

# EXPLAINING THE EMERGENCE OF COOPERATIVE PHENOMENA

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Phase transitions, such as spontaneous magnetization in ferromagnetism, are the most fundamental *cooperative* phenomenon in which long-range orders emerge in a system under special conditions. Unlike *collective* phenomena which are mere collections of processes (or actions) mostly accountable by statistical averages of the micro-constituents' properties, they are results of genuine cooperation in which unique properties emerge for the whole system that are not such simple averages. In this paper I investigate what the problem of phase transitions is, how it is solved by a mathematical maneuver, i.e. taking the *thermodynamic limit*, and whether the solution is sound and rigorous as claimed.

**1. Introduction.** Phase transitions are one of the two main *cooperative phenomena* studied in *thermostatistics* (or thermo-statistical physics) (cf. Stanley 1971; Emch 1977; Toda, Kubo et al. 1983), the other being irreversible processes. They are so called because they are results of cooperative interactions among microscopic objects.<sup>1</sup> Many other cooperative phenomena come under scientists' scrutiny: the growth patterns of plants, the behavioral structures of insect colonies, the ups and downs of financial markets, & etc., all of which are to be explained via the understanding of how the micro-constituents act and interact as individuals and what the conditions are under which such interactions give rise to the macro-phenomena (while the macro-micro division is relative to the field of study).

In the natural hierarchy of macrosystems ranked according to their complexities, cooperative phenomena in thermostatistics are the simplest (because the thermo-statistical division is the most basic macro-micro division in nature). Therefore, the ways in which they are explained must contain some fundamental elements that explanations of higher-level cooperative phenomena share. It is with this point in mind, I embark in this paper on a philosophical analysis of the theory of phase transitions, or (for lack of space) its theoretical core, aiming at showing the difficulty of having a *rigorous* explanation of a typical cooperative phenomenon.

**2. The Problem of Phase Transitions.** Giving a rigorous account of phase transitions in purely thermodynamical terms encounters no real conceptual problems (Stanley 1971: 1-9), but it evokes no micro-constituents and therefore provides no useful illustration for our topic. However, it provides features of the phenomena at the macro-level which all micro-explanations must recover. For a system of fluid which may be in, *inter alia*, the phase of solid, liquid, or gas and whose states are determined by  $P$  (pressure),  $\sigma$  (density), and  $T$  (temperature), the regions of pure phase are separated by surfaces in the  $P\sigma T$  (phase) space on which two or more phases coexist in equilibrium. For a system of magnets whose states are determined by three analogous variables:  $B$  (external field),  $m$  (magnetization per constituent),  $T$ , the regions of pure phase are also separated by surfaces in the  $BmT$  space on which two or more phases coexist in equilibrium. Quasi-equilibrium changes of a macrosystem are represented by smooth (i.e. analytic everywhere) curves in the phase space except on those surfaces where the lack of analyticity represents at least a first-order phase transition. For instance, for a certain value of  $T$ , we have a  $\sigma P$  curve for a fluid representing the change of its  $\sigma$  with its  $P$ . The curve is smooth until it hits the phase transition line between liquid and gas where different values of  $\sigma$  corresponds to the same  $P$  of the system, namely,  $\sigma$  is still continuous but  $\sigma/P$  ( $P/\sigma$ ) is not (i.e. *non-analytic*). Similarly, with a ferromagnet at a certain  $T$ , the  $mB$  curve is analytic except at the transition line of  $B = 0$  where different values of  $m$  corresponds to the same  $B (= 0)$ . In general, phase transitions as thermodynamic phenomena are shown as *non-analyticities* or *singularities* of a macrosystem's main thermodynamic variables. This is a feature that any micro-explanations of phase transitions must recover.

For such an explanation, we begin with a brief sketch of the most general and shared features of our model (Toda, Kubo et al. 1983: ch. 2). A dynamical system,  $S$ , is represented by a phase space,  $\Gamma$ , and a parameter family of homomorphisms or diffeomorphisms (the flow):  $\phi_t: \Gamma \rightarrow \Gamma$  ( $t \in \mathbb{R}$ ), where each  $\gamma \in \Gamma$  denotes a state of  $S$  and  $\phi_t$  dictates how  $\gamma$  evolves in  $\Gamma$  (a dynamics). As a phase space,  $\Gamma$  is equipped with a  $\sigma$ -algebra of subsets,  $\mathcal{A}$ , and a normalized measure,  $\rho$ , on  $(\Gamma, \mathcal{A})$  such that  $\rho(\Gamma) = 1$  and  $\forall t, \forall A \in \mathcal{A}, \rho(\phi_t(A)) = \rho(A)$ , i.e. it is invariant under the flow. In other words, a dynamical system  $S$  is given by a triple:  $(\Gamma, \phi_t, \rho)$ , where  $\phi_t$  and  $\rho$  are

determined in part by S's Hamiltonian. The state of equilibrium is a special macrostate of S in which no macro-dynamical process takes place in  $S^2$ , and so  $\phi_t$  plays no role. The measure,  $\rho$ , which in this case is also known as the equilibrium probabilistic measure (e.p.m.) can be obtained in different circumstances under the assumption that S is equally probable to be in any of the possible microstates compatible to the given macroscopic constraints. Depending on the constraints imposed, we end up with different types of e.p.m.'s. (i) A *microcanonical ensemble* represents isolated macrosystems, and because of that its e.p.m. is  $r_{mic} = d(H - E_0)$  (where H is the system's Hamiltonian and  $E_0$  its total energy). (ii) A *canonical ensemble* is one in which the system it represents exchanges energy with outside but not molecules, and its e.p.m. is  $r_{can} = \exp(-bH)$ , where  $b = 1/kT$  (k - the Boltzmann constant). (iii) A *grand canonical ensemble* can be seen as a canonical ensemble where the exchange of molecules with outside is also permitted, and its e.p.m. is  $r_{gran} = \exp[-b(H - \mu N)]$ , where  $\mu$  is the chemical potential and N the total particle number. Then, all macro-quantities are weighted (by the proper e.p.m) averages of the corresponding micro-quantities. For any system, S, we select an e.p.m. of the ensemble which best describes S, and then for any thermodynamic function, f, of S,

$$\langle f \rangle = (\rho ds)^{-1} \int f \rho ds \text{ or } (\rho_i)^{-1} \sum_i f_i \rho_i, \text{ or } \langle \hat{f} \rangle = (Tr \hat{\rho})^{-1} Tr(\hat{f} \hat{\rho}),$$

depending on whether S is continuously classical or discretely classical or quantum<sup>3</sup>. Therefore, these equations provide the link for an explanation of a macrosystem via its micro-constituents. Depending on whether or not the Hamiltonians, H's, contain terms for the interaction among molecules, the LHS (i.e.  $\langle f \rangle$ ) of these equations, which is purely macroscopic, is explained by the RHS of the same equations as either a cooperative or merely a collective process.

The factors that normalize the averages, i.e.  $Z$  (or  $\Xi$ ) =  $(\rho ds)$  or  $(\rho_i)$  or  $Tr(\rho^A)$ , are known as the partition functions ( $Z$  corresponds to  $\rho_{can}$  and  $\Xi$  to  $\rho_{gran}$ ) and are especially useful because most integrable phase functions, such as pressure, entropy and energy, turn out to be the same as the partial differentiation of the partition functions with respect to the appropriate parameters. For instance, in the canonical ensemble, if we define free energy,  $F$ , as  $F = -\ln Z/b$ , then we have, the pressure:  $P = -[\partial F / \partial V]_T$ , the entropy:  $S = -[\partial F / \partial T]_V$ ,<sup>4</sup> and the internal energy:  $U = F - TS$ . And in the grand canonical ensemble, we have the pressure as

$$P = (\beta V)^{-1} \ln X \quad \text{and} \quad N = z \frac{1}{X} \ln X \quad (1)$$

Therefore, in principle, the thermodynamic properties of a system is determined once its partition function is known, and the partition function is known once the Hamiltonian of the system is given and the ensemble chosen. However, what is in principle the case is far from so in practice. The entire enterprise of thermostatics is built on the ingenuity of finding the right model for a certain type of macrosystems such that the Hamiltonian of the model is complex enough to approximate them but not so complex as to render the calculation of the partition function infeasible.

We are now ready to appreciate the problem of phase transitions in its most general form. I have mentioned earlier that a phase transition shows up as a non-analyticity of some thermodynamic function. In the case of a liquid-gas transition, for instance, there must be a break of a system's  $P$  with respect to its  $\sigma$  (at a certain  $T < T_c$  (the critical temperature)). If we can calculate  $P$  from the partition function (via eq. 1), we only need to see if a break appears in  $P$  at the proper temperature. But here is the rub.

Suppose (cf. Yang & Lee 1952; Griffiths 1972; Penrose 1979) that we have a classical system which occupies a finite region  $\Lambda \cap \Gamma$  with a volume  $V$  (determined by  $\Lambda$ ). Further, we suppose that the intermolecular interaction has the potential,  $\Phi(\mathbf{r})$ , such that it is *stable* (i.e. the total potential  $U(\mathbf{r}_1 \dots \mathbf{r}_N) \geq -cN$ , where  $c > 0$  is a constant) and *strongly tempered* (i.e.  $\Phi(\mathbf{r}) \rightarrow 0$  for large  $\mathbf{r}$ ). It follows from the stability condition that inside  $V$ , only a finite number (say  $N_{\max}$ ) of molecules can coexist. The grand canonical partition function can be derived as follows:

$$X_{\Lambda} = \sum_{N=0}^{N_{\max}} \frac{1}{N!} \int_{\Lambda} \dots \int_{\Lambda} \exp[-\beta(H_N - \mu N)] = \sum_{N=0}^{N_{\max}} \frac{1}{N!} \exp(\beta \mu N) \sum_{i=1}^N \exp(-\beta H_i) = \sum_{N=0}^{N_{\max}} z^N Z_N,$$

where  $z = \exp(\beta \mu)$  and  $Z_N = \sum_{i=1}^N \exp(-\beta H_i)$  is the partition function for an canonical ensemble.

By expanding it in terms of  $z$ , we obtain the following polynomial,

$$X_{\Lambda}(z) = 1 + zZ_1 + \frac{1}{2} z^2 Z_2 + \dots + z^{N_{\max}} Z_{N_{\max}}, \quad (2)$$

which, from the above expression of  $Z_N$ , have only non-negative coefficients. This means that there exists no positive real root,  $z_i$ , for the equation,  $\Xi_N(z) = 0$ .

Now, from eq. 1, we have, with a given temperature  $T$ , the pressure of the system as  $P_L = (bV)^{-1} \ln X_L$  and its density as  $S_L = \frac{N_L}{V} = \frac{z}{V} \frac{1}{z} \ln X_L$  (or in other words,  $\sigma_\Lambda = z (bP_L) / z$ ). Both can only have non-analytic (or singular) points at the roots of  $\Xi_N(z)$ , and therefore do not have such points at any positive real value of  $z$ . By eliminating  $z$  between the above expressions of  $P_\Lambda$  and  $\sigma_\Lambda$ , we may (in principle) obtain  $P_\Lambda$  as a function of  $\sigma_\Lambda$ , which is again analytic. It is also proved that  $P_L / S_L \rightarrow 0$  and is analytic.

One can also construct a similar argument for magnetic systems by using the isomorphisms of  $P_\Lambda \times B_\Lambda$  and  $\sigma_\Lambda \times m_\Lambda$  (where  $m_\Lambda = M_\Lambda / N_{\max}$ ) which reaches the same conclusion: no phase transition (e.g. spontaneous magnetization) takes place in magnets as long as they are of finite size (more on this in detail in section 4). So, the problem becomes: how is this possible?

**3. The Rigorous Solution: Thermodynamic Limit (TL).** There exist in the literature two ways of giving a rigorous solution to the problem, in both of which the idea of TL is essential. The first considers infinite systems from the beginning (cf. Emch 1977; Penrose 1979: 1957-72) while the second begins with a finite system and then consider what happens when the system's volume goes to infinity while keeping its density constant. The first general solution in the latter approach is given in the 1952 paper of Yang and Lee (cf. Yang & Lee 1952). The central claim is that the sort of non-analyticity which defines phase transitions may appear when we conceptually let the system in question to increase its size (in any non-bizarre manner) to infinity while keeping its density finite (i.e. taking the TL). To follow this idea, whose justification we shall discuss in detail later, one needs at least to show (i) that the limits of those integrable phase functions exist, and (ii) that non-analyticity appears in the appropriate functions. At this level, the proofs are strictly for claims of existence, not for what the limits are and where the non-analyticity occurs, which can only be determined in special models, as we shall see in the next section.

For a finite system with a stable and strongly tempered potential, Yang and Lee proved two theorems, which can be simplified and combined into one as follows.

[T1] In a region in the complex  $z$ -plane which contains all real  $z > 0$ , if  $V_\Lambda \searrow$  in such a way that its surface area increases no faster than  $V^{2/3}$ , then

$$\lim_{\substack{L \rightarrow \infty \\ V \rightarrow \infty}} \frac{1}{V} \ln X_L (= bP), \lim_{\substack{L \rightarrow \infty \\ V \rightarrow \infty}} \frac{\eta}{V} \left( \frac{1}{V} \ln X_L \right) (= S/z), \quad \lim_{\substack{L \rightarrow \infty \\ V \rightarrow \infty}} \frac{\eta^2}{V^2} \left( \frac{1}{V} \ln X_L \right), \textcircled{2}$$

exist and are analytic for all positive real  $z$  (the first item is also monotonically increasing along  $z$ ), *except at those  $z$ 's such that  $X_L(z) = 0$  (i.e. the roots).*

Noting that the first item is proportional to  $P$  and the second  $\sigma$ , [T1] essentially says that any system satisfying the constraint will be in a pure phase except possibly at those  $z_i$ 's which are roots. If no roots lie on the positive real axis of  $z$ , there are no multiple phases and hence no phase transitions (at least they are not represented by the functions). One must note the generality of this theorem: besides the density being finite and the interaction stable and tempered, little else is assumed<sup>5</sup>.

We know from the previous section that for a finite system,  $\Xi_\Lambda(z) = 0$  can never have positive real roots. The trick is that taking TL makes the number of terms of the polynomial infinite and so is the number of roots. Thus, we have the following.

[T2] When  $V_\Lambda \searrow$ , (i) the number of roots of  $\Xi_\Lambda(z) = 0$  becomes infinite which may force some  $z_i$  onto the positive real axis of  $z$ ; and (ii) at which points,  $P(z)$  is still continuous but  $\sigma(z)$   $P/z$  is not (or similarly for magnetization,  $F(B)$  is continuous but  $m(B) = F/B$  is not). In other words, at TL and a certain  $T$ , it is possible that  $P(z)$  or  $m(B)$  become nonanalytic.

However, one must deal with specific models if one wants to know where rigorously a phase transition occurs in a system.

**4. Rigorous Solutions for Special Systems.** The simplest systems in the literature are classical *lattice systems*, the majority of which can be studied under the *Ising model* which has one form to represent a species of magnets (i.e. ferro-(or antiferro-)magnets) and another a species of fluid (i.e. lattice gas). The model was not invented for deriving rigorous results of TLs, but it turned out to be ideal for such purposes, and its lattice gas model allows us to apply rigorous results obtained in magnets to fluids or vice versa.

The Ising model of a magnet (obviously of finite sizes) describes it as a macrosystem satisfying the following conditions.

- i. It consists of  $N$  fixed sites each of which is occupied by a spin-1/2 particle which can be in one of two possible states: spin-up ( $\sigma_i = +1$ ) and spin-down ( $\sigma_i = -1$ ). It therefore occupies a finite region,  $\Lambda$ , in the configuration space with a volume,  $V_\Lambda$ .
- ii. The interaction between two sites is given exclusively by the terms:  $J_{ij}\sigma_i\sigma_j$ , for every site  $i$  or  $j = 1, \dots, N$ , where  $J_{ij} > 0$  if sites  $i$  and  $j$  are nearest neighbors and  $J_{ij} = 0$ , otherwise.
- iii. The Hamiltonian of the system, therefore, is given by:

$$H_L = - \sum_{\langle i,j \rangle} J_{ij} S_i S_j - B \sum_i S_i \quad (3)$$

where  $B$  is the external magnetic field and  $\langle i,j \rangle$  means pairs of nearest neighbors only.

Since the total number of the spins in an Ising system is constant, we use the partition function of the canonical ensemble, i.e.,  $Z_L = \sum_{S_1} \otimes \sum_{S_N} \exp(-\beta H_L)$ , for sites,  $1, 2, \dots, N \in \Lambda$ , and we then have the

free energy,  $F_L = -(\beta)^{-1} \ln Z_L$  and the magnetization,

$$m_L = \frac{1}{N} \sum_{i=1}^N \frac{1}{2} \langle S_i \rangle = - \frac{1}{N} \frac{\partial F_L}{\partial B}, \quad (4)$$

namely, the rate of change of the system's free energy with the change of the external field alone.

To get a model of lattice gas, imagine that all the spin-1/2 particles are replaced either by a gas particle or an empty site (at most one gas particle is allowed at each site), and instead of the spin,

$\sigma_i = 1$  or  $-1$ , we have the occupation number of a site,  $n_i = 1$  or  $0$ , depending on whether it is filled or empty. If we assume, as in the magnet model, nearest-neighbor interactions only, i.e.,  $\Phi_{ij} < 0$  if sites  $i$  and  $j$  are nearest neighbors and  $\Phi_{ij} = 0$ , otherwise, where  $\Phi_{ij}n_in_j$ , ( $i$  or  $j = 1, \dots, N$ ) is the interaction Hamiltonian, then the two models are related by the simple identification,  $S_i = 2n_i - 1$ . It is obvious that the grand canonical ensemble should be used for lattice gas systems and by substituting the above expressions for the corresponding ones in a magnet's Hamiltonian (eq. 3), free energy and magnetization (eq. 4), we get the Hamiltonian, the pressure and the particle-number of a lattice gas. Because of this formal equivalence of the two forms of the Ising model, one can prove a result in the magnet case and transfer it directly to lattice gas, and then if some restrictions of the latter can be relaxed (so as to make the model closer to the usual gas models) without forfeiting the result, we would have proven it in general!

There are many kinds of magnetic materials, chiefly among them are paramagnets and ferromagnets (or anti-ferromagnets). Materials of both kinds become magnetized under the influence of an external magnetic field, but paramagnets cease to have any magnetization once the field is reduced to zero while ferromagnets, however, retain a certain residue magnetization; and moreover, when the field is reduced to zero in two opposite directions, the residue  $M$  of a ferromagnet assumes different values. This is also known as the phenomenon of *spontaneous magnetization*, whose existence is well confirmed by experiments and accounted for by a purely thermodynamical (i.e. phenomenological) theory. However, as I mentioned earlier, a thermostistical theory of finite Ising systems predicts the impossibility of such a phenomenon. There are two different ways of seeing the details of this point.

In one way (Griffiths 1972: 50-55), it is a natural consequence of the impossibility I explained in section 2. First, we may recall the parallel (given at the beginning of section 2) between the pressure  $P$  and the density  $\sigma$  of a fluid and the external field  $B$  and the magnetization  $m$  of a magnet respectively. If a phase transition in fluids is represented by a non-analyticity of  $P$  with respect to  $\sigma$  (or vice versa), then that in magnets can be represented by an non-analyticity  $m$  with respect to  $B$ . To see this, we rewrite the Hamiltonian of an Ising system as

$$H^*_L = - \sum_{\langle i,j \rangle} J_{ij} S_i S_j - B \sum_i S_i \quad (S_i = \pm 1)$$

. Since



the energy of any system is only determined up to a constant,  $H^*_\Lambda$  is equivalent to  $H_\Lambda$  (eq. 3).<sup>6</sup> Then the canonical partition function for the ferromagnets becomes  $Z^*_\Lambda = \sum_{N=0}^{N_{max}} z^N Z_N$ , which has rigorously the same form as the one used in the Yang-Lee theorem except now  $z = \exp(-\beta B)$  (instead of  $z = \exp(\beta m)$ ). Now, we can replace the  $Z_\Lambda$  with the above  $Z^*_\Lambda$  to get  $F^*_\Lambda$  and therefore obtain the result from eq. 4 that  $m_\Lambda$  is proportional to  $-\partial F^*_\Lambda / \partial B$ . Applying our discussion in section 2 to this equation we see that as long as  $\Lambda$  is finite, there cannot be any singularity in  $m_\Lambda$  with respect to  $B$  at a given  $0 < T < T_c$ . Hence, there is no spontaneous magnetization at  $B = 0$  (when  $0 < T < T_c$ ), contrary to the well established fact.

The other way (Goldenfeld 1992: 49-52; Griffiths 1972: 59-63) uses the property of up-down-reversal symmetry of an Ising system. If we reverse the direction of  $B$  and every spin, we have, from eq. 3,  $H_\Lambda(B, J, \{S_i\}) = H_\Lambda(-B, J, \{-S_i\})$ ; therefore, it is easy to see that  $Z_\Lambda(B, J, T) = Z_\Lambda(-B, J, T)$ , and so  $F_\Lambda(B, J, T) = F_\Lambda(-B, J, T)$ . Then, it is immediately obvious that  $m_\Lambda(B) = -m_\Lambda(-B)$ ; and when  $B = 0$ , we have  $m_\Lambda(0) = -m_\Lambda(0) = 0$  (there is no other possibility). Hence, no spontaneous magnetization, which is a very general result since the proof uses only the up-down-reversal symmetry.

To see where a spontaneous magnetization (and therefore ferromagnetism) at  $T > 0$  is possible in the Ising model, Lee and Yang (Lee & Yang 1952) proved another theorem as a result of applying their general theorems to the case of Ising model (for both magnets and lattice gas).

[T3] Given an Ising system of magnet (or lattice gas) with  $J_{ij} \geq 0$  (or  $\Phi_{ij} \geq 0$ ),  $Z_\Lambda$  (or  $Z^*_\Lambda$ ) = 0, only if  $|z| = 1$ , namely, all the roots of the partition function lie on a circle in the complex  $z$ -plane whose radius is of unit length.

As  $V_\Lambda \rightarrow \infty$ , the collection of roots on the unit circle becomes denser and denser until eventually one of them 'pinches' the positive real axis, whereby a singularity at  $z = 1$  occurs. From [T2] and because  $z = \exp(-\beta B)$ , we have that a phase transition at a temperature  $T > 0$  is only possible in an Ising system at  $B = 0$ . In other words, at TL the *symmetry* mentioned above may *break*

at  $B = 0$  so that  $m_-(B)$  when  $B \searrow 0^+$  is not equal to zero nor to  $m_-(B)$  when  $B \nearrow 0^-$ , where  $m_-(B) = \lim_{\Lambda \searrow \emptyset} m_\Lambda(B)$ . Note that we *cannot prove* that a phase transition (or symmetry breaking) must occur at  $B = 0$  (when  $0 < T < T_c$ ), and thus could not explain why it actually occurs by [T3]. The  $z_i$ 's on the circle of  $|z| = 1$  becoming dense as  $V \searrow \emptyset$  does not imply that every point on the circle eventually becomes a root; and therefore the perforation of the positive axis is not guaranteed by taking TL. In fact a one-dimensional Ising system is proven not to have phase transition at TL. To have a phase transition at  $T = T_c$ , an Ising system must have  $\geq 2$  dimensions. In the case of a 2-dimensional system,  $F = \lim_{\Lambda \searrow \emptyset} F_\Lambda$  can be rigorously solved so that not only we know at what temperatures the symmetry breaks (i.e.  $F = F(B=0)$  have different values for directions from which  $B = 0$  is approached) but what happens rigorously within the regions where phase transitions take place (i.e. *critical phenomena*) (cf. Onsager 1944; Yang 1952).

**5. Of the Thermodynamic Limit.** First, one may doubt whether the approaches described above are solutions to the problem at all, for the problem is really this: *while most if not all actual macrosystems are finite, thermostatics predicts rigorously that no such systems could possibly exhibit the phenomenon of phase transitions*. Taking TL, one may argue, appears to be avoiding rather than solving the problem. Therefore, it seems obvious that just to provide a TL solution is not enough, one must also argue that it is indeed an explanation for the existence of phase transitions.

The prevailing response to such a request is that TL serves as a good *approximation* because actual macrosystems contain so many constituents that they are practically indistinguishable from infinite systems. One may also mention that such a method of approximation is not infrequently used in physics. When we apply differential calculus to study rigid bodies in mechanics and fluids in hydrodynamics, are we not similarly assuming that since, for instance, the molecules are so numerous on a surface of some solid object that it can be considered as continuous? To a certain extent this response is right. More precisely, the justification goes as follows. The Ising model is a mathematical theory in which a great deal of idealization conditions are assumed. When it turns out that no finite Ising system admits multiple phases in equilibrium, and hence, no phase transitions, it does not mean

that no phase transitions occur in actual magnets or lattice gases (if there are such gases). It simply means that actual phase transitions are not rigorously the non-analyticities of pressure or free energy of some Ising systems. However, since the actual magnets or lattice gases are very close to infinite Ising systems (which are proven to be well-behaved systems, i.e., having well-defined thermodynamical quantities) because their micro-constituents are so numerous and densely populated, taking TL on an Ising system provides a good approximate account of the actual phenomena. This is clearly analogous to the case of applying calculus to *almost continuous* bodies (i.e. those which contain a large number of very small particles of constant masses). Take the mass  $M$  of such a body. It is in fact not a continuous quantity and so any theoretical quantity that calls for its differentiation,  $dM$ , or derivative,  $dM/dx$  ( $x$  being some continuous parameter) is not possible, just as phase transition as the non-analyticity of pressure or free energy is not possible in a finite Ising system. But because the body is so densely populated with molecules, it is from a macroscopic point of view approximately continuous, so that a continuous function of  $M$  gives a good approximation.

On the other hand, the two cases are dissimilar in some important and relevant aspects. For instance, while in the case of applying calculus, the approximation is clearly asymptotic, it is not so in the case of phase transitions. Suppose we have a body of volume  $V^*$  which has finite particle density. For any  $V_1 < V_2 < V^*$ , we have the average value of  $\Delta M/\Delta V = (M_2 - M_1)/(V_2 - V_1)$ , and  $dM/dV = \lim_{\Delta V \rightarrow 0} \Delta M/\Delta V$ . Taking  $\Delta V \rightarrow 0$  to be a sequence of  $\Delta V$ 's one smaller than the next until it vanishes,  $\Delta M$  becomes zero at some  $\Delta V$  as long as  $M$  is not continuous, but the denser the body becomes the smaller the  $\Delta V$  has to be before  $\Delta M$  vanishes and the closer  $\Delta M/\Delta V$  approaches  $dM/dV$ . Hence, as the body becomes denser,  $\Delta M/\Delta V$  approaches  $dM/dV$  asymptotically as  $\Delta V \rightarrow 0$ . This is not true with TL. Until the limit is reached, the pressure or the free energy of any macrosystem is analytic. The non-analyticity is not at all asymptotically reached by the process of taking TL. At no stage of this process is non-analyticity (representing a phase transition) roughly or approximately defined; very much unlike the case of  $\Delta M/\Delta V$  where at each step towards the limit, it is not only well-defined but closer to the limit,  $dM/dV$ . To see this point from a different angle, let us analyze the Yang-Lee theorem (e.g. [T3]) again. It says that when TL is taken, the number of roots,  $z_i$ , which all lie on the unit circle in the complex  $z$ -plane becomes infinite, and so one of them may puncture the positive real

z-axis and thereby creates a singularity. There is no asymptotic behavior in the distribution of these roots as their number increases. So, as long as it is finite, the system, no matter how big, may be theoretically no closer to having a non-analytic point than any smaller systems.

Another aspect of the dissimilarity is the opposing perspectives the two cases adopt. Even though in both cases we are concerned with macroscopic properties, in the former about calculus we want to essentially ignore the fine discontinuous structure of the body in question, while in the latter about phase transitions we need to preserve the micro-constituents and their structures. The stability condition prevents us from even theoretically putting too many molecules or sits into a finite volume; hence, we need to push the volume to infinity while keeping the density constant. Further, we should note that to have continuous thermodynamical quantities, such a pressure, temperature and entropy, one does not need to take the TL. The collective appearance of a finite molecular system is mathematically continuous and mostly analytic. TL is necessary only when dealing with cooperative phenomena such as phase transitions and irreversible processes. Therefore, *TL can be taken as a theoretical trademark that distinguishes cooperative from merely collective phenomena.*

Thus, we may conclude at this point that TL may provide the right approximation in general, but exactly how it approximates the actual phenomenon of phase transitions is still a question.

Second, taking TL is said to be necessary for eliminating the effect of boundaries (Sklar 1993, 78-81; Griffiths 1972, 10-12; Toda et al 1983, 127), but such a statement can be misleading<sup>7</sup>. On the one hand, this is true but only if a single phase is possible (e.g.  $0\text{ C} < T < 100\text{ C}$  for water); on the other hand, if multiple phases are possible (e.g.  $T = 0\text{ C}$ ) and so are phase transitions, the boundaries matter even if we take the TL on the system in question. Some (Griffiths 1972: 42) even define phase transitions as long-range orders even when the boundaries are infinitely far away. Therefore, taking TL is either not necessary (because a single phase can be well understood in a large but finite system or in a system connected to a reservoir) or necessary but not for eliminating boundaries (because for phase transitions what we need is precisely how boundaries work even if they are infinitely far away).

Third, one may question TL's explanatory value. What does it reveal for or supply to our understanding of phase transitions as a cooperative phenomenon? To say that phase transitions only occur at TL with a system of more than one-dimension is misleading, to say the least. Unlike the

claim that one-dimensional Ising system contains no multiple phases which can in fact be true, the above statement can never; so how can it explain anything that actually happens? To see TL's role, let us review the whole scheme for phase transitions. Equilibrium thermostatics (classical and quantum) is constructed primarily on single phase systems. It is always a question (or a test) for the theory whether multiple phases in equilibrium can be represented by a single function (such as pressure and free energy). Without additional stipulations on the internal structure of and the interactions among a system's constituents, it is obvious, as explained earlier, that the answer is negative if the system is finite. There certainly are possible types of interactions among, and/or arrangements of, a given system's molecules so that non-analyticities arise even if the system is finite, but the two conditions, (strong or weak) tempering and stability, are so natural and any other additional constraints so implausible from a microscopic point of view that pursuit in this direction seems unreasonable. This is why TL becomes a much preferred option if the approximation argument we evaluated earlier in this section is sound. Therefore, TL by itself has no explanatory import; it merely provides a necessary condition under which other causally relevant factors, such as the arrangement of molecules (or sites) and the nature of their interactions, can give an explanation that is approximately true.

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## Notes

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<sup>1</sup> Cooperative phenomena must be carefully distinguished from collective phenomena. By the latter I mean a mere collection of processes (or actions) while the former are results of genuine cooperation or interaction. While collective phenomena abound in thermostatics, e.g. having a temperature, a pressure, or even a volume, cooperative ones are scarce. Furthermore, while it is easy to reduce a magnitude of the collective aspects of a system, such as the system's temperature, to those of the constituents, such as the velocities of the molecules, a reduction in cooperative phenomena is usually much more difficult.

<sup>2</sup> A precise and comprehensive definition equilibrium is difficult and even controversial matter. Here, we'll have to make do with some crude characterization, such as no macro-dynamical processes and no temperature difference among any two parts.

<sup>3</sup> Here the integration is over  $\Gamma$ , and the sum over the whole discrete spectrum; and the hatted quantities are the corresponding quantum operators and  $\text{Tr}(\cdot)$  is the trace operator.

<sup>4</sup> Since the free energy is clearly an ensemble-average, all the other functions obtained from it via partial differentiations are certainly also ensemble-averages. Therefore, I shall not use the bracket for such functions unless the context does not make it clear.

<sup>5</sup> The requirement that the area of the surface of  $V$  increases no faster than  $V^{2/3}$  simply means that a system of which [T1] applies should not be enclosed in a surface whose area is proportional to  $R^s$ , where  $R$  is the one-dimensional size of the surface (e.g. its radius) and  $s > 2$ . Since  $s = 2$  is the number of dimensions of most surfaces, it must take a great deal of twists, such as in a sponge, to make a surface whose area goes beyond that.

<sup>6</sup> This maneuver is also justified if one notes formal equivalence of the magnet model and the lattice gas model, while in the latter the partition function is a grand canonical function which resembles  $Z^*_\Lambda$  below that has exactly the form of a grand canonical partition function.

<sup>7</sup> I thanks Gérard Emch for pointing this out to me.