

Finite-size effects at first-order phase transitions observed in adsorbed oxygen films

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(Received 2 December 1988)

At a first-order phase transition the specific-heat signal is of δ -like shape. However, this is true rigorously only for systems with infinite dimensions. For finite systems the specific heat is rounded, the degree of rounding depending on the size of the system. Model systems to investigate such rounding effects are physisorbed layers. Such layers are always finite, since substrate properties make adsorption sites of only finite size available. Recent theoretical investigations study the finite-size effects of temperature-driven first-order phase transitions by analyzing various moments of the energy distribution. The theoretical results describe the rounding of the singularities and the shifts in the location of the specific-heat maxima in a manner which is suitable for immediate comparison with experimental results. The only unknown fit parameter is the system size. The present paper describes fit results for physisorbed O₂ layers. The presently determined experimental system size is found to be in good agreement with that size known from neutron diffraction studies.

There are some basic differences in the behavior of phase transitions which are intimately correlated to their order. At a second-order transition, the characteristic correlation length of the system diverges. For a first-order transition, however, no such diverging length exists. The diverging correlation length means that short-range properties of the system become increasingly irrelevant when the system approaches its transition point. Therefore second-order phase transitions can show universal critical behavior. Since for a first-order phase transition there is no diverging length this kind of phase transition shows much less universality.

The singularities of the specific heat, e.g., observed at second-order phase transitions are closely linked to the divergence of the correlation length. The singularities observed at first-order phase transitions have their origin in coexisting phases where the conversion of one phase into the other is accompanied by the consumption of latent heat. Other than with a second-order phase transition there is no critical region and no critical exponent. What are the consequences of finite-size effects on the behavior of phase transitions? In the case of a second-order phase transition the increase of the correlation length will eventually be limited by the finite dimension of the system; that is, the correlation length of a finite system does not diverge. In the case of a first-order phase transition even at the transition point the correlation length is equal to only a few-lattice-spacings distance and therefore it is normally not limited by the size of the system.

Finite-size effects cause the singularities of both kinds of phase transitions to be rounded and the transition temperatures to be shifted. Second-order transitions are rounded and their transition temperatures shifted according to $\propto L^{-1/\nu}$; first-order transitions are rounded and shifted according to $\propto L^{-d}$ which means that correlation length and volume (area), respectively, rule rounding and shifting.

There is by now a well-established physical theory which describes how finite-size effects influence second-

order phase transitions; the influence on first-order transitions has attracted attention only very recently.¹⁻⁷

Contrary to the theoretical situation there are few experimental contributions which deal with finite-size phenomena in two-dimensional systems.^{8,9} The present paper describes adsorbed films as experimental systems which allow the study of finite-size effects and the test of theoretical predictions. These films have finite dimensions since their coherent layer size is limited by the substrate which is a foil of compressed graphite with a large specific surface. It is a characteristic feature common to all such large area substrates that they have only finite coherent adsorbing regions delimited from each other by grain boundaries, etc. Since these boundaries are sites of much stronger adsorption the particles placed at these sites generally do not participate in phase transitions, although they contribute to the heat capacity and to the other physical properties of the film. The substrate most commonly used for the preparation of such systems is graphite and its subspecies (grafoil, papyex, foam, ZYX) which differ significantly in their homogeneity, their degree of unique orientation, and their domain sizes. This kind of substrate consists of small crystallites the faces of which become the adsorption planes. Finite-size effects of the adsorbed system originate from the edge lengths of those faces. Typical lengths are from 100 to 1000 Å.

We reinvestigate formerly published¹⁰ specific-heat data of O₂ films for finite-size effects. The films were adsorbed on grafoil sheets. This substrate is anticipated to have mean characteristic edge lengths of about 100 Å. Thus the maximum size of one coherently adsorbed patch should be limited to about $100 \times 100 \text{ Å}^2$ on an average.¹¹ When this is compared with sizes one is used to in the case of three-dimensional systems, we foresee very small system sizes; therefore these films are anticipated to be favorable candidates to reveal pronounced finite-size effects. We concentrate on that part of the phase diagram (O₂ films/grafoil) which resembles phases of a classical van der Waals system. The triple and melting lines corre-

spond to the coverage range between $\rho \approx 0.25$ and 1. These lines are known to reveal sharp specific-heat anomalies. Typical examples are depicted in Figs. 1(a) and 1(b) for the triple line ($\rho = 0.51$) and the melting line ($\rho = 0.89$), respectively;^{10,12-16} refer to these papers for a detailed description of the liquid and solid phases and for more details of the phase diagram of adsorbed O₂ films. The triple and melting lines are clearly first-order transition lines since for both lines phase equilibrium between the liquid and the solid phase has been observed in scattering experiments.¹³ For the triple line we would ideally anticipate δ anomalies, for the melting line we would in principle anticipate mesalike anomalies whose width is predetermined by the width of the temperature interval of coexisting solid and liquid phases. In case of a melting line which is only weakly temperature dependent the mesalike anomalies will approximately assume a pseudo- δ -like shape. This then would render it difficult to distinguish points in the phase diagram which are to be attributed to the triple line or the melting line, respectively.

Table I (columns 1-6) shows the data we obtained by analysis of the experimental specific-heat results near both transition lines.¹⁰ The phase transitions start with a T_c^{exp} which is coverage independent. This is consistent with the assumption of a triple line ($0.35 \leq \rho \leq 0.71$). Then the specific heat shows peak positions at successively increas-

ing transition temperatures indicating that the triple line terminates somewhere beyond $\rho = 0.71$. We determined the limiting coverage between the triple and the melting lines to be about $\rho_1 = 0.73$; this coverage corresponds also to the density of the liquid phase.¹⁰ The coverage dependence of the melting line is only weak. Between $\rho = 0.75$ and 0.98 the melting temperature increases by $\Delta T = 0.66$ K which is to be compared with ≈ 26 K (2.6%).

We mention that in going from $\rho = 0.35$ to 0.68 the anomalies become successively slimmer. The minimum FWHM is 0.49 K (Table I, column 4). Between $\rho = 0.68$ and 0.71 this trend is stopped and then reversed, the anomalies now broaden more and more finally reaching a FWHM of 1.2 K at the end of the melting line (Table I, last row). The ups and downs of the entropy jumps ΔS of the latent heats A are considered to merely express the data scatter. It may not be attributed to a trend which has physical meaning.

Next we compare the experimental findings with the theoretical results. Theoretical results which allow the immediate comparison with experimental data are due to Challa, Landau, and Binder.⁷ We aim at the fit of the system's size b . To this end we fit the number of particles L participating in the phase transition. Challa *et al.* study the finite-size effects of temperature-driven first-order transitions by analyzing various moments of the energy

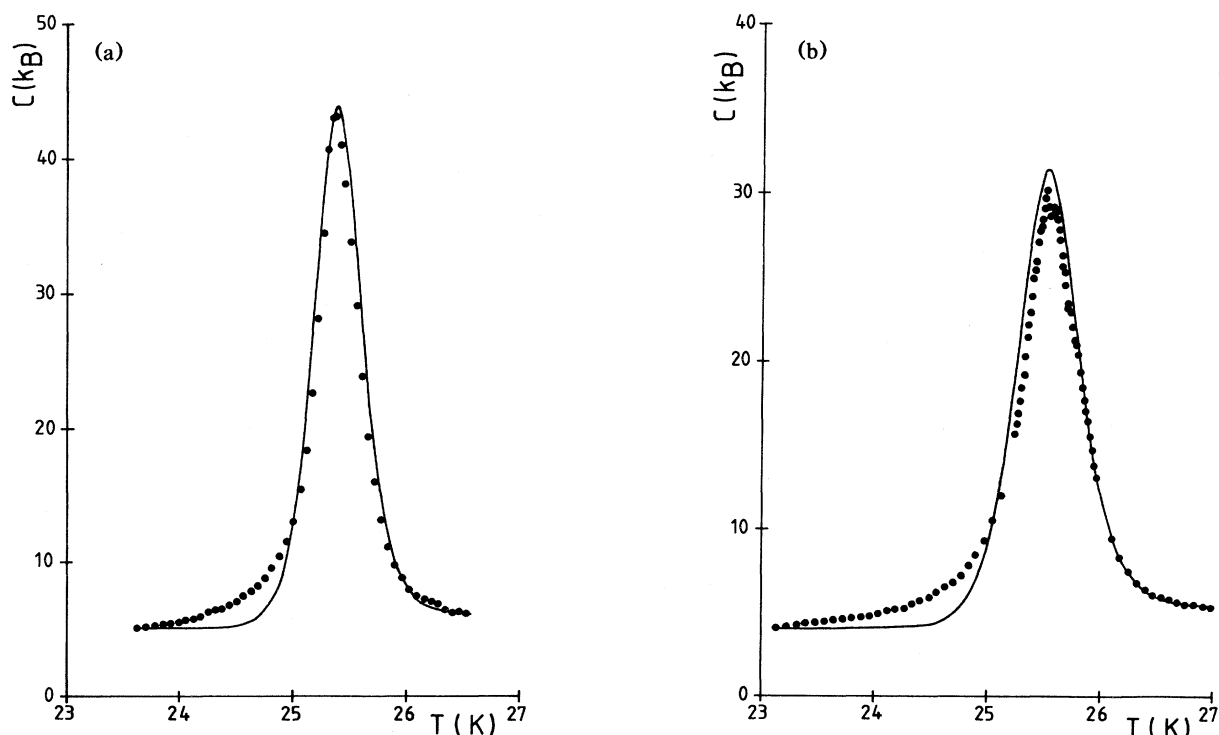


FIG. 1. Specific heat particle O₂ in units of k_B as a function of temperature. Dotted curve: experimental results, line: theoretical results. The coverage was $\rho = 0.51$ [(a), triple line] and $\rho = 0.89$ [(b), melting line]. The experimental $C_{\text{max}} = C(T = T_c^{\text{exp}})$ is fitted to the maximum of Eq. (1). The parameters of the theory (Ref. 7), C_+ and C_- , are assumed to correspond to the outermost left- and right-hand points of the experimental curve, respectively. After choosing $q = 2$ or 3 one gets L from Eqs. (1) and (2). There is good agreement between the fit and the experimental curve, apart from the fitted curve being somewhat slimmer than the experimental one. This becomes particularly evident for that part which lies below T_c where the experimental curve does not agree with the calculated one.

TABLE I. Analysis of the experimental specific-heat results.

ρ^a	T_c^{exp} (K)	C_{max} (k_B)	ΔT^b (K)	ΔS^c (k_B)	A^d ($k_B K$)	L^e		T_c^{exp} ($L \rightarrow \infty$)		ΔT_c^f		b^g (Å)
						$q=2$	$q=3$	$q=2$ (K)	$q=3$ (K)	$q=2$ (K)	$q=3$ (K)	
0.35	25.42	39.8	0.63	0.88	22.4	13	13	25.31	25.24	0.11	0.17	47
0.51	25.39	43.2	0.54	0.82	20.8	15	15	25.31	25.26	0.08	0.14	54
0.68	25.33	41.5	0.49	0.80	20.3	...	15	...	25.20	...	0.13	54
0.71	25.33	39.7	0.56	0.81	20.5	...	14	...	25.18	...	0.15	50
0.75	25.34	40.2	0.56	0.70	17.8	...	17	...	25.22	...	0.12	61
0.80	25.36	36.1	0.52	0.71	17.9	...	16	...	25.22	...	0.14	58
0.84	25.42	32.3	0.65	0.75	19.1	...	14	...	25.26	...	0.17	50
0.89	25.51	30.2	0.86	0.73	18.6	14	14	25.41	25.34	0.10	0.17	50
0.93	25.69	27.4	0.99	0.79	20.3	...	12	...	25.47	...	0.22	43
0.95	25.85	26.9	1.15	0.75	19.4	...	12	...	25.63	...	0.22	43
0.98	26.00	25.9	1.20	0.76	19.8	...	12	...	25.78	...	0.22	43

^aIn units of the coverage of the $\sqrt{3}$ structure.

^bWidth at $C_{\text{max}}/2$ (FWHM); lattice contribution subtracted.

^cEntropy jump solid-liquid.

^dLatent heat $A = \Delta ST_c$.

^eFit for $q=2$ only done for selected coverages.

^f $\Delta T_c = T_c^{\text{exp}}(L) - T_c$.

^g $b = L \times (\text{area of one particle})^{1/2}$

distribution. The distribution function is approximated by the superposition of the two weighted Gaussian functions. The rounding of the singularities and the shifts in the location of the specific-heat maxima are predicted and the characteristic features of a first-order transition are identified. The specific heat is described by⁷

$$C_L(T) = (a_+ C_+ + a_- C_-) / (a_+ + a_-) + \{a_+ a_- L^d [(E_+ - E_-) + (C_+ - C_-) \Delta T]^2 / [k_B T^2 (a_+ + a_-)^2]\}, \quad (1)$$

where $a_+ = \{(C_+)^{1/2}\} e^x$ and $a_- = \{(C_-)^{1/2}\} q e^{-x}$; q is the number of ordered states at the transition point coexisting with the disordered state. The subscripts $+$ and $-$ refer to the high- and low-temperature phases, respectively, d is the dimensionality of the system (presently $d=2$), and k_B is Boltzmann's constant. x is given by $x = -\Delta F L^d / 2k_B T$. $\Delta F = F_+ - F_-$ and $F_{\pm} = E_{\pm} - TS_{\pm}$ are free energies. Then $\Delta F = -(E_+ - E_-) \Delta T / T_c$, $\Delta T = T - T_c$. $E_+ - E_-$ is the latent heat and C_{\pm} are the specific heats above and below the transition, respectively. The temperature shift in the location of the specific-heat maximum is described by⁷

$$T_c(L) - T_c = \{k_B T_c^2 \ln[q(C_-/C_+)^{1/2}]\} / (E_+ - E_-) L^d, \quad (2)$$

where T_c and $T_c(L)$ are the transition temperatures of the infinite and the finite systems, respectively.

Inspection of formulas (1) and (2) reveals that the only experimentally unknown parameter is the number (L^d) of particles involved in the phase transition. We analyze the behavior of the specific-heat results by fitting Eqs. (1) and (2) to our experimentally found data points. The analysis is also applied to coverages beyond $\rho \approx 0.71$, since for the present adsorption system up to coverages of $\rho = 1$ the melting line virtually behaves like a triple line.¹⁰ We vary L and we aim at a maximum agreement between the experimentally determined $C_{\text{max}} = C(T = T_c^{\text{exp}})$ and the $C_{L,\text{max}}$ deduced from Eq. (1). Note that $C_{L,\text{max}}$ responds sensitively to a variation of L . In detail we proceed as follows. First we deduce an approximate L . With the help of Eq. (2) we then calculate the shift ΔT_c of the transition temperature. Only the smaller one of both roots of the

quadratic equation has physical meaning. By subtracting ΔT_c we then reduce the experimental $T_c^{\text{exp}}(L)$ to $T_c^{\text{exp}}(L \rightarrow \infty)$. Note that the anomaly described by Eq. (1) is centered around $T_c(L)$. This T_c is inserted into Eq. (1) and we arrive at a better approximation for L . With the next approximation for ΔT_c we calculate the final L .

The right-hand columns (7-13) of Table I list the fit results for L , $T_c^{\text{exp}}(L \rightarrow \infty)$, ΔT_c , and the mean edge lengths b of the adsorption patches the particles of which participate in the phase transition. Columns 7 and 8 indicate that L does not significantly depend on coverage. Moreover, it nearly does not depend on the choice of q , used here as a parameter.

The figures for ΔT_c show (columns 11 and 12) that there is only a small difference of about 0.5% between the transition temperature of the experimental (finite) system and the hypothetical (infinite) system. ΔT_c obviously depends on coverage. At low coverage it weakly tends to become smaller assuming the minimum value near ρ_1 . Then it increases finally reaching $\Delta T_c = 0.22$ K at $\rho = 0.93, 0.95$, and 0.98 . The FWHM reveals similar behavior. We do not yet understand if this behavior has physical meaning. The increase of ΔT_c may be an artifact of the inherent but still latent trend of the anomalies to assume a mesalike shape.

Figures 1(a) and 1(b) compare the experimental results (dots) with the specific heat calculated with the help of Eq. (1) (line). There is fair agreement between the experimental findings and the theoretical prediction. The theoretical curve is somewhat slimmer than the experimental one. At $T < T_c$ the discrepancy becomes especially evident. Far off the phase transition the specific heat

should assume the Debye value which is $(2+2)$ degrees of freedom times $1k_B$ equal to $4k_B$ plus minor contributions due to the molecule's rotation around its z axis and its vibration perpendicular to the substrate surface. The sum may well be very close to that value which was experimentally observed ($5k_B$). This means that the outermost left- and right-hand points of the experimental curve should correspond to temperatures where the phase transition did not yet start or is just over, respectively. Therefore, we identify those points with C_- and C_+ of the theory. Presumably, in this way we underestimate these figures somewhat, since Monte Carlo calculations revealed that at least for the Potts model C_- and C_+ are to be localized much closer to the critical point of the phase transition.⁷

Column 13 of Table I lists the sizes of the patches undergoing the phase transition. These figures are based on the L 's of column 8. The presently determined values for b are between 43 and 61 Å. Former independently done experimental observations (scattering experiments) report b for grafoil to be between 100 and 120 Å.¹¹ In order to explain the difference by roughly a factor of 2 between both system sizes we may argue in accordance with Callaway and Schick^{8,9} that presumably only one half of the adsorbed particles take part in the phase transition, since the other half is adsorbed on sites of strong binding or is otherwise trapped. The reasoning of these authors is based on experiments and calculations done for adsorbed helium films, but we may hope that it also gives hints for the present situation; under the aspects discussed here it should not matter whether we consider helium or oxygen films. Callaway and Schick investigated finite-size effects of helium films and the relation of their properties to characteristic substrate sizes by real-space renormalization-group methods. They found that about 50% of the adsorbed helium particles did not take part in the order-disorder transitions at $T_c \approx 3$ K of those films since a large part of the particles had been trapped on sites of strong binding. This result suggests that we may distin-

guish "idle" and "nonidle" particles present in the O_2 film. All particles are assumed to contribute to the Debye-type part of the specific heat and only the nonidle particles to that part of the specific heat which reflects critical behavior. The assumption that all particles contribute to the Debye-type part of the specific heat is supported by the observation that the outermost left- and right-hand points of the experimental specific-heat curve are very close to the anticipated Debye values. Unfortunately, it seems difficult to do a more quantitative argumentation and to do a recalculation of the specific heat on the basis of the division of the adsorbed particles into those which participate in the phase transition and those which do not. Note that the anomalies displayed in Figs. 1(a) and 1(b) and all data of Table I are based on normalized heat-capacity data, i.e., to calculate the specific heat the heat capacity has been divided by the number of particles actually adsorbed. To make allowance for the division in idle and nonidle particles the heat capacity in the critical region is to be normalized to the number of nonidle particles and in the noncritical region to the number of all adsorbed particles. Despite those difficulties we nevertheless foresee the reevaluated fit to result in a considerably larger edge length so that the presently fitted size would become closer to that anticipated on the basis of the diffraction studies.

In summary we conclude that the experimentally observed blurring of the specific-heat anomalies is consistently explainable by the theoretical investigation of Challa, Landau, and Binder. The fitted system size is in fair agreement with that which was determined in former studies. This means that finite-size effects are the reason that the O_2 film does not show infinitely high but blurred anomalies.

The author thanks Professor K. Binder for a critical reading of the manuscript.

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