

**MMAT 305**  
**PHASE TRANSFORMATIONS IN SOLIDS**

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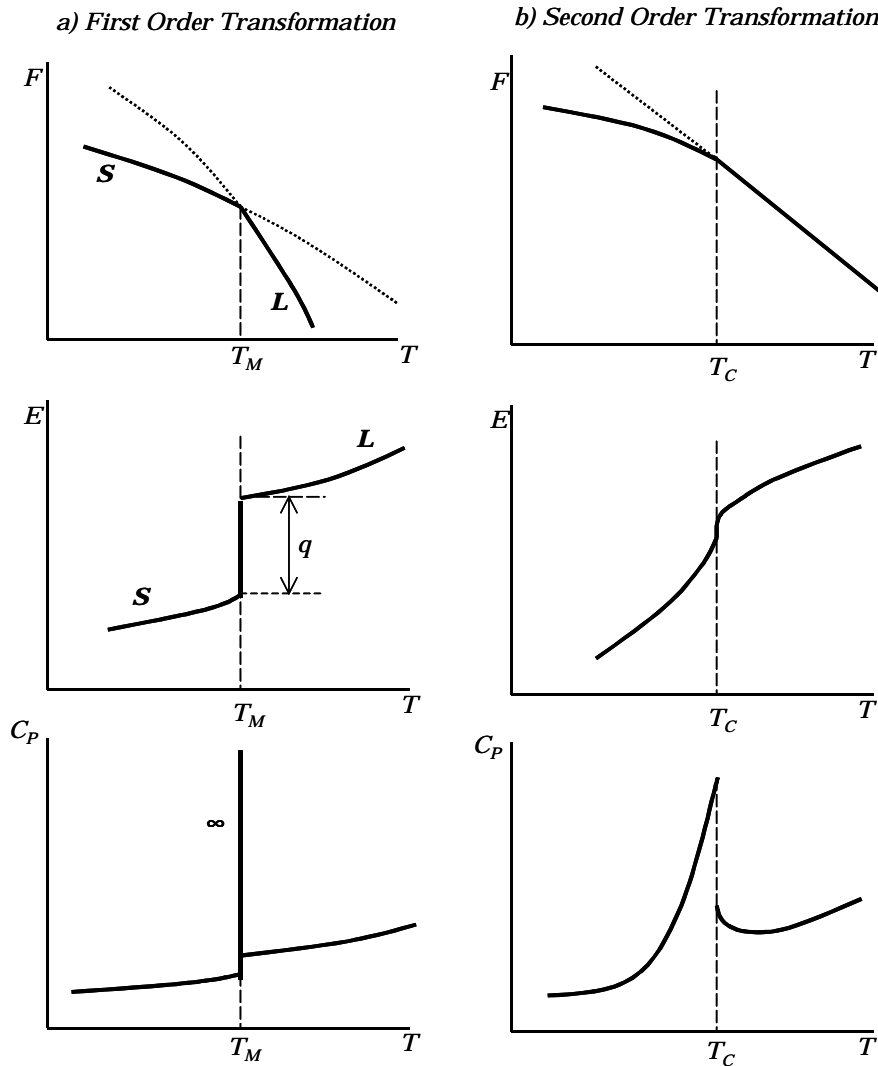
**Order-Disorder Transformations**

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# Order-Disorder Transformations

## 1. Introduction

For first order transformations, the entropy is discontinuous. It is represented graphically by the slope of the free energy-temperature curve. As shown in Figure 1a, the transformation from solid to liquid or liquid to solid at the melting point  $T_M$  involves a discontinuous change in the slope,  $\Delta S$ . Because the free energies of the solid and the liquid at  $T_M$  are equal,  $\Delta F=0$  and the “jump” in the entropy  $\Delta S$  must necessarily correspond to a change in internal energy,  $\Delta E=T_M\Delta S$ , which is the latent heat  $q$ , i.e.,  $\Delta S(T_M)=q/T_M$ .



**Figure 1.** Thermodynamic characteristics of first and second order transformations.

For second order transformation, there is no discontinuity in the entropy, i.e., no abrupt change in the slope of the free energy vs. temperature curve at the transition temperature  $T_c$  (Figure 1b). The capacity, however, does change. Graphically, the capacity is represented by the change in the curvature.

Consider a binary alloy of atoms A and B (Figure 2).

A	B	A	B	A	B
B	A	B	A	B	A
A	B	A	B	A	B
B	A	B	A	B	A
A	B	A	B	A	B
B	A	B	A	B	A

**Figure 2.** A completely ordered lattice of atoms.

Now, change pairs of atoms A-B atoms, so that an atom A is moved from sub-lattice 1 to sub-lattice 2 and an B atom is moved from sub-lattice 2 to sub-lattice 1 (Figure 3).

A	B	A	B	A	B
B	A	B	A	A	A
A	A	B	B	B	B
B	A	B	A	B	A
A	B	A	B	A	B
B	A	B	A	B	A

**Figure 3.** A partially ordered lattice of atoms.

Consider the concentration  $C$  of “wrong” pairs, or misplaced pairs of atoms. In a totally ordered state  $C=0$ , while in a totally disordered state  $C=1/2$ . It is convenient to define an *order parameter*  $\eta$  such that  $\eta=1$  for the completely ordered state and  $\eta=0$  for the completely disordered state. In the previous example of a binary alloy of A and B atoms, the order parameter is related to the concentration of pairs placed on the “wrong” sub-lattice through:

$$C = \frac{1}{2}(1 - \eta)$$

## 2. Interacting and Non-interacting Systems

To illustrate the difference between interacting and non-interacting systems, let us focus our attention to a very similar system, the Frenkel defects. Frenkel defects can be visualized as pairs placed on the “wrong” sub-lattice. The crystal can be viewed as two interpenetrating sub-lattices: one of atoms A and one of interstitial sites  $i$  (consider that the sub-lattice 2 is the lattice of interstitial sites and replace B atoms with interstitials in Figure 2). The energy of such a system is given by:

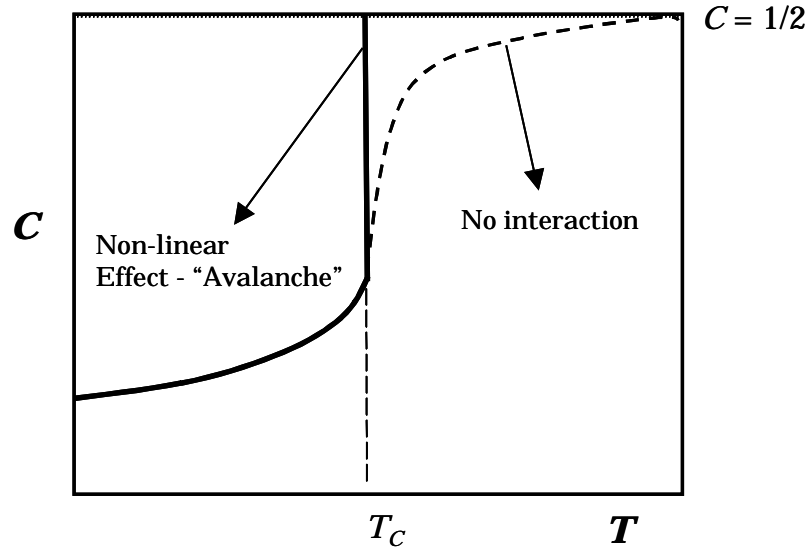
$$E = \varepsilon_p CN$$

where  $\varepsilon_p$  is the energy of a single pair,  $C$  is the concentration of pairs, and  $N$  is the total number of atoms (which is in this example equal to the total number of pairs). This simplified expression for the energy of a system of Frenkel pairs assumes *no interaction between vacancies*. This is clearly an oversimplification. When there are large number of vacancies in the crystal, there are fewer bonds to break when removing an atom. It is, therefore, *easier* to create a vacancy in the presence of many other vacancies. A highly disordered system tends toward more disorder (so called the “*avalanche*” effect, shown in Figure 4). In general, one can model the energy of such a system by adding higher order terms to the linear energy expression for the non-interacting system:

$$E = \varepsilon_p CN - AC^2$$

Ferromagnetic as well as ferroelectric materials show a similar behavior. Consider a system of magnetic dipoles, all aligned in the same direction ( $\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow$ ). As the temperature is increased, the order parameter will decrease. Dipoles will begin to assume a random orientation ( $\uparrow\downarrow\uparrow\uparrow\downarrow\uparrow\downarrow\downarrow\uparrow\uparrow$ ). In the ordered state, when all the dipoles are aligned, there is a strong net magnetic field produced as a result of the combined fields of the

individual dipoles. This net magnetic field makes an anti-parallel dipole *energetically unfavorable*. As dipoles begin to flip due to increased thermal vibrations as the temperature is raised, the net magnetic field decreases. This means that flipping a dipole from the parallel to the anti-parallel orientation is *easier* when the system is less ordered. Again, when this system is in a disordered state, the change in energy due to interaction causes the system to tend to further disorder.



**Figure 4.** Concentration of “wrong” pairs for interacting and non-interacting systems.

### 3. The Anti-phase Boundary

A completely ordered system is shown in Figure 5. All A atoms are on sub-lattice 1 (squares) and all B atoms are on sub-lattice 2 (circles). In this case, the probability of finding an A atom on a sub-lattice 1 site is unity while the probability of finding a B atom on sub-lattice 1 is zero. For this case, the order parameter  $\eta=1$ . If the system were in a state of complete disorder,  $\eta=0$ , then the probability of finding an A atom on sub-lattice 1 and the probability of finding a B atom on sub-lattice 1 would be equal.

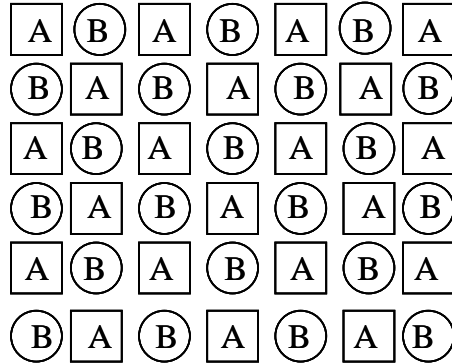
*Complete Order*             ${}^1P_A=1, {}^1P_B=0, {}^2P_A=0, {}^2P_B=1, \eta=1$

*Complete Disorder*         ${}^1P_A=1/2, {}^1P_B=1/2, {}^2P_A=1/2, {}^2P_B=1/2, \eta=0$

Relating the probability to find a given atom on a given sub-lattice site gives:

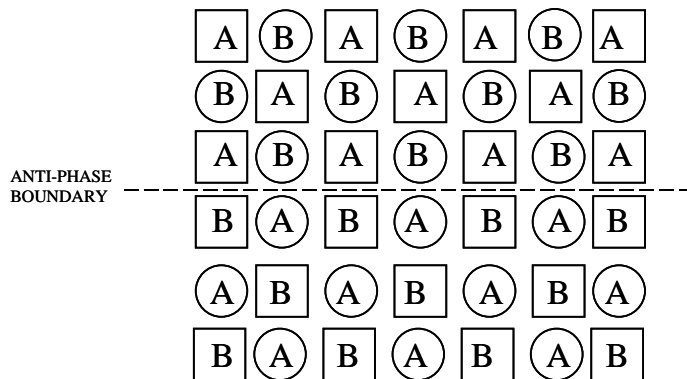
$${}^1P_A = \frac{1}{2}(1 + \eta) \text{ and } {}^1P_B = \frac{1}{2}(1 - \eta)$$

where  ${}^1P_A + {}^1P_B = 1$  which implies that all sub-lattice 1 sites are occupied.



**Figure 5.** A completely ordered system with A atoms on sub-lattice 1 (squares) and B atoms on sub-lattice 2 (circles).

Now consider a crystal with all the atoms in the “wrong” sub-lattices. By the above definitions, the order parameter of such a system must be  $\eta = -1$  and the system is again *completely ordered*. When two adjacent regions in a crystal display this property, the boundary between the two regions is called an *anti-phase boundary* (APB, Figure 6).



**Figure 6.** The anti-phase boundary.

As stated before, the order parameter for one region is  $\eta = 1$  while in the other region  $\eta = -1$ . However, the order parameter of the whole system is not well defined. The order parameter, in this case, is a local property and cannot be accurately represented by an average over a larger region containing APBs.

## 4. Bonding Energy

If the energy associated with an atom bonding with its neighbors in a binary alloy is considered, it is obvious that the AA, BB, and AB bonds may have different energies associated with them [ $\epsilon_{AA}$ ,  $\epsilon_{BB}$ ,  $\epsilon_{AB}(=\epsilon_{BA})$ ]. To determine whether or not atoms A and B will form a solid solution, one must evaluate

$$\Omega = \epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})$$

If  $\Omega < 0$ , then the two atoms mix because *on average* AA and BB bonds require more energy than AB and BA bonds. If, however,  $\Omega > 0$ , then the AB bonds require more energy and mixing is energetically unfavorable. Thus the two species separate.

## 5. Thermodynamic Theory

Having developed some understanding of the nature of order-disorder transformations and having introduced the concept of the order parameter  $\eta$ , we would now like to express the standard thermodynamic functions such as the free energy ( $F$ ), entropy ( $S$ ), internal energy ( $E$ ), and the heat capacity ( $C_p$ ) in terms of  $\eta$ . The approach that will be outlined below is known as the *Bragg-Williams* solution. The process will be analogous to the approach previously used, for example, to determine the equilibrium vacancy concentration and the contribution of vacancies to the heat capacity of a crystal. The method consists of “constructing” the degeneracy of the system from basic combinatorics and taking the logarithm to find the entropy as a function of the order parameter, and then establishing the total energy of the system as a function of  $\eta$  given the definition of  $\eta$  and some specific information about the system. The free energy is then constructed in the usual manner:

$$F(\eta) = E(\eta) - T \cdot S(\eta)$$

Imposing the equilibrium condition requires that  $F(\eta)$  be minimum so that the derivative of  $F$  with respect to the order parameter is evaluated and set equal to zero:

$$\partial F / \partial \eta = 0$$

From this relation, one can solve for the *equilibrium order parameter* at a certain temperature, i.e.,  $\eta_0(T)$ , to determine the temperature dependence of the order parameter. The equilibrium

value of  $\eta$  is then substituted back into the general equations for  $F$ ,  $E$ ,  $S$ , and  $C_P$  to establish the thermodynamic functions as a function of the equilibrium order parameter.

Now, let us determine  $E(\eta)$  and  $S(\eta)$  for a binary alloy of A and B. Let:

$N_A$  = the number of A atoms= $N/2$

$N_B$  = the number of B atoms= $N/2$

$N$  = total number of atoms in the system

${}^1N$  = the number of type 1 sub-lattice sites

${}^2N$  = the number of type 2 sub-lattice sites

${}^1N_A$  = the number of A atoms on sub-lattice 1

${}^1N_B$  = the number of B atoms on sub-lattice 1

${}^2N_A$  = the number of A atoms on sub-lattice 2

${}^2N_B$  = the number of B atoms on sub-lattice 2

If we consider a crystal with no vacancies and interstitials, then:

$${}^1N_A + {}^2N_A = N_A = N/2$$

The multiplicity of such a system is:

$$\omega = \frac{{}^1N!}{{}^1N_A! {}^1N_B!} \cdot \frac{{}^2N!}{{}^2N_A! {}^2N_B!}$$

For the internal energy of the system, we assume that the energy is the sum of the energies of pairs of nearest neighbors. The energy of such a system is simply:

$$E = \varepsilon_A N_A + \varepsilon_B N_B + \varepsilon_{AA} N_{AA} + \varepsilon_{BB} N_{BB} + \varepsilon_{AB} N_{AB} + \varepsilon_{BA} N_{BA}$$

where  $\varepsilon_A$  and  $\varepsilon_B$  are the “self-energies” of atoms A and B, respectively, and will be ignored for the purposes of this analysis. The number of A-A and A-B bonds can be written as:

$$N_{AA} = z {}^1N_A {}^2P_{A-A}, \quad N_{AB} = z {}^1N_A {}^2P_{B-A}$$

where  $z$  is the coordination number (for a simple cubic lattice  $z=6$ , BCC  $z=8$ , FCC  $z=12$ ), and  ${}^2P_{A-A}$  is the probability of finding an A atom in sub-lattice 2 next to an A atom. Similarly,  ${}^2P_{B-A}$  is the probability of finding a B atom in sub-lattice next to an A atom. This is a simplification of the problem since we assume no interactions between “misplaced” atoms. Thus, it is assumed that the probability of finding an A atom on a sub-lattice 2 is only a function of the number of A atoms and the number of sub-lattice 2 sites. This lack of interaction really

describes a lack of *short-range* order. The concentration of atoms A and B expresses information about *long-range* or *global* order. To state this assumption more rigorously:

$${}^1P_{A-A} = {}^1P_{A-B} = {}^1P_A = {}^1N_A / N_A, \quad {}^2P_{A-A} = {}^2P_{B-A} = {}^2P_A = {}^2N_A / N_A$$

It should be noted that in reality,  ${}^1P_{A-A} \neq {}^1P_{A-B}$  as well as  ${}^2P_{A-A} \neq {}^2P_{B-A}$  due to short-range order. Using this approximation, we have

$${}^1N_A = N_A {}^1P_A = \frac{N}{2} {}^1P_A, \quad \text{and} \quad {}^2N_A = N_A {}^2P_A = \frac{N}{2} {}^2P_A.$$

Substituting back into the equation for  $N_{AA}$ , we get:

$$N_{AA} = z \frac{N}{2} {}^1P_A {}^2P_A = z \frac{N}{8} (1 - \eta^2)$$

where we used the relations  ${}^1P_A = {}^2P_B = (1/2)(1 + \eta)$  and  ${}^2P_A = {}^1P_B = (1/2)(1 - \eta)$ . A similar treatment of  $N_{BB}$  yields:

$$N_{BB} = z \frac{N}{2} {}^1P_B {}^2P_B = z \frac{N}{8} (1 - \eta^2)$$

which is reassuringly equal to  $N_{AA}$  as it must be for the case where  $N_A = N_B$  and  ${}^1N = {}^2N$ . For  $N_{AB}$  and  $N_{BA}$  we have:

$$N_{AB} = z {}^1N_A {}^2P_B = z \frac{N}{2} {}^1P_A {}^2P_B = z \frac{N}{8} (1 + \eta)^2$$

$$N_{BA} = z {}^1N_B {}^2P_A = z \frac{N}{2} {}^1P_B {}^2P_A = z \frac{N}{8} (1 - \eta)^2$$

Substituting these relations back into the original expression for the energy of the system:

$$E = \varepsilon_{AA} N_{AA} + \varepsilon_{BB} N_{BB} + \varepsilon_{AB} N_{AB} + \varepsilon_{BA} N_{BA}$$

yields:

$$E(\eta) = \varepsilon_{AA} z \frac{N}{8} (1 - \eta^2) + \varepsilon_{BB} z \frac{N}{8} (1 - \eta^2) + \varepsilon_{AB} z \frac{N}{8} [(1 - \eta)^2 + (1 + \eta)^2]$$

$$= (\varepsilon_{AA} + \varepsilon_{BB}) z \frac{N}{8} (1 - \eta^2) + \varepsilon_{AB} z \frac{N}{8} [(1 - \eta)^2 + (1 + \eta)^2] = \frac{Nz}{8} (\varepsilon_{AA} + \varepsilon_{BB}) - \frac{Nz}{4} \eta^2 \left[ \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} - \varepsilon_{AB} \right]$$

after re-arranging terms. The internal energy can then be expressed as:

$$E(\eta) = E(0) - \frac{Nz}{4} \Delta E \eta^2$$

where

$$E(0) = \frac{Nz}{8} (\varepsilon_{AA} + \varepsilon_{BB}) \quad \text{and} \quad \Delta E = \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} - \varepsilon_{AB}.$$

Having expressed  $E$  as a function of the order parameter, we return now to the expression for the multiplicity first in order to determine an expression for the entropy and second to express the entropy as a function of the order parameter. The entropy of the system is given by:

$$S = k \ln \omega$$

where

$$\omega = \frac{{}^1N!}{{}^1N_A! + {}^1N_B!} \cdot \frac{{}^2N!}{{}^2N_A! + {}^2N_B!}$$

Thus:

$$S = k[\ln({}^1N!) + \ln({}^2N!) - \ln({}^1N_A!) - \ln({}^1N_B!) - \ln({}^2N_A!) - \ln({}^2N_B!)]$$

Now using the Stirling's approximation <sup>†</sup> we obtain the following mess:

$$S = k[{}^1N \ln({}^1N) - {}^1N + {}^2N \ln({}^2N) - {}^2N - {}^1N_A \ln({}^1N_A) + {}^1N_A - {}^1N_B \ln({}^1N_B) + {}^1N_B - {}^2N_A \ln({}^2N_A) + {}^2N_A - {}^2N_B \ln({}^2N_B) + {}^2N_B]$$

Recalling that

$${}^1N_A = \frac{N}{4}(1 + \eta), \quad {}^1N_B = \frac{N}{4}(1 - \eta), \quad {}^2N_A = \frac{N}{4}(1 - \eta), \quad \text{and} \quad {}^2N_B = \frac{N}{4}(1 + \eta)$$

and gathering like terms, the equation for the entropy takes a more palatable form:

$$S(\eta) = -kN \left[ \frac{1}{2}(1 + \eta) \ln \frac{1}{2}(1 + \eta) + \frac{1}{2}(1 - \eta) \ln \frac{1}{2}(1 - \eta) \right]$$

The total free energy of the system is then given by:

$$F(\eta) = E(0) - \frac{NZ}{4} \Delta E \eta^2 + kTN \left[ \frac{1}{2}(1 + \eta) \ln \frac{1}{2}(1 + \eta) + \frac{1}{2}(1 - \eta) \ln \frac{1}{2}(1 - \eta) \right].$$

To determine the equilibrium order parameter  $\eta_0$  as a function of temperature, we minimize the free energy with respect to the order parameter, i.e.,

$$\frac{\partial F(\eta_0)}{\partial \eta} = 0, \quad \frac{z\Delta E}{2kT} \eta_0 = \frac{1}{2} \ln \frac{(1 + \eta_0)}{(1 - \eta_0)}.$$

This is a transcendental equation and cannot be solved easily in closed form. It can be solved, however, without difficulty using numerical or graphical methods. To find the solution of this problem, let us make first the following substitution:

$$T_c = \frac{z\Delta E}{2k}$$

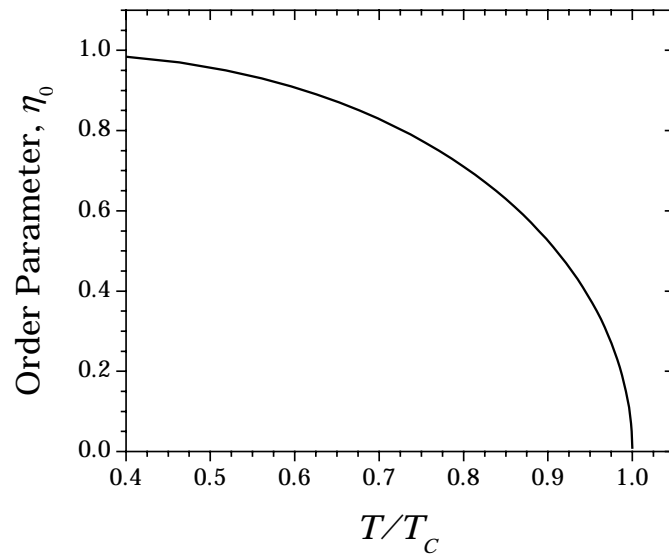
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<sup>†</sup>  $\ln N! = N \ln N - N$  for  $N \gg 1$

such that

$$\frac{T_c}{T} = \frac{1}{2\eta_0} \ln \frac{(1+\eta_0)}{(1-\eta_0)}$$

where  $T_c$  is a critical temperature and its meaning will be obvious later. We then graph  $T/T_c$  as a function of  $\eta_0$  and then swap axes to obtain the variation in the equilibrium order parameter as a function of the normalized temperature  $T/T_c$  (Figure 7).



**Figure 7.** Equilibrium order parameter vs. the normalized temperature  $T/T_c$ .

As it can be seen, when the  $T/T_c=1$ , the order parameter tends to 0. This defines the transition temperature from the (partially) ordered state ( $T/T_c<1$ ) to the disordered state ( $T/T_c>1$ ). This phase transition temperature is also known as the Curie temperature which can be also verified by taking the second derivative of the free energy:

$$\frac{\partial^2 F(\eta)}{\partial \eta^2} = -\frac{Nz}{2} \Delta E + \frac{kTN}{1-\eta^2}.$$

Close to  $\eta=0$

$$\left. \frac{\partial^2 F(\eta)}{\partial \eta^2} \right|_{\eta=0} = -\frac{Nz}{2} \Delta E + kTN = -kN(T_c - T) = \begin{cases} > 0 & T > T_c \\ < 0 & T < T_c \end{cases}.$$

Therefore,  $\eta=0$  corresponds to minimum free energy if  $T>T_c$  (disordered state stable) and maximum free energy if  $T<T_c$  (ordered state stable).

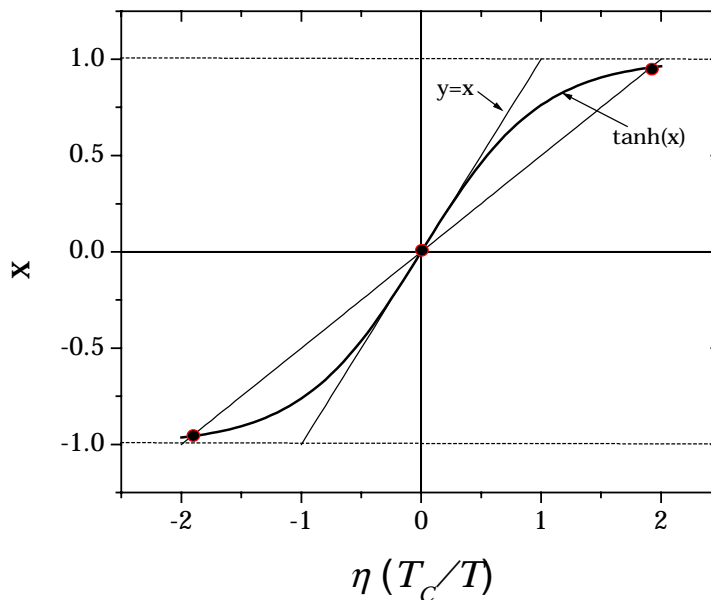
The equation for the equilibrium order parameter can be re-arranged, and using the definition of the hyperbolic tangent it can be re-written as:

$$\eta_0 = \tanh \frac{\eta_0 T_C}{T}$$

and setting  $x = (T_C \eta_0) / T$  it becomes

$$\frac{T}{T_C} x = \tanh x$$

which can be solved easily by graphical methods. The exact solutions to the equilibrium order parameter as a function of temperature are given by the intersections of a line with slope  $T/T_C$  and the hyperbolic tangent function as shown in Figure 8.



**Figure 8.** Graphical determination of the equilibrium order parameter.

If  $T > T_C$ , then the line  $(T/T_C)x$  has a slope greater than unity and thus intersects  $\tanh(x)$  only at the origin. This corresponds to a single solution,  $\eta_0 = 0$ . This result makes sense: above the critical temperature and at equilibrium, the only stable state is one of complete disorder. If  $T < T_C$ , then the line intersects  $\tanh(x)$  at two values of  $\eta$ , one positive and one negative corresponding to two symmetric (phase and anti-phase) solutions for the equilibrium order parameter.

Now that we have determined the equilibrium order parameter at a given temperature, we can evaluate the internal energy and the capacity of the system at that particular temperature:

$$\frac{E(\eta_0)}{N} = \frac{E(0)}{N} - \frac{z}{4} \Delta E \eta_0^2 = \frac{E(0)}{N} - \frac{1}{2} T_c \eta_0^2$$

In the above equation the term  $E(0)$  term represents energy not associated with order-disorder, such as the phonon energy, while the contribution to the energy from the order-disorder varies as the square of the order parameter. It should be noted that the energy of the system in a completely disordered state, i.e.,  $\eta_0=0$ , is given by  $E(0)$ . To determine the heat capacity at a given temperature as a function of equilibrium order parameter, we use the definition of the capacity:

$$C_p = \frac{\partial E}{\partial T} = \frac{1}{N} \frac{\partial E(0)}{\partial T} - T_c \eta_0 \frac{\partial \eta_0}{\partial T}$$

However, since we cannot write an exact solution for the equilibrium order parameter as a function of temperature without employing numerical methods, we cannot state exact solutions for the internal energy or the heat capacity at a given temperature. Instead, we have to employ some approximations and evaluate the equilibrium order parameter over specific ranges of  $\eta_0$ .

First we consider the case when  $\eta_0 \ll 1$ , near complete disorder. We re-write the configurational entropy:

$$S(\eta) = -kN \left[ \frac{1}{2}(1+\eta) \ln \frac{1}{2}(1+\eta) + \frac{1}{2}(1-\eta) \ln \frac{1}{2}(1-\eta) \right]$$

using the Taylor expansion of the natural logarithm:

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots$$

$$\ln(1-x) = -x - \frac{x^2}{2} - \frac{x^3}{3} - \frac{x^4}{4} - \dots$$

and we obtain:

$$S(\eta) \cong -kN \left[ -\ln 2 + \frac{\eta^2}{2} + \frac{\eta^4}{12} \right]$$

neglecting terms higher than the fourth order. Substituting back into the equation for the free energy yields ‡:

$$F(\eta) \cong E(0) - NkT \ln 2 + \frac{1}{2} kN(T - T_c)\eta^2 + \frac{1}{12} kNT\eta^4.$$

Taking the derivative with respect to the order parameter and setting it equal to zero yields the equilibrium order parameter:

$$\frac{\partial F(\eta)}{\partial \eta} = 0 = k(T - T_c)\eta_0 + \frac{1}{3} kT\eta_0^3$$

or finally

$$\eta_0 = \pm \sqrt{3 \left( \frac{T}{T_c} - 1 \right)}.$$

Now let us consider the case for  $\eta_0 \cong 1$ , i.e., near complete order. The equilibrium order parameter is given by:

$$\frac{T_c}{T} = \frac{1}{2\eta_0} \ln \frac{(1 + \eta_0)}{(1 - \eta_0)}$$

which reduces to:

$$\frac{T_c}{T} \cong \frac{1}{2} \ln \frac{2}{(1 - \eta_0)}$$

for  $\eta_0 \cong 1$ . Therefore,

$$\eta_0 \cong 1 - 2 \exp\left(-\frac{2T_c}{T}\right).$$

## References

1. L. Guttman, *Order-Disorder Phenomena in Metals*, in Solid State Physics Vol. 3, F. Seitz and D. Turnbull ed., pp. 145-223 (1956).
2. L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Pergamon Press, 1958.
3. M. A. Krivoglaz and A. Smirnov, *The Theory of Order-Disorder Transformations*, MacDonald and Co, London, 1964.

‡ This approach constitutes the basis of Landau theory of phase transformations, which will be discussed in the next chapter.