# THE THERMODYNAMICS OF PHASE EQUILIBRIUM: FROM THE PHASE RULE TO THE SCALING LAWS

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## ABSTRACT

In recent years the author has advanced a conceptual structure based on the generalization of Gibbsian thermodynamics and statistical mechanics. The purpose of this paper is to bring this theory up-to-date by harmonizing it with the recent developments in the theory of critical phenomena.

## 1. INTRODUCTION

At the turn of the century thermodynamics and statistical mechanics had their well defined logical structure. Thermodynamics was supposed to be macroscopic and non-statistical; its microscopic foundations was expected to be given by means of 'reduction' to statistical mechanics.

The rich developments of this century wrought havoc with these neat categories, and present research pays, at best, lip-service to the traditional logical structure.

One would like to hope that science can create order in the chaos of experience, but unfortunately, successful scientific activity tends to create a chaos of its own. A logical structure, to be of real use must be flexible enough to cope with this complex situation. If such a structure can be developed at all, this is likely to happen in successive approximations, in terms of manageable steps.

It seems to me that a modernized form of Gibbsian thermodynamics can provide the point of departure for such a programme. A few years ago I published a volume entitled *Generalized Thermodynamics*[1] to report on progress achieved along these lines†.

I am grateful for the opportunity to summarize my thoughts at this meeting, particularly because significant developments occurred since the completion of my report which render its updating desirable.

I am alluding to the remarkable expansion in the exploration of the phenomena in the neighbourhood of the critical point[2-4]. The critical point was discovered a little over a hundred years ago by Andrews, and was presumably so named because of its critical role with respect to the possibility of condensing a gas which appears 'permanent' at higher temperatures. Such points are 'critical', however, for a deeper reason as well. In their

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† I shall use the term GTD to designate generically any of the theories within this overall structure.

critical states substances reach the limits of their thermodynamic stability, and many of their measured properties exhibit a singular behaviour, the quantitative description of which poses extreme demands on experimentalist and theorist alike. The intensive activity of the last few years came about thanks to breakthroughs in experimental and theoretical techniques. Within theory, these involve the treatment of singular functions by means of the so-called critical point exponents[2,3].

Since critical points play an important role in GTD, the emergence of these new techniques enables me to sharpen my argument and eliminate unsatisfactory approximations formerly used out of expediency.

I have to confine myself to a somewhat impressionistic sketch of a number of ideas without any pretence of proving specific statements. However, I made an effort to line up the ideas so as to bring out their interdependence, and would like to hope that the parsimony in detail will further this end.

One of the problems arising in this connection is taking a new look at the relation of statistical mechanics to thermodynamics. My thesis is that we are dealing with two complementary aspects of the structure of matter which have to be used jointly in a carefully dovetailing pattern. At the outset statistical mechanics starts with structureless permanent point particles and thermodynamics with cells localized in space time. Both pictures are capable of refinement and their ultimate relation should be inferred from the careful analysis of experience, rather than from some preconceived opinion about what is more 'fundamental'.

The structure of GTD has a hierarchic character built up in a step-by-step procedure. Section 2 is devoted to the outline of a theory denoted by MTE, an abbreviation suggested by 'macroscopic thermodynamics of equilibrium'. Actually, MTE denotes a precisely defined deductive system developed in ref. 1, whereas, following current practice, the term thermodynamics is used in a somewhat vague generic sense. The situation is similar for STE (statistical thermodynamics of equilibrium) discussed in Section 3, along with some quantum mechanical considerations. Up to this point the rigour of the developments compares favourably with that expected in classical thermodynamics. The pace is changed somewhat in Section 4 in which approximate methods are admitted in order to handle some detailed properties of critical points which are beyond the reach of the rigorous methods.

The discussion is limited to time independent phenomena. Although GTD can account for a variety to time dependent processes, the situation has not matured to the point of admitting a concise presentation.

In view of the fact that I am attempting to survey a vast range of subjects, I beg to be excused for not supplying a thorough bibliography. The material of sections 2 and 3 is developed in detail in ref. 1. My minor excursion into the recent theory of critical point exponents is adequately documented in refs 2–4.

## 2. MACROSCOPIC THERMODYNAMICS OF EQUILIBRIUM (MTE)

We start with the fundamental equation

$$U = U(X_1, X_2, \ldots X_{r+1}) \tag{1}$$

expressing the energy in terms of the extensive variables which for the time being we choose to be the entropy $S$, the mole numbers of the $c$ independent components and the volume $V$. To be more precise, we assume that we are dealing with what Gibbs called the primitive fundamental equation corresponding to a single homogeneous phase.

We see that

$$r = c + 1 \tag{2}$$

We single out the volume $V = X_{r+1}$ as a 'scale factor' and define the densities:

$$x_k = X_k/V, u = U/V \tag{3}$$

The intensities conjugate to the $X_k$ are defined:

$$P_k = \partial u/\partial X_K \tag{4}$$

Although superficially it does not seem to offer anything new if we solve equation 1 for the entropy and write the fundamental equation in the entropy scheme

$$S = S(X_1, X_2, \ldots X_{r+1}) \tag{5}$$

with the appropriate definition of intensities:

$$\pi_k = \partial s/\partial X_K \tag{6}$$

the parallel use of the two schemes is important because they serve to describe reversible and irreversible processes respectively. While the energy scheme is more convenient in the theory of phase equilibrium, the entropy scheme is indispensable for a smooth transition to STE.

The choice of densities and intensities for the description of thermodynamic systems seems simple enough from the point of view of an elementary theory. It is a common experience that thermodynamic systems can be 'scaled'. Although this property is, strictly speaking, inconsistent with the discrete structure of matter it is nevertheless assumed in the standard thermodynamic formalism. I like to express this by saying that one assumes the validity of the *principle of scale invariance*. This principle along with the conservation laws and the extremal principles, form the backbone of the formalism of MTE. The traditional tests of thermodynamics pay little if any attention to this principle, maybe because of reluctance to consider principles of limited validity. Yet, in spite of its fundamental importance, scale invariance is limited for more than one reason. Such limitations arise because of surface effects, and as a consequence of long range forces; a serious breakdown sets in at atomic scales. Many interesting problems arise from the requirement of handling situations in which one or the other of these restrictions becomes effective. We shall consider some of these questions below.

Scale invariance, or the physical homogeneity of a phase, finds expression in the mathematical homogeneity of the fundamental equation. This leads to

$$U = \sum_1^{r+1} X_k P_k \tag{7}$$

and

$$P_{r+1} = u - \sum_1^r x_k P_k \tag{8}$$

Assuming that equation 2 can be solved for $x_k$ we obtain

$$P_{r+1} = \omega(P_1, P_2, \ldots P_r) \tag{9}$$

Note that

$$x_k = -\partial\omega/\partial P_k \tag{10}$$

We examine the response of the system around equilibrium in terms of the relations:

$$\delta P_i = \sum_1^r u_{ik}\delta x_k \tag{11}$$

where

$$u_{ik} = \partial^2 u/\partial x_i \partial x_k = \partial P_i/\partial x_k \tag{12}$$

and

$$\delta x_i = \sum_1^r \omega_{ik}\delta P_k \tag{13}$$

where

$$\omega_{ik} = \partial\omega/\partial P_i \partial P_k = \partial x_i/\partial P_k \tag{14}$$

The matrices $\|u_{ik}\|$ and the reciprocal $\|\omega_{ik}\|$ are called the stiffness and the compliance matrix respectively.

A thermodynamic system is in a state of normal stability if the stiffness matrix is positive definite. The matrix can be brought to diagonal form with the diagonal elements:

$$\lambda_k = \frac{D_k}{D_{k-1}} = \left(\frac{\partial P_k}{\partial x_k}\right)_{P_1, P_2, \ldots P_{k-1}} \qquad k = 1, 2, \ldots r \tag{15}$$

Here the $D_k$s are the principal minors of the stiffness matrix. Normal stability requires that all the $\lambda_k$ be positive.

We note that the use of densities and intensities for the specification of the system are entirely equivalent, provided

$$D_r = \frac{\partial(P_1, P_2, \ldots P_r)}{\partial(x_1, x_2, \ldots x_r)} \neq \begin{cases} 0 \\ \infty \end{cases} \tag{16}$$

and equations 11 and 13 respectively are soluble. The case $D_r = 0$ is precluded in states of normal stability, but this does indeed occur at critical points, and $D_r = \infty$ is realized near absolute zero.

In order to explain the meaning of this 'breakdown' of the theory we resort to the artifice of associating intensities with infinite reservoirs, and describe systems in terms of their densities. Under these conditions the breakdown of conditions 16 makes excellent sense. The case $D_r = 0$ is

understood by recognizing that at critical points the densities of the system are subject to abnormally large fluctuations.

The nature of the anomaly near absolute zero is also easily understood. At sufficiently low temperatures the entropy of a system becomes constant, and below such a characteristic temperature the extensive parameters are no longer uniquely associated with the temperature of the environment. This is the basis for the notorious difficulties of low temperature thermometry.

In order to account for the more general situations in which densities and intensities do not uniquely determine each other, we have the plausible option of assuming this relation to be statistical. This idea is followed up in the next section.

Meanwhile we conclude this section by pointing out that the Gibbs phase rule follows at once from equation 9. Consider, indeed, a hetero-geneous system of $f$ phases in equilibrium. The intensities have to satisfy an equation of the type 9 for each phase. The space of intensities has the dimension

$$\delta = r + 1 - f = c + 2 - f \geqslant 0 \tag{17}$$

where $\delta$ is called also the number of thermodynamic degrees of freedom.

It can be shown (see ref. 1, p 155) that critical states cannot arise unless two distinct phases become identical at the point in question. It follows from here that a one-component system can have only an isolated critical point. Thus the classical theory cannot account for lambda-points which form a line in the $P/T$ diagram. The necessary extensions of the theory will be discussed in the next section.

## 3. STATISTICAL AND QUANTUM MECHANICAL CONSIDERATIONS

The considerations of the last section suggest the development of a statistical theory in which the extensive variables of a system are considered as random variables. Randomness enters the picture because of the coupling between system and reservoir involving the exchange of the quantities $X$. The random variables are assumed to be statistically independent from each other in the following sense: the values of the same quantity measured at discrete instances of time are independent from each other, and so are values associated with different systems coupled to the same reservoir. These requirements are the statistical expressions of the state of equilibrium. For a detailed discussion of this approach I refer to Tisza and Quay[5] who have shown that the elaboration of this picture yields under very general and at the same time realistic assumptions the grand canonical distribution function (d.f.)

$$dF(X \,|\, \pi) = dG(X) \exp[-\varPhi(\pi) - \Sigma \pi X] \tag{18}$$

The vertical bar indicates that the d.f. is conditioned by the intensities of the reservoir. $G(X)$, a function depending only on the properties of the system, is the so-called structure function. Its differential $dG$ is the number of linearly independent eigenfunctions of the Schrödinger equation. The function $\varPhi$ depends on the properties of the system and on the intensities $\pi_1, \ldots, \pi_r$ of the

reservoir; $\Sigma \pi X$ is short for $\sum_{\mathrm{T}} \pi_K X_K$. All the functions involved contain the volume of the system as a constant parameter. The normalization of $dF$ yields

$$e^{\Phi} = \int e^{-\Sigma X\pi} dG(X) \tag{19}$$

This equation has a pivotal role, exhibiting the connection of all the relevant major theories. Thus suppose we start with the Hamiltonian of the system involving the phase space coordinates of structureless particles:

$$H = H(q_1, \ldots q_f, p_1, \ldots p_f) \tag{20}$$

Then proceeding from here to the Schrödinger equation we arrive at the structure function $G(X)$. Equation 19 then yields the entire formalism of MTE. We have indeed for the entropy

$$S = k(\Phi + \Sigma X\pi)$$
$$= k \int dF \ln dF/dG$$

and the potential of the grand canonical d.f.

$$\Omega = V\omega = -kT\Phi$$

Note that whereas the structure function may have discontinuities in the case of a discrete spectrum, the Laplace–Stieltjes transform 19 yields an absolutely continuous differentiable $\Phi$. (Only the critical points call for special consideration.)

Contrary to the traditional foundations of thermodynamics on the basis of statistical mechanics, there is no need to assume that the system has a large number of degrees of freedom in order to arrive at the continuous differential–geometrical representation of thermodynamics. Of course, the large number of degrees of freedom does appear in the reservoir.

The formalism generated along the lines indicated has been called STE, short for statistical thermodynamics of equilibrium. Its main point can be simply stated: The formalism of MTE remains valid even in the statistical case, provided we replace the macroscopic extensive parameters with the canonical averages of the corresponding random variables.

I briefly note that the formalism admits also another interpretation. We consider the system as a measuring device, as a sensor that explores the intensities of the environment. Since in STE, the connection between the measured extensive quantities and the intensities is statistical, the latter can only be *estimated* from the former. The elaboration of this idea leads to interesting thermodynamic results[5].

I wish to point out here a curious analogy. As we go from MTE to STE we can no longer attribute simultaneous sharp values to the extensive and intensive variables. This uncertainty is governed by Boltzmann's constant just as the somewhat similar uncertainty of quantum mechanics is governed by Planck's constant.

The connection between the mechanical and thermodynamic formalisms provided by equation 19 still leaves many questions unanswered. It is a major challenge for statistical mechanics to prove that, assuming reasonable intermolecular forces, one can actually justify the scale invariance of MTE in the so-called thermodynamic limit. A great deal has been achieved in this direction, but the discussion of these results is outside the scope of this paper.

Although the procedure outlined above brings about the transition from the mechanical to the thermodynamic variables introduced above, the choice of the latter is not wide enough to account for the situations of greatest current interest. Thus we have no parameters as yet to describe, say, crystal symmetry. To achieve this further enrichment we have to use the well known Born–Oppenheimer (B–O) approximation. I like to call this procedure rather the B–O *transformation*, because it achieves the transition from the particle Hamiltonian to other Hamiltonians specified in terms of the spatial configuration of the nuclei. Please note the plural in this statement. It is indeed of capital importance that the B–O transformation leads often to different 'branches', say corresponding to white tin and grey tin, and each of these leads through equation 19 to one of the primitive fundamental equations that is to be used in the determination of heterogeneous equilibrium.

This approach opens up a new avenue for introducing additional parameters into the fundamental equation in a systematic fashion. In statistical mechanics the criterion for choosing such parameters is: take additive invariants (or also permutational invariants in the case of identical particles). This means in practice, the number of particles, momentum and angular momentum. In the present case we are authorized to take also translational invariants. (See p 186 of ref. 1). We obtain thus the important parameter of long range order, called quasi-thermodynamic, because it has no conjugate intensity.

Another important extension of the theory is to magnetic (and electric) systems. It is easy to join the couple $M, H$ (magnetic moment and field) in analogy to density and chemical potential, to the formalism. It is a surprising aspect of recent studies[2–4] that this analogy is valid in a quantitative sense which goes considerably beyond the requirements of the thermodynamic analogy. It is therefore worth while to point out that this precise analogy is obtained only under carefully selected experimental conditions. Whereas pressure, temperature and chemical potential are constant over a heterogeneous system in equilibrium, this is true for the magnetic field only for special geometrical conditions. This is connected with the fact that the long range dipolar forces interfere with scale invariance. We note that the Ising model, although expressed originally in the language of magnetic systems, does not contain the disturbing dipolar interaction. Among its most important applications are cases in which the magnetization is interpreted as a quasi-thermodynamic order parameter.

## 4. CRITICAL POINTS

From the experimental point of view critical points in the phase diagram correspond to states in which two distinct modifications, such as liquid and vapour, or domains of opposite magnetization merge into a homogeneous phase.

According to thermodynamic theory critical points are *stable* states in which the determinant of the stiffness matrix vanishes. In terms of the symbols introduced in Section 2 we have two equivalent statements:

$$D_r = 0, \lambda_r = (\partial P_r/\partial X_r)_{P_1, \ldots P_{r-1}} = 0 \tag{21}$$

States satisfying these relations are called *spinodal*. In general, they are on the boundary of the metastable and unstable regions, and qualify as critical equilibrium points only when they are on the boundary of the normal region of stability. Here the system escapes instability by splitting into distinct modifications, and we see that the empirical definition is equivalent to the one based on thermodynamic stability.

This equivalence is, in fact, a theorem and enables us to predict that the compliance coefficients are singular. (This conclusion cannot be reached from the empirical definition alone.) In the case of a one component fluid we have

$$\lambda_1 = \left(\frac{\partial T}{\partial s}\right)_\rho = \frac{T}{c_v}, \qquad \lambda_2 = \left(\frac{\partial \mu}{\partial \rho}\right)_T = \frac{1}{\rho^2 \kappa_T} \qquad (22)$$

where $c_v$ and $\kappa_T$ are the specific heat and the compressibility respectively. At the critical point $\lambda_2 = 0$, $D_2 = 0$ implies

$$\alpha, \kappa_T, c_p \rightarrow \infty \qquad (23)$$

where $\alpha$ is the expansion coefficient. These conclusions are borne out by experiment. It is noteworthy that they follow from the vanishing of the determinant of the stiffness matrix, and there is no need to assume that the elements themselves vanish. The latter situation arises in the case of an accidental degeneracy with $\lambda_1 = \lambda_2 = 0$. Such a degenerate situation actually prevails in the Ising model, but in this case the degeneracy comes about because of the symmetry between the states of opposite magnetization.

Accordingly, when I discussed these matters some ten years ago, I duly stressed the difference between the Ising model and the real fluid[6]. At that time it was believed that the $c_v$ of fluids is finite at the critical point. The situation was entirely reversed as, shortly thereafter, more precise measurements showed that the specific heat $c_v$ is logarithmically divergent, in close analogy with the Ising model. We can hardly avoid the conclusion that the two cases exhibit similar symmetries. While the symmetry between the co-existing liquid and vapour modifications is by no means evident, such a symmetry has actually been predicted by the well known lattice gas model of Lee and Yang[9]. It is a surprise, however, that this model should prove not only manageable, but also more realistic than the van der Waals model of pairwise interacting particles.

In order to give justice to the hidden symmetry of the fluid it is important to use the density $\rho$, with the chemical potential $\mu$ as the conjugate variables instead of the more customary $V$, $P$[7]. Note that in MTE and STE the choice of variables is not entirely conventional, because this choice determines the type of exchange process that underlies the coupling of systems.

At this point we have arrived at the conclusion of the rigorous theory. Details have to be put in from experiment, from statistical mechanical calculations and also from approximate methods within GTD. The following is hardly more than a list of well known procedures with a few evaluating remarks.

### (i) Van der Waals theory

This is a wonderful *tour de force* arriving from a simple particle picture at the gross features of a fluid system. However, the method of Maxwell con-

struction has been incorrectly identified with the rigorous Gibbs theory. Differences of principle are pointed out on p 161 of ref. 1.

### (ii) Internal field theory

By introducing an internal field depending on the magnetization, $P$. Weiss generalized the concept of intensity in order to cope with the limitations of scale invariance. This method was greatly developed by Landau and a further improved modern version is found in ref. 2.

The proper microscopic model to interpret the molecular field theories is the cellular model. Assuming the cells to be statistically independent corresponds to the trivial scale invariant case. The internal field theory is one step better, and takes an average interaction effect of neighbouring cells into account. What is neglected is the correlation of actual states. The inclusion of the correlations is achieved in the next approximation.

### (iii) Ornstein–Zernike theory

This theory takes intercellular correlations into account and provides an excellent description of critical light scattering. Corrections required by the best experiments seem to be no more than marginal.

### (iv) The Ising model

This is the cellular model simplified to make rigorous calculations possible. It has been developing into the prototype for most critical points. It was Onsager's rigorous calculations that led to the discovery of the critical point exponents as the proper analytical tools to account for critical phenomena.

### (v) Critical point exponents

The introduction of this technique represents a turning point in the thermodynamic theory of critical points. Under normal conditions the thermodynamic fundamental equation is an extremely smooth function and the method of power series expansion is entirely justified. When using this method in his theory of continuous transitions, Landau did not suspect that these transitions might be singular. In contrast, my own approach was always centred around the importance of singularities, but lacking the proper technique I chose to confine myself in GTD to results of a topological nature, leaving details to statistical mechanics. However, in the last few years the new technique developed to a point where it can no longer be ignored by students of thermodynamics. In view of the wealth of results opened up for study I can do no more than whet your appetite for further study.

The underlying mathematical idea is simple enough. In order to make power series expansion applicable we modify as follows:

$$f(x) \approx |x|^{\lambda}(1 + ax + \ldots)$$

where $x$ tends to zero at the critical point and $\lambda$ is the critical point exponent. Logarithmically divergent functions are associated with an exponent $\lambda = 0$. The relevant variable is often the temperature expressed in terms of the reduced variable: $t = (T_c - T)/T_c$. The same symbols are used for the

thermodynamically analogous exponents for fluids, magnetic systems and more general order--disorder transformations. Here are some examples:

$$c_v \sim |t|^{-\alpha}$$
$$(\rho_G - \rho_L) \quad \text{or} \quad M \sim |t|^{\beta} \tag{24}$$
$$\rho^2 \kappa_T = \left(\frac{\partial \rho}{\partial \mu}\right)_T \quad \text{or} = \left(\frac{\partial M}{\partial H}\right)_T \sim |t|^{-\gamma}$$

In the case of $\alpha$ and $\gamma$ it is conventional to use primed indices below and unprimed above the critical point.

The first question that comes to mind is: how good are such representations? I confine myself to referring to *Figure 1* taken from a recent paper by M. Giglio and G. B. Benedek[8][†].



$$\gamma'_{vapour} = 1.244 \pm 0.017$$
$$\gamma'_{liquid} = 1.228 \pm 0.028$$
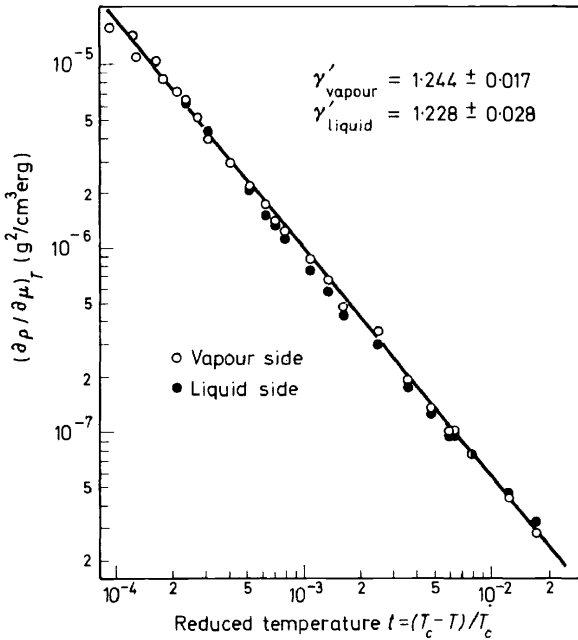
o Vapour side
● Liquid side

*Figure 1.* Plot of $(\partial \rho/\partial \mu)_T$ along the vapour and liquid sides of the coexistence curve of xenon as a function of the reduced temperature $t = (T_c - T)/T_c$. Open circles show vapour side; closed circles show liquid side.

The second point is that inserting the representations 24 into the standard thermodynamic formalism yields inequalities such as the Rushbrooke inequality:

$$\alpha' + 2\beta + \gamma' \geqq 2 \tag{25}$$

† I am indebted to the authors for letting me use their remarkably accurate results. They pointed out to me in a personal communication that the quality of their plot depends very markedly on the use of the variables $\rho$, $\mu$. The constancy of the two exponents and their coincidence is lost in the plot of the conventional compressibility. This confirms the suggestion of Chase and Tisza[7].

Such inequalities are borne out by experiment, and indeed they have proved helpful in spotting errors in the determination of exponents.

More recently a number of so-called scaling laws have been proposed which tend to bring about a greatly increased coherence in the field. I confine myself to referring to the scaling law proposed by Kadanoff[2] which can be explained most simply in the present context.

Kadanoff considers an Ising model of lattice constant $a_0$ and defines a cell of size $La_0$ satisfying the relation

$$1 \ll L \ll \xi/a_0 \tag{26}$$

where $\xi$ is the coherence length. Kadanoff argues that the properties of the site and cell will be identical provided we scale the magnetic field $H$ and the reduced temperature as follows:

$$\tilde{H}/H = L^x$$

$$\tilde{t}/t = L^y \tag{27}$$

$\tilde{H}$, $\tilde{t}$ refer to the intensities effective in the cell description, whereas $H$, $t$ refer to the site. The main result is that all nine exponents mentioned above can be expressed in terms of $x$ and $y$. The situation in this respect is remarkably good. Small discrepancies only arise in connection with the exponent of the correlation length describing, say, the extent of the short range order of spins on the paramagnetic side of the critical point. However, this pehnomenon is already a long way from the traditional domain of thermodynamics. Assuming that the scaling law will continue to hold up under the close scrutiny it is being subjected to, we can rationalize its meaning within GTD as follows: We known that the scale invariance of the macroscopic system must be limited, because any subdivision must stop at the single site; the scaling law is a generalization of the principle of scale invariance, to which it can be reduced if $x$ and $y$ are set equal to zero.

## CONCLUSIONS

Generalized thermodynamics is a flexible framework accommodating many theories beyond those traditionally considered. Thus open systems and their fluctuations can be rigorously handled without invoking specific microscopic models. The extension of Gibbsian phase theory is consistent with the recent results concerning the phenomena in the neighbourhood of the critical points. The technique of critical point exponents made many of the classical procedures of approximation obsolete. However, this affects only various approximations to the main theory. Thus the shortcomings of the van der Waals theory are often ascribed incorrectly to the Gibbs theory. Although the latter is also in need of corrections and additions, when all this is done, the basic structure of the theory is seen to be considerably strengthened.

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