# SOME THEORETICAL ASPECTS OF PHASE TRANSITIONS

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Thermodynamics alone puts but few limitations on the nature of phase transitions. Coupled, however, with a statistical mechanical interpretation, it provides occasionally some insight into this nature.

Consider the usual simple proof that the Helmholtz free energy, $A(V,T)$ can never have a region in which the plot against $V$ at constant $T$ is concave downward, i.e. for which $(\partial^2 A/\partial V^2)_T < 0$. Suppose there were such a region, *Figure 1*. We draw the straight line tangent at $V_1$ and at $V_2 > V_1$. Consider a system of volume $V$ $(V_1 < V < V_2)$ then a distribution with
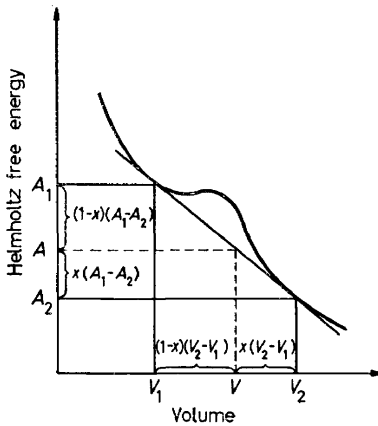


*Figure 1*

weight fraction $x = (V_2 - V)/V_2 - V_1)$ occupying the volume $xV_1$ and with fraction $(1 - x) = (V - V_1)/(V_2 - V_1)$ occupying the volume $(1 - x)V_2$ will have total volume $V$. Provided the system is so large that the interfacial free energy can be neglected, the total free energy will be $A = xA_1 + (1 - x)A_2$, namely it will lie on the straight line between the two volumes $V_1$ and $V_2$. But since the equilibrium condition at fixed $V$ and $T$ is that $A$ be a minimum, the two-phase system will be the equilibrium state for all volumes between $V_1$ and $V_2$.

Since $P = - (\partial A/\partial V)_T$ is constant along the line, the two-phase region has a constant pressure. For the sketch shown, since $(\partial^2 A/\partial V^2)_T > 0$ at both $V_1$ and $V_2$, the compressibilities, $K = - V(\partial V/\partial P)_T = V/(\partial A^2/\partial V^2)_T$ approach finite values at the phase transition.

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The argument is conclusive for thermodynamic equilibrium. However, the inverse conclusion, which is sometimes drawn, that if there is a phase transition there must exist some uniquely defined continuous $A(V,T)$ curve above the straight portion, is unjustified. This conclusion is sometimes extrapolated from the remarkable success of the simple van der Waals equation which shows the familiar $P-V$ loop in the condensation region, corresponding to just such a continuous $A-V$ curve with $A$ concave downward. The conclusion is further substantiated by the fact that in many, if not all, cases the metastable region can be traced experimentally beyond the transition volumes. However, these metastable curves are never followed into the region where $A$ is concave downward, $(\partial P/\partial V)_T > 0$.

It is my opinion that no such continuous $A-V$ curve has any unique meaning. The usual description is that such a continuous $A-V$ curve is that which would obtain if the system were constrained to a uniform density. However, the problem arises as to how uniform is uniform. If $(\partial^2 A/\partial V^2)_T < 0$ fluctuations of any kind in the density lead to a more stable configuration, and since positive surface free energies are meaningless between regions differing in a continuous parameter for infinitesimal differences in that parameter, the fluctuations on a molecular level will be stable. In short, even if the system is constrained to a lattice with one molecule per site, the equilibrium configuration will have the molecules at the cell corners with as many clustered together as the assumed lattice allows. The value of $A$ will depend on the lattice structure assumed and will be utterly different if a lattice permitting two or more molecules per cell is considered.

An interesting example of a phase transition in which the metastable curves for the two phases can be traced to overlapping volumes is that of some experiments made by the use of electronic computers on hard sphere molecules. These have been made by Alder and Wainwright in Livermore and by Wood in Los Alamos, the latter following a method first used by Metropolis, Rosenbluth, Rosenbluth, Teller and Teller.

The computers treat an infinite system of hard spheres, the initial positions and velocities of which are exactly periodic in cubic cells containing $n$ molecules, so that for all future time the system is constrained to have no density fluctuations nor energy fluctuations in any volume containing exactly an integral number of these cubic cells. In different experiments the number $n$ is chosen as 4, 8, 16, 32, . . . 512, the latter being the largest number treated. The results are essentially independent of $n$ for $n \geqslant 32$. Alder and Wainwright ask the computer to tell them the positions and velocities after time $t$ by actually computing the results of all collisions. Wood uses the $M R^2 T^2$ method, by which random displacements with the appropriate weighting are made. The number of random moves in this case plays a similar role to the time $t$ in the other computation. In both cases the pressure $P$ is computed from the pair distribution in space, and the results of the two methods are essentially identical.

At sufficiently large volumes the $P-V$ curve is quite normal. At volumes considerably larger than close packing a strange phenomenon occurs. For the order of $10^5$ moves or more the computed $P$ shows the normal small fluctuation around some average value, $P_{cr}(V)$, but then suddenly jumps to a

larger value, and fluctuates around the new average of $P_g(V)$ for another $10^5$ or more moves. In at least one case a return to $P_{cr}$ was observed. The spatial distribution that leads to $P_{cr}$ is that of small displacements from the arrangement of a close-packed lattice, and few if any exchanges of the positions of the molecules occur. (Since the initial positions chosen are those of a close-packed lattice the " phase " with $P_{cr}$ always appears initially.) If $V$ is sufficiently large the distribution goes over in a few moves (that is in some $10^3$ moves) to the distribution corresponding to $P_g(V)$.

Unfortunately, the free energy $A_{cr}(V)$ of the " phase " for which the pressure is $P_{cr}(V)$ cannot be obtained. That of the other " phase " is obtained from the $P_g(V)dV$ integral to the perfect gas limit where the integration constant is known. The function $A_{cr}(V)$ is left with an unknown integration constant, and the " equilibrium " pressure at which the transition occurs is unknown. However, since the negative slope

$$- (\partial A_g / \partial V)_T = P_g(V)$$

of the " gas phase " is much greater than that of the " crystalline phase " at low $V$ values, it is clear that the two curves, $A_g$ and $A_{cr}$ must intersect, leaving a region concave downwards.

By an ingenious method Wood has "compressed" the metastable gas phase to low $V$ values, and the distribution appears to go over into something resembling that of a body-centred cubic lattice.

Now it appears to me to be clear that the behaviour of this system shows that the " gas " or " fluid " phase has a positive surface free energy in contact with the " crystalline " phase.

In the discussion of the phase transition one proves that a transition occurs at equilibrium if the $A-V$ curve is such that a tangent to it at two volumes $V_1$ and $V_2$ falls below the curve. However, the statement is only true if the surface free energy is neglected. This is always legitimate if the system is large enough, and under no constraint of uniform density. If, however, the surface free energy is positive, and a sufficiently large proportion of the system is at the interface, the argument would fail. The systems dealt with in these computer experiments are such that uniform density is maintained in cubic cells containing $n$ molecules, and always $n < 10^3$. The system can become two-phase only by dividing every cell into the two phases. Counting that at least one molecular layer in each phase is at the interface, even for $n = 10^3$ one would have 200 molecules in each cell at an interface bisecting the cell, and another 200 at the interfaces with the adjacent cell. In all, about half the molecules would be at interfaces. If the surface free energy is positive it is clear why the system does not show the phase separation and the consequent volume range of constant $P$ value. But unless the surface free energy were positive separation would occur. It seems evident that there are two distinct phases, crystalline and fluid, for these hard sphere molecules, and that the two phases have a positive surface free energy.

One might parenthetically remark that for this (classical) system the energy is purely kinetic and independent of volume. The whole dependence of $A$ upon $V$ lies in the entropy term, as does the surface free energy.

Could the calculations be carried out sufficiently long the relative entropies in the two phases could be evaluated by comparing the " times" spent in each phase. The transitions are so rare that this is impractical.

The foregoing discussion indicates that in the normal first-order transition the free energies of the two phases show a normal behaviour as the transition is approached. Abnormal increase in the compressibility or in the heat capacity is not to be expected. If such an abnormal " pre-transition " rise in either or both were observed it would indicate that the stable phase has, in its structure, some premonition of the approaching calamity. Such premonitory behaviour might be described as fluctuations in the stable phase, $a$, of groups of molecules into the arrangement of phase $b$. If $\Delta\mu$ is the difference, $\mu_b - \mu_a$, in the free energies per molecule for the two phases, the probability that a given set of $n$ molecules would be in phase $b$ would be $\exp - n(\mu_b - \mu_a)/kT$ were there no surface effects. The number on the interface is of order $n^{2/3}$, and if the interfacial free energy per (the area of one) molecule is $\sigma$ then another factor of order $\exp - n^{2/3}\sigma/kT$ is introduced, which is the only remaining factor at the transition point for which $\mu_a = \mu_b$. We might decide that the new phase is unrecognizable unless it is at least the size of a cube with four molecules on the edge, having 8 molecules in the interior as the new phase, and the remaining $64 - 8 = 56$ molecules on the surface. The chance that a given set of 64 molecules is in such a fluctuation is then of the order $\exp - 56\sigma/kT$, which is hardly appreciable unless $\sigma/kT$ is indeed very small. Using a rather small interfacial tension of 13 dyn/cm and an area of 10 Å$^2$ per molecule, $\sigma = 1\cdot3 \times 10^{-14}$ erg, $\sigma/k$ is 100°K, so that $\sigma/kT$ is of order $\frac{1}{3}$ at room temperature.

We may conclude that if two phases have a reasonable interfacial tension the fluctuations in either of the phases that presage the transition will be negligible. The situation is utterly different if the interfacial tension is extremely small, and were it, perchance, to become identically zero in value, we would expect a continuous rise of the heat capacity and of the compressibility to infinite values as the transition is approached.

The order of a phase transition is traditionally defined as that of the lowest derivative of the Gibbs free energy, $G$, which becomes discontinuous at the transition. First-order transitions are those for which there are non-zero first derivative discontinuities by the amounts $\Delta S$ and $\Delta V$, whereas for second order transitions these are continuous but the next derivatives are discontinuous, so that $C_p$, $K$ and $\beta$ jump in value. The definition has the advantage of mathematical simplicity and apparent uniqueness, even if, on the one hand rather varied phenomena are classed as the same order, and on the other hand the order is not always easy to assign unambiguously from the experimental behaviour.

There exists an old objection to the possibility of existence of true second-order (or any even order) transitions. The objection is probably best answered by the apparent experimental existence of a considerable number of clear cases. However, it deserves mention with the probable theoretical answer.

The objection is that, on a $G-T$ plot, the continuation of the curve for the phase of higher $C_p$, and therefore of greater concavity downward, lies at a lower free energy $G$ than that of the phase which is observed to be

stable. The obvious answer is that the continuation does not exist. Physically, one assumes that there is some natural parameter which is a function of the state $T$ and $P$, the change of which contributes terms to the heat capacity and compressibility, *etc.*, and which reaches some " dead-end stop " at the transition, so that beyond the transition it remains constant at this limiting value. Actually, as far as I know, all cases of second-order transitions for which there is a mechanistic physical explanation do have a natural parameter of this type. In the lambda transition of liquid helium the two-fluid model has this parameter as the fraction of superfluid, which reaches the natural limit of zero at the transition. Transitions explained by the onset of what one describes as free rotation have also such a parameter in the fraction of " freely rotating " molecules, which cannot exceed unity. In the case of superconductivity the parameter is the " energy gap " above the Fermi surface, which decreases to zero at the transition.

Unfortunately for so simple an explanation, any naïve interpretation of it would require the heat capacity to be completely normal on the side of the transition for which the parameter takes its constant limiting value. This is seldom the case, and in most experimentally known cases the heat capacity rises abnormally from both sides as the transition is approached.

Even the mathematical definition of a second-order transition runs into at least semantic difficulties when applied to the liquid helium case. The heat capacity rises logarithmically to infinity from both sides as the transition is approached. Since the rise is logarithmic the heat absorbed in the interval between $T_{tr} - \epsilon$ and $T_{tr} + \epsilon$ goes to zero as $\epsilon$ vanishes, so that the transition is not first order. In the sense that the two heat capacities at $T_{tr} - \epsilon$ and at $T_{tr} + \epsilon$ differ by a non-zero constant as $\epsilon$ decreases, there is a " jump " in the heat capacity, but at the transition it is between two infinite values.

There is one rigorous statistical mechanical statement that can be made linking the order of the transition and the distributions of molecules on the two sides of the transition. The statement is simplest in the classical case when the kinetic energy is always $(\frac{1}{2})kT$ per degree of freedom. The molecular distribution may be described by a hierarchy of probability density functions for increasing numbers, $n$, of molecules. The first of these $\rho_1(r)$ gives the probability density of finding a single molecule at $r$ and the second, $\rho_2(r_1, r_2)$, is the probability density of finding simultaneously one molecule at $r_1$ and a second at $r_2$. In an $n$th order transition the probability density function, $\rho_n$, for $n$ molecules is discontinuously different on the two sides of the transition, but the functions for fewer than $n$ molecules remain continuous.

Finally I may mention one interpretation of what appears to be a second-order transition in some glasses, presented by Dr J. H. Gibbs at the Gordon Research Conference on Liquids in the summer of 1959. On cooling, most glasses show abnormally high heat capacities, and on " freezing " there is a sudden drop of the heat capacity. The entropy drops on cooling abnormally rapidly in the range of high heat capacity, then at a normal rate for lower temperatures, but usually stays well above the entropy of the crystalline material and approaches a positive non-zero value at absolute zero. The sudden change of heat capacity is primarily or solely due to the enormous

increase in viscosity and consequent almost zero rate of the internal reorientations toward the stable ordered structure.

However, some polymer glasses, the polymer of which can also be obtained as crystals, have a total decrease of entropy in this abnormal heat capacity range which takes them to essentially the same entropy as the crystal. Below the " transition " their heat capacities are closely the same as that of the crystal, and, if the crystal entropy is zero at absolute zero one concludes that the glasses approach (practically) zero entropy at absolute zero. If these facts are correct one must conclude that the " transition " occurs as the disorder entropy of the glass approaches zero.

In order to believe this at all one must remember that a vanishingly small entropy is still consistent with a considerable number of states in a macroscopic system. Since $S = k \ln \Omega$, a value of $\Omega$, the number of microscopic states, as large as $10^{10^{20}}$ which is still a considerable number, would give an immeasurably small entropy in one mole of material.

Now Gibbs sets up the highly complicated expression, using the quasi-chemical approach, for the number of disordered complexions, $\Omega$, as a function of the difference, $\Delta E$, in energy between the glass and crystal, which in turn is determined by the number of " misplaced " links. The details of the calculation are quite complicated. However, the expression for $\ln \Omega$ extrapolates to zero, $\Omega$ to unity, at a value of $\Delta E$ greater than zero. In reality, of course, the approximate expression, which might be quite good for large $\Delta E$ fails at low values, where certain unique configurations corresponding to the partial crystalline order begin to have importance, and configurations for all $\Delta E > 0$ exist, indeed in great numbers, but not greater than, say, $10^{10^{20}}$. The glass system follows the approximate equation prediction fairly well for large $\Omega$ values, decreasing $\Delta E$ and $\Omega$ with lowering temperature, and finding it increasingly difficult to diffuse to the lower energy sites as $\Omega$ decreases and their number becomes smaller. This same decrease in sites available causes a rapid decrease in fluidity. By the time $\Omega$ had decreased to $10^{10^{20}}$ the molecules can no longer find the few peculiar configurations of really low energy, and the fluidity has sunk correspondingly. But by this time the configurational entropy has become immeasurably small.

Whether the picture indeed corresponds to reality I am not in a position to assert. In any case I find it plausible. The essential feature is that the low configurational entropy is adduced as a cause of the decrease in fluidity, the decrease in fluidity occurs at the same point as the true $S$ versus $\Delta E$ curve changes character, and this occurs at an entropy so small as to be negligible.