Inequalities Relating Critical Exponents

Hanif Bayat Movahed*
Department of Chemistry, University of Toronto
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During modern era of critical phenomena, several inequalities between critical exponents have been derived. However most of these inequalities depend on some assumptions. Beside this, some of these inequalities can be replaced by equalities. Several solved classical models as well as some recent theories have helped us to check the validity of these inequalities. To check these inequalities in lab, experiments should be done in very close temperature to the critical temperature and therefore there have been difficulty to check precisely these inequalities. However, there have been enough results to study the behaviors of these inequalities as well as the critical exponents.

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INTRODUCTION

Critical Phenomena

The critical point for fluid system is the specific temperature and pressure, in which the phase transition between liquid and gas stop to exist. After passing critical point, at higher temperatures and pressures, it is possible to convert a liquid to a gas continuously without using energy for the phase transition. The critical point in magnets (or Curie point for ferromagnetic) is defined in similar way to the critical point in fluids [1]. Bellow the critical temperature, if the system at non-zero magnetic field is approached to the magnetic field of zero ($H = 0$), M will not be zero. However at the critical temperature or higher temperatures, ($T \geq T_c$), the graph of $H - M$ will be continuous and at magnetic files of zero ($H = 0$), magnetization will be zero ($M = 0$). The critical phenomena is related to the behavior of the systems around the critical point.

critical exponents

As we become close to the critical point, some of the quantities of the system are related to the temperature as $f(T) \sim (T - T_c)^\beta$ for some exponents of β. The similar behaviors may be seen not as a function of temperature, but as a function of some other quantities of the system $f(x) \sim (x)^\beta$. These exponents (β) are called the critical exponents. For example, the order parameter ($\rho_L - \rho_G$) in fluids and zero field magnetization M in magnets can be described as a function of $T - T_c$. However, commonly instead of $T - T_c$, $\epsilon \equiv \frac{(T-T_c)}{T_c}$ is used [1].

In practice M, ($\rho_L - \rho_G$) or the other functions of ϵ can have more general form of [1]

$$f(\epsilon) = A(\pm\epsilon)^\beta(1 + B(\pm\epsilon)^x + ...) \quad (1)$$

where $x > 0$ and the sign behind ϵ depends on the definition of the critical exponent and how the approach to the critical temperature is made. Generally depends on the direction of an approach to the critical temperature, the critical exponent can get different values. If an approach is made from a temperature above or bellow T_c, $+\epsilon$ and $-\epsilon$ should be used respectively. Considering Eq. (1), the critical exponent of β is naturally defined as [1]

$$\beta \equiv \lim_{\epsilon \to 0} \frac{\ln f}{\ln(\pm\epsilon)} \quad (2)$$

The significance of these critical exponents is based on the universality of them. This means in the theoretical models they do not depend on the details of the physical system and they mainly depend on the dimension of the system. However, according to the experimental results, which are presented later in this paper, the values are not exactly the same for the real different materials, but they are close to each other and it is possible to find some universal relations between these exponents.

MODERN ERA OF CRITICAL PHENOMENA AND CRITICAL EXPONENT INEQUALITIES

While some people may claim that the modern era of critical phenomena started in the 1940s, most people think during the period of 1964-1972 a revolution happened in our understanding of critical phenomena [1], [2]. The main idea was to focus on the region near the critical point (instead of looking at the whole phase diagram) and find different universal relations between the critical exponents. These relations arise from the fundamental thermodynamics (by considering statistical mechanics) and therefore they are valid for any systems [1], [2]. For describing the rates of divergence of thermodynamics properties close to the cortical point several inequalities have been derived.

Definition of Common Critical-Point Exponents for Fluids and Magnetic Systems

Before trying to present the relations between critical-point exponents, we should describe briefly the definitions of some of the most famous critical exponents for fluids and magnets [1]. α and α' are defined as

$$C_V \sim (\epsilon)^{-\alpha}, C_V \sim (-\epsilon)^{-\alpha'}, C_H \sim (\epsilon)^{-\alpha}, C_H \sim (-\epsilon)^{-\alpha'} \tag{3}$$

where C_V and C_H are heat capacities at a constant volume and a constant magnetic field respectively. β is defined as

$$(\rho_L - \rho_G) \sim (-\epsilon)^{\beta}, M \sim (-\epsilon)^{\beta} \tag{4}$$

where ρ_L, ρ_G and M are density of liquid, density of gas and zero-field magnetization respectively. γ and γ' are defined as

$$K_T \sim (\epsilon)^{-\gamma}, K_T \sim (-\epsilon)^{-\gamma'}, \chi_T \sim (\epsilon)^{-\gamma}, \chi_T \sim (-\epsilon)^{-\gamma'} \tag{5}$$

where K_T and χ_T are isothermal compressibility and isothermal susceptibility. δ is defined as

$$(P - P_c) \sim |\rho_L - \rho_G|^{\delta} sgn(\rho_L - \rho_G), H \sim |M|^{\delta} sgn(M) \tag{6}$$

where P and H are pressure and magnetic field respectively.

While there are some other critical exponents, the above components are enough to present some of the most rigorous inequalities. Later, we will present the definitions of some other exponents also.

The Rushbrooke Inequality

The Rushbrooke inequality can be considered as the most famous inequality between critical exponents. This inequality was proposed by Rushbrooke in 1963 as a discussion remark at the end of some one else seminar [1]. The inequality is as follows:

$$\alpha' + 2\beta + \gamma' \geq 2 \tag{7}$$

Rushboork did not make any special assumption to prove eq. (7). The proof is based on the relation

$$C_H - C_M = T \frac{\left(\frac{\partial M}{\partial T}\right)_H^2}{\left(\frac{\partial M}{\partial H}\right)_T} \tag{8}$$

and since C_M must be positive, it can be concluded that

$$C_H \geq T \frac{\left(\frac{\partial M}{\partial T}\right)_H^2}{\left(\frac{\partial M}{\partial H}\right)_T} \tag{9}$$

Is it an equality? While Rushbrooke presented the above relation as an inequality, according to several solved models as well as some experimental data, the value of $\alpha' + 2\beta + \gamma'$ is equal to two and therefore many people believe that the eq.(7) is an equality. However the attempts to prove this guess theoretically, have been unsuccessful till now. From the definitions of α', β and γ', it is clear that the approach to the critical temperature, T_c, is made from the bellow of T_c.

Landau theory, scaling theory, Ising model (two and three dimensional), Essam and Fisher work on gap exponents, van der Waals theory and mean field theory all predict the Rushbrooke inequality as an equality. By considering the error bonds of experiments, almost the same prediction has been found by experiments. [1] [3] [4]

However, Rushbrooke showed that if we define $R \equiv \lim_{\epsilon \to 0} \frac{C_M}{C_H}$, then if $0 \leq R < 1$ then Rushbrooke relation will be an equality and the value of $\alpha' + 2\beta + \gamma'$ is two. But if $R = 1$, then the Rushbrooke relation fails to be an equality anymore [5].

We present several models and experimental results later in this paper and their predictions for the Rushbrook inequality are discussed.

Griffiths Inequality

Griffiths presented several inequalities between the critical exponents, however the most famous one is presented in 1965 and it describes the relation between α',β and δ [1] [6]. The inequality is as follows:

$$\alpha' + \beta(1 + \delta) \geq 2 \tag{10}$$

Again for this inequality, solved models as well as the experimental results predict the value of almost two or less than two for $\alpha' + \beta(1 + \delta)$. Initially it was thought that the experimental results violate this inequality [7], but in situations like this one can conclude that the experimental measurements did not extend to the temperatures close enough to T_c [1]. Moldover in 1969 [8] concludes that $\alpha' \sim 0.15$ and by this value $\alpha' + \beta(1 + \delta)$ become 2.01 and therefore it obeys the eq. (10).

Not independent from the Rushbrooke and Griffiths inequalities (eqs.(7) ,(10).), Griffiths has proved [1] that

$$\gamma' \geq \beta(\delta - 1) \tag{11}$$

The above relation, which is known as Widom inequality (or equality), initially was conjectured by Widom as an equality in 1964 [9]. By combining eq. (11) as an equality with eq. (7), we can derive eq. (10). However Widom derived this equality based on some experimental results and also by making an assumption that the behavior of the (P-T) isochores near the critical point [6] [9], which is not a solid fact [6]. Griffiths proof for Widom inequality is also based on some assumptions such as $(\frac{\partial H}{\partial M})_T$ is a non-decreasing function of $M \geq 0$ for $T \leq T_c$ [1].

Other Inequalities

Griffiths proved several other inequalities such as $\gamma(\delta + 1) \geq (2-\alpha)(\delta-1)$ and $\gamma'(\delta+1) \geq (2-\alpha')(\delta-1)$. There are some other inequalities between other critical exponents of ν,ν', η, ϕ and ψ also. Where ϕ and ψ are defined at $T = T_c$ when $H \to 0$, while in Rushbrooke inequality it was $H = 0$ and $T \to T_c$, and they are as follows:

$$C_H \sim H^{-\phi} \sim M^{-\phi\delta} \tag{12}$$

$$S(H) \sim -H^{\psi} \sim M^{\psi\delta} \tag{13}$$

and $\zeta = \psi\delta - 1$. ν, ν' and η in magnets are defined as follows:

$$\zeta \sim \epsilon^{-\nu}, \zeta \sim (-\epsilon)^{-\nu'}, \Gamma(r) \sim |r|^{-(d+\eta-2)} \tag{14}$$

where ζ, $\Gamma(r)$ and d are correlation length, pair correlation function and dimensionality respectively. [1]

All these proofs of inequalities are based on some most probably true assumptions, that have not been generally established (such as the last paragraph assumption for $(\frac{\partial H}{\partial M})_T$). Beside the previous inequalities, there are some other famous inequalities. For example, Coopersmith derived the bellow equation between ϕ, ψ and δ as fellows:

$$\phi + 2\psi - \frac{1}{\delta} \geq 1 \tag{15}$$

But since the exponents ϕ and ψ rarely measured, it is hard to talk more about this inequality. The proof of the Coopersmith inequality does not depend on any unproved assumption. [1]

From other famous inequalities, one can name Fisher and Josephson inequalities. Fisher proved several inequalities in his 1969 paper [10] such as

$$\gamma \leq (2 - \eta)\nu, 2 - \eta \leq d\frac{\delta - 1}{\delta + 1} \tag{16}$$

and

$$2 - \eta \leq \frac{d\gamma'}{2\beta + \gamma'} \leq \frac{d\gamma'}{(2 - \alpha')} \tag{17}$$

While Fisher himself, introduce his work as "Simple rigorous proofs are given for the inequalities..." [10], they are based on some assumptions such as positivity of the correlation functions for all temperatures and any non-negative magnetic field [1].

Except Rushbrook and Griffiths inequalities, which are really rigorous and unproved assumptions are not used in their proofs, almost all other inequalities are based on some plausible, but not generally proved assumptions [1]. However as discussed earlier, because of lots theoretical and experimental evidences, those inequalities can be considered as equalities.

CRITICAL EXPONENTS BY SOLVED MODELS

In this part, we will discuss some of the models which predict the values of the critical exponents and we will check their predictions for the discussed inequalities.

Classical Models (van der Waals theory of fluids, molecular field theory of a magnet and Landau theory)

The named theories and models are called classical, since there are the earlier theories of critical-exponents. All these models give the same value for α', β, γ' and δ as 0, $\frac{1}{2}$, 1 and 3 respectively and therefore all these models predict the Rushbrooke and Griffiths inequalities as equalities [1] [3]. These models also predict that $\alpha = \alpha'$ and $\gamma = \gamma'$. However these values of critical exponents are completely different from experimental results, for example β for most of experimental results have a value between 0.3 to 0.4 [1].

Ising Model

In Ising model, the magnetic moments are classical and a system is a collection of spins, which can get only 1 or -1 values. Onsager's solution for two dimensional Ising model give the values of α', β, γ' and δ as 0, $\frac{1}{8}$, $\frac{7}{4}$ and 15 respectively. Using these results, the value of $\frac{15}{8}$ for $\alpha' + 2\beta + \gamma'$ is found, which is very close to two. For Griffiths inequality the value of $\alpha' + \beta(1+\gamma)$ will be two, which shows it as an equality. However the same as the introduced classical models, experimental results violate these theoretical results. [1]

For the three dimensional Ising model, no one has yet solved it and therefore the values for critical exponents are based on some approximations. The approximated values of α', β, γ' and δ are $\frac{1}{16}$, $\frac{5}{16}$, $\frac{21}{16}$ and 5 or $\frac{1}{8}$, $\frac{5}{16}$, $\frac{20}{16}$ and 5 respectively [1]. Again Rushbrooke inequality is concluded as an equality and for Griffiths inequality the value of $\alpha' + \beta(1+\gamma)$ will be $\frac{31}{16}$ and 2, which suggest it again as an equality. Again the predicted values are not in agreement with experimental values. According to more recent work of Mayer [11] on dilute Ising model, the values of 0.110 , 0.325 and 1.240 were obtained for α, β and γ respectively. These values are in a very good agreement with experimental results and if we assume that $\alpha = \alpha'$ and $\gamma = \gamma'$, the value of $\alpha' + 2\beta + \gamma$ will be 2.000.

Scaling Law Theory of Exponents

Static scaling law or homogenous function approach, by adding a reasonable axiom, have found non-numerical values for the critical exponents [1]. This added axiom mainly states that for the generalized homogenous function of the Gibbs potential near the critical point

$$G(\lambda^a\epsilon, \lambda^b H) = \lambda G(\epsilon, H) \tag{18}$$

for any value of λ. By using this axiom, critical exponents values were calculated based on two scaling parameters,

a and b. [1] [3]

The calculated values for α', β, γ' and δ are $2-\frac{1}{a}$, $\frac{1-b}{a}$, $\frac{2b-1}{a}$ and $\frac{b}{1-b}$. By considering these values, both Rushbrooke and Griffiths inequalities become equalities. By considering scaling law theory, the Coopersmith inequality (eq.(15)) become an equality also.

Some other theories

Critical exponents can be found from n-Vector model. Guida and Zinn-Justin in 1998 estimated critical exponents of the N-vector model by using some new ideas in the context of the Borel summation techniques [12]. The values for α, β and γ are predicted as -0.12, 0.36, 1.39 and 4.8 [12] and if we assume that $\alpha' = \alpha$ and $\gamma = \gamma'$, it predicts the Rushbrooke inequality as an equality. In other work by Zinn-Justin and Guillou, by finding the critical exponents for the n-Vector model in three dimensions from field theory, the values of 0.365, 1.38 and 4.803 for β, γ and δ were found [13] [14].

EXPERIMENTAL VALUES FOR THE CRITICAL EXPONENTS

As discussed previously, experimental results do not violate the Rushbrooke and Griffiths inequalities. Some of these values are presented in the following tables

Fluids	α'	β	γ'	δ	α	γ
CO_2 [1]	~ 0.1	0.34	~ 1.0	4.2	~ 0.1	1.35
Xe [1]	< 0.2	0.35	~ 1.2	4.4	–	1.3
N_2 [15]	–	0.327 ± 0.002	–	–	–	1.23 ± 0.01
Ne [15]	–	0.327 ± 0.002	–	–	–	1.25 ± 0.01

Magnets	$\alpha' or \alpha'_S$	β	δ	α	γ
Ni [1]	-0.3	0.42	4.22	0	1.35
EuS [1]	-0.15	0.33	–	0.05	–
FeF_2	–	0.325 [16]	–	0.111 [17]	1.25 [18]
CoF_2	–	0.305 [19]	4.94 [20]	0.109 [20]	1.22 [19]

From the above results, it is clear that the values of critical exponents depend on the materials and the initial hope that these values may be universal, is not true. As can be seen in the above tables, almost all the times the Rushbrooke and Griffiths inequalities become equalities. For example for CO_2 the value of $\alpha' + 2\beta + \gamma'$ is equal to 1.78, which is lower than two, however by considering experimental error bar, we can assume that this can reach two; or for FeF_2 if we assume that $\alpha = \alpha'$ and $\gamma = \gamma'$, then the value of $\alpha' + 2\beta + \gamma'$ become 2.01 which is completely close to 2.

* Electronic address: hbayat@chem.utoronto.ca

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