2 V_A(r) \quad (2)$$

which is the celebrated VdW excess free energy for fluid-like or disordered phases. Historically various choices for ρ_0 have been made. Here we will put ρ_0 at a value halfway between its upper limit, the crystal close-packing density, and its lower limit, the second virial coefficient value of ρ_0 . How this is to be done for a d -dimensional system is discussed in more detail elsewhere [1]. In an ordered crystal-like phase the distribution of sites runs over the discrete set of neighbours $\{\mathbf{r}_j\}$ of the particle located at the origin, $\bar{\rho}(\mathbf{r}) = \sum_j \delta(\mathbf{r} - \mathbf{r}_j)$ whereas $\alpha(\rho)$ is a decreasing function of ρ which vanishes at the maximum density for which the ordered phase can exist, here the density of crystal close packing ρ_{cp} . In view of the anisotropy of the crystalline phase we write $\alpha(\rho)$ as the product of three one-dimensional factors:

$$\alpha(\rho) = \left(1 - \left(\frac{\rho}{\rho_{cp}}\right)^{1/3}\right)^3$$

whereby equation (1) reduces to

$$f_{ex}(\rho, T) = -k_B T \ln\left(\left(1 - \left(\frac{\rho}{\rho_{cp}}\right)^{1/3}\right)^3\right) + \frac{1}{2} \sum_j V_A(r_j) \quad (3)$$

which is the excess free energy for ordered (crystalline) phases as advocated in [2]. The free-energy expressions (2) and (3) can be easily generalized to d -dimensional systems [1]. They contain no unspecified parameters except those which characterize the attractions ($V_A(r)$) and the ordered structure considered. They contain very basic physics but only in an approximate way. The simple analytic form of (2) and (3) allows explicit expressions to be obtained for many thermodynamic properties [1, 2, 3].

3. Phase transitions

As is well known, equation (2) embodies a simple but realistic description of the disorder–disorder or liquid–gas transition [2]. What is however not obvious from (2) is that the liquid will not always exist, even when the temperature is below the critical point temperature predicted by (2). For a complete description one has indeed to allow the ordered phases described by (3) to compete with the disordered phases described by (2). As shown in detail in [3], for attractions with a sufficiently short range the resulting order–disorder transition will then always pre-empt the original disorder–disorder transition. These results corroborate similar results obtained from more sophisticated theories [4]. This can be understood by observing that the order–disorder HS transition (corresponding to $V_A(r) = 0$) controls the more general ($V_A(r) \neq 0$) order–disorder transition whereas, as shown in [1, 3], the HS transition obtained from (2) and (3) is already fairly realistic (see table 1). When the range of $V_A(r)$ becomes extremely small, equation (3) leads moreover to a VdW loop in the free energy of the ordered phase. This again corroborates results from more sophisticated theories and from computer simulations [4]. Equations (2) and (3) do provide us with a highly flexible and fairly realistic description of the phase transitions which can occur in any system of particles with pair interactions which can be described as a HS repulsion plus an arbitrary attraction, $V_A(r)$.

Acknowledgment

MB acknowledges financial support from the Fonds National de la Recherche Scientifique (Belgium).

References

- [1] Baus M, Coussaert T and Achrayah R 1996 *Physica A* at press
- [2] Daanoun A, Tejero C F and Baus M 1994 *Phys. Rev. E* **50** 2913
- [3] Coussaert T and Baus M 1995 *Phys. Rev. E* **52** 862
- [4] See, e.g.,
Bolhuis P and Frenkel D 1994 *Phys. Rev. Lett.* **72** 2211
Tejero C F, Daanoun A, Lekkerkerker H N W and Baus M 1994 *Phys. Rev. Lett.* **73** 752