

Phase transition in expanded matter

S. M. Stishov

Institute of Crystallography, Russian Academy of Sciences, 117333, Moscow

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The gas–liquid phase transition falls in the category of transitions which occur in expanded matter as the result of a local volume instability. In general, these transitions are not accompanied by changes in the state of aggregation of the matter. A phase transition in expanded matter is controlled by the behavior of the bulk modulus. The relation between the interaction energy and the temperature plays no special role.

The general volume dependence of the interaction energy in a real many-body system is known to be about the same for particles quite different in nature.

By “interaction energy” here we mean that part of the total energy of the system which does not include the energy of thermal motion or the zero-point energy. This part of the total energy can appropriately be called the “potential energy” E . For systems containing free electrons, the kinetic energy of the electrons is regarded as a constituent part of the interaction energy (or potential energy).

This similarity is not, of course, a matter of pure chance. It is instead dictated by the stability conditions for the matter. It is thus not surprising that the reaction of matter to a change in external conditions has several universal features, one of which is a liquid–gas phase transition. This transition occurs in “expanded” matter, i.e., in matter whose volume V is greater than the equilibrium value (V_0) corresponding to the conditions $P=0$ and $T=0$, where P is the pressure and T is the temperature.

In this letter we show that a phase transition in expanded matter is a consequence of a local volume instability which unavoidably occurs in a many-body system for known interparticle interaction laws. The corresponding phase transition is unavoidably linked with a change in the state of aggregation of the matter; it can be a gas–gas, liquid–gas, or liquid–liquid transition.

To determine the physical nature of a phase transition in expanded matter, we consider Fig. 1, which is a general plot of the volume dependence of the potential energy E , the pressure $P = -(\partial E/\partial V)_T$, and the bulk modulus $K = -V(\partial P/\partial V)_T$. These curves are drawn for the particular case of a Lennard–Jones crystal at $T=0$ and $P=0$ (we are ignoring the contribution of the zero-point energy to the pressure and the bulk modulus, as we are completely justified in doing in the case of heavy particles). The distinctions between a crystal and a state of matter without spatial order are unimportant in the present context.

We see that all three curves in Fig. 1— $E(V)$, $P(V)$, and $K(V)$ —are similar in shape, in accordance with the functional form of the interaction energy. The bulk modulus K , which controls the stability of the matter, decreases rapidly with increasing volume, goes negative, goes through a minimum, and then slowly tends toward

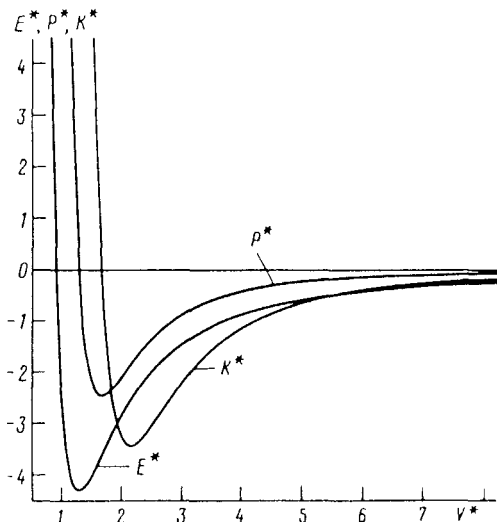


FIG. 1. The reduced energy E^* , the reduced pressure P^* , and the reduced bulk modulus K^* versus the reduced volume for a Lennard-Jones crystal. The curves were calculated from the expression¹ $E^* = 12.131V^{*-4} - 14.454V^{*-2}$.

zero. The condition for stability of the matter [$K > 0$ or $(\partial P / \partial V)_T < 0$] imposes a fundamental limitation on the possibility of an omnidirectional expansion of an object, to a comparatively small increment in volume. Accordingly, the parts of the corresponding curves in Fig. 1 which lie outside the stability region are not observable at $T = 0$.

A very different situation arises during the thermal expansion of an object. The thermal component of the bulk modulus K obviously stabilizes the state of the matter.¹⁾ A glance at the $K(V)$ curve in Fig. 1 shows that two cases are possible here: $T \gg T_c$ and $T < T_c$, where T_c is a characteristic temperature above which the bulk modulus K is always positive (this is essentially the critical temperature of the phase transition). At $T < T_c$ there exists a region of "forbidden" volumes, in which the condition for the existence of a homogeneous object is violated [$(\partial P / \partial V)_T > 0$], and the matter decomposes into two phases, differing in density (this is a first-order phase transition). A more detailed analysis would of course be required in order to say anything definite about the nature of these phases. We should point out that the situation outlined above corresponds essentially perfectly to the behavior of matter in the van der Waals model. This is not surprising, in view of the genetic relationship between the corresponding models of the interparticle interaction.

How is this question resolved in the classical van der Waals theory? In the van der Waals model, repulsive forces are modeled by an interaction of hard spheres, so they do not contribute to the potential energy of the van der Waals object. As a result, the van der Waals equation has an exceedingly simple structure. We can write this equation in the form

$$P = T / (V - b) - a / V^2. \quad (1)$$

The first term on the right-hand side is the thermal pressure. This term is always positive. The second term is correspondingly the potential pressure. This term is always negative. The quantities a and b are constants.²

The famous van der Waals loop, which arises at all temperatures below a critical temperature, is evidence that unstable states, for which we have $(\partial P/\partial V)_T > 0$, arise. Right at the critical point, according to the condition $(\partial P/\partial V)_T$ [see Eq. (1)], the thermal and potential components of the derivative $(\partial P/\partial v)_T$ cancel out exactly.

It is generally assumed that the van der Waals theory describes a liquid-gas phase transition. However, it is not difficult to show, with the help of Eq. (1), that the van der Waals theory contains, in addition to T_c , another characteristic temperature (the same is true of other, equivalent models), $T' \simeq 0.84T_c$, above which the pressure of the system never vanishes. Accordingly, at $T > T'$ the system has no bound states (the free energy does not have a minimum). It is customary to think of a liquid and a gas as bound and unbound states, respectively; if we do this, we would conclude that a phase transition just below T_c in the van der Waals models is a gas-gas transition. In this connection, we should point out that the definitions of condensed matter and a gas as bound and unbound states are contradictory, if only because the propensity of matter to undergo crystallization does not depend on the temperature.³

In determining the state of the matter below, we will make use of the ratio $\gamma = E/kT$, which characterizes the state of the matter for given thermodynamic parameters, and which does not invoke the condition $P=0$. The conditions $\gamma \gg 1$ and $\gamma \ll 1$ undoubtedly make it legitimate to speak in terms of a condensed state or a gaseous state of matter. Although the situation is less definite at values $\gamma \simeq 1$, we will use the condition $\gamma = 1$ as a natural boundary between the condensed gaseous states of matter.

Let us go back to the van der Waals model. Working from the condition $(\partial P/\partial V)_T = 0$ at $T = T_c$ and $V = V_c$, and using Eq. (1), we find $T_c = 2a/V_c(1 - b/V_c)$. Using $V_c = 3b$, and noting that a/V_c is the interaction energy E of van der Waals matter, we finally find

$$T_c \simeq 0.9E(V_c) \quad (2)$$

or

$$\gamma \simeq 0.9.$$

In other words, at the critical point the temperature is essentially equal to the interaction energy or, in the case at hand, the energy of adhesion of the matter. For a volume different from a critical volume we can evidently use the approximation

$$T > |E| \quad \text{for} \quad V > V_c \quad (3)$$

and

$$T < |E| \quad \text{for} \quad V < V_c.$$

On this basis we can assume that the van der Waals theory, with all possible reservations, does indeed simulate a liquid-gas phase transition.

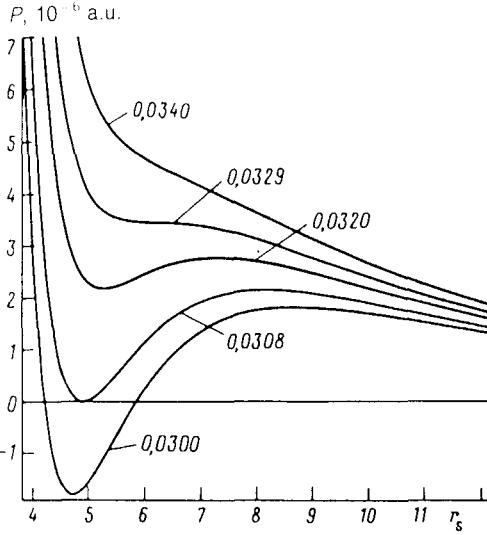


FIG. 2. van der Waals isotherms in the model of a single-component plasma [see expression (6)]. Here P is the pressure, in atomic units, $2Ry/a_0^3$, where Ry is the rydberg, a_0 is the first Bohr radius, and r_s is the radius of a sphere containing one particle, expressed in units of a_0 . The temperature values on the isotherms are in units of double rydbergs. The critical isotherm corresponds to a temperature $T=0.0329$.

How general is this situation? In other words, will relations (2) and (3) hold for other interaction laws?²⁾ Let us consider a classical system of point charges on a uniform neutralizing background (this is the model of a classical one-component plasma). The total energy of this system, E_t , is written in the form

$$E_t = 3/2kT - \alpha r_s, \quad (4)$$

where α is the Madelung constant, and r_s is the radius of a sphere containing one charge. This radius is found from the condition $(4/3)\pi r_s^3 = V/N$, where V is the volume of the system, and N is the number of charged particles.

Since the variation of the Madelung constant is generally small, we assume that it is independent of the thermodynamic conditions. We assign it a value of 0.9, which corresponds to the interaction of a point charge with a uniformly distributed charge of the opposite sign in a spherical cell. (The numerical value of α plays no particular role in this case.) Furthermore, ignoring the contribution of spatial correlations to the pressure, we find the equation of state

$$P = 0.239T/r_s^3 - 0.072/r_s^4, \quad (5)$$

where r_s is expressed in units of the first Bohr radius, and the pressure is in atomic units. The first term on the right side of (5) is the pressure of an ideal gas; the second term is the pressure of a system of point charges.

It is simple to verify, with the help of Eq. (5), that this system does not undergo a phase transition, although it does have an instability at small values of r_s (Ref. 4). The reason is that, as r_s is reduced, the thermal pressure in (5) increases too slowly to overcome the instability caused by the Coulomb term. However, if we assume that the neutralizing background is a degenerate electron gas, we find that the system becomes stable, and the equation of state becomes

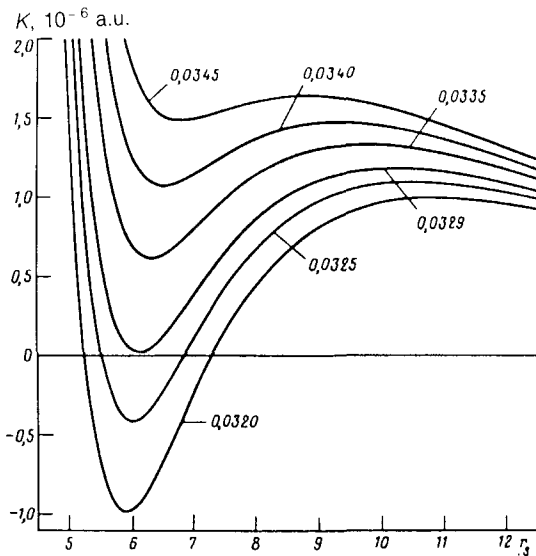


FIG. 3. Behavior of the bulk modulus $K = -V(\partial P/\partial V)_T$ near the phase transition in the model of a single-component plasma [see (6)]. The units of measure are explained in Fig. 2. The critical isotherm ($T = 0.0329$) corresponds to the case in which the $K(V)$ curve is tangent to the abscissa.

$$P = 0.239T/r_s^3 - 0.072/r_s^4 + 0.1759/r_s^5, \quad (6)$$

where the third term on the right is the Fermi pressure of the electron gas.

It follows from Fig. 2 that Eq. (6) has all the distinguishing features of the van der Waals equation. Figure 3 shows how the bulk modulus K vanishes at the critical point. The critical point has the coordinates $T_c = 0.033$ a.u. ($\sim 10^4$ K), $r_s = 6.18$. The value of the interaction energy of the critical point is $E = -0.12$ a.u., so we have a ratio $\gamma = T_c/E \approx 0.3$.

In the model which we are discussing here, the phase transition is thus totally unrelated to a change in the state of aggregation of the matter, and it is a liquid-liquid transition. Near the first-order phase transition, these two liquid phases obviously differ only in density. Note also that assertions of this sort are meaningful near the critical point, where the abrupt change in volume at the transition is small. At low temperatures the volume of the low-density phase may be so large that the condition $T/E > 1$ is satisfied, regardless of the situation at the critical point.

The model discussed above is too simplified to be compared directly with any real system, unless we consider the matter comprising white dwarfs such a system. Nevertheless, it does have some bearing on the situation in liquid metals. In particular, one might be led to believe that the corresponding transition in liquid metals would be a liquid-liquid phase transition if there were no effects associated with a metal-insulator transition (Ref. 5). Note in this connection that simple estimates show⁶ that the ratio of the temperature to the potential energy at the critical point is very small ($T_c/E \approx 0.03$) for alkali metals.

In conclusion we would like to stress once more that a phase transition in expanded matter is a consequence of a volume instability and is controlled by the

behavior of the bulk modulus. The particular relation which holds between the critical temperature T_c and the interaction energy E plays no special role in this case; it may correspond to a gas-liquid, gas-gas, or liquid-liquid transition, depending on the particular particle-particle interaction. On the other hand, since the onset of instabilities is due solely to the behavior of the second derivative of the interaction energy with respect to the volume, one cannot make the unconditional assumption that nature has no other types of interactions which would prevent an instability of the type considered here. The phase diagram of matter with a specific interaction of that sort would have a completely different form.

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¹The zero-point energy plays a role of this sort in quantum matter at $T=0$.

²It is apparently no secret that a van der Waals loop can arise in systems other than systems with a short-range repulsion.

³One might suggest that that stability region of expanded metallic matter is controlled by the relation $E \simeq I$, where E is the interaction energy, and I the ionization potential. At $I/|E| > 1$, an insulating state apparently becomes unfavorable.

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