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Crossover between displacive and order-disorder phase transition

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Abstract

The phase transition in a 3D array of classical anharmonic oscillators with harmonic nearest-neighbour coupling (discrete ϕ^4 model) is studied by Monte Carlo (MC) simulations and by analytical methods. The model allows to choose a single dimensionless parameter a determining completely the behaviour of the system. Changing a from 0 to $+\infty$ allows to go continuously from the displacive to the order-disorder limit. We calculate the transition temperature T_c and the temperature dependence of the order parameter down to $T = 0$ for a wide range of the parameter a. The T_c from MC calculations shows an excellent agreement with the known asymptotic values for small and large a. The obtained MC results are further compared with predictions of the mean-field and independent-mode approximations as well as with predictions of our own approximation scheme.

In this approximation, we introduce an auxiliary system, which yields approximately the same temperature behaviour of the order parameter, but allows the decoupling of the phonon modes.

Our approximation gives the value of T_c within an error of 5% and satisfactorily describes the temperature dependence of the order parameter for all values of a.

1. INTRODUCTION

One of the basic classification schemes for structural phase transitions consists in assigning it to the order-disorder or the displacive type. The displacive transition can be described as a freezing of a phonon mode, which shows "critical softening" at the phase transition point. The occurrence of a soft mode is often used as criterion for a displacive transition in a real systems, since the frequency of the phonon modes is accessible by spectroscopic experiments.

In the order-disorder case, there are two or more locations for each atom in the unit cell. Occupation numbers for these locations are the same above the transition temperature, and differ below. Formally, as in the displacive case, the system can be described in "phonon" language.

There is a simple model which shows that one can go from the order-disorder to the displacive type *continuously* [1]. This model can be defined as a 3D cubic lattice of classical anharmonic 1D oscillators with nearest-neighbour harmonic coupling [2, 3, 4, 5, 6, 7]:

$$V = \frac{A}{2}\sum_n x_n^2 + \frac{B}{4}\sum_n x_n^4 + \frac{C}{2}\sum_{n,n'}(x_n - x_{n'})^2\sigma(n,n'), \tag{1}$$

A, B, and C are model parameters, the indices n and n' run over all oscillators, $\sigma(n,n')$ is equal to 1 for neighbouring particles and vanishes elsewhere. The system undergoes a phase transition from the higher symmetry to the lower symmetry phase at a certain temperature T_c for any $A < 0, B > 0, C > 0$, *i.e.* the statistical average of each coordinate x_n takes a non-zero value $\eta =< x_n >$ below T_c and vanishes above. It is often convenient to express the potential (1) as

$$V = \sum_n v(x_n) - C\sum_{n,n'} x_n x_{n'}\sigma(n,n'), \tag{2}$$

with an "on-site" single particle potential

$$v(x) = \frac{A'}{2}x^2 + \frac{B}{4}x^4, \quad A' = A + 12C\ . \tag{3}$$

It is known that the behaviour of the system is governed by the ratio

$$a = -A/C. \tag{4}$$

At small $a > 0$ the system shows a displacive phase transition, while for large a the system behaves as the Ising model, which shows a typical order-disorder phase transition. The transition temperatures T_c in the limit cases are known from Ising-model and self-consistent phonon calculations, to be respectively [2, 4, 8, 9]:

$$T_c(a \downarrow 0) \approx 2.64C|A|/B,$$
$$T_c(a \to +\infty) \approx 9.12C|A|/B, \tag{5}$$

assuming here and further that the temperature is expressed in energy units (the Boltzman constant equal to 1). On the other hand, despite of the important role of the above model in the theory of the structural phase transitions [2], the actual dependence of $T_c(a)$ is not known. The results of previous molecular dynamics and Monte Carlo studies are collected in Figure 1. They obviously do not give a consistent quantitative picture. So far the analytical study was restricted to the mean-field approach. [2, 10].

Recently, it was observed that the knowledge of the dependence $T_c(a)$ can be useful in the quantitative analysis of the properties of crystalline $Sn_2P_2S_6$ which has a ferroelectric phase transition showing simultaneously features typical for both the order-disorder and displacive type [11].

The aim of this paper is to establish this dependence of $T_c(a)$ as well as the temperature behaviour of the order parameter. Let us stress that, similarly to some related papers [4, 5, 6, 7], we are not interested here in details of critical behaviour in the very vicinity of the phase transition. Critical behaviour of this model is thoroughly described for example in the reference [2].

The paper is organized as follows. Section 2 describes our MC simulations performed for a wide range of values of the parameter a. In section 3, we first compare the MC results with rather poor predictions of the standard decoupling schemes and suggest an improved self-consistent equation for the order parameter that allows to calculate both the transition temperature and the order parameter with a reasonable accuracy for all values of a.

2. MONTE-CARLO SIMULATIONS

For numerical simulation it is convenient to re-scale coordinates and energy units. This allows to reduce the potential energy (1) into the form

$$V_{\rm red} = -\frac{a}{2}\sum_n x_n^2 + \frac{a}{4}\sum_n x_n^4 + \frac{1}{2}\sum_{n,n'}(x_n - x_{n'})^2\sigma(n,n'), \tag{6}$$

with a single dimensionless parameter $a = -A/C$. Then the re-scaled order parameter at zero temperature is equal to 1 for any $a > 0$.

The typical size of the array of atoms studied in our MC simulations is $10 \times 10 \times 10$ atoms, with periodic boundary conditions. We perform Monte-Carlo steps consecutively for each atom, and accept (or reject) them accordingly to

standard criteria. Additionally, we perform "magic" steps for the case of large a, when the sign of the coordinate of the given atom may flip. These steps allow the system to thermalize in the order-disorder limit as well. We calculate the square of the order parameter as the average

$$\eta^2 = N^{-1/2} < X_0^2 - X_1^2 >, \tag{7}$$

where $X_k = N^{-1/2} \sum x_n e^{ikn}$ is the Fourier transform of x_n, N is the total number of particles.

For the case of an infinite slab, $N^{-1/2} X_1^2$ is negligible, and (7) gives purely the square of the order parameter. For a finite slab, the term X_1^2 allows to remove fluctuations from the high-temperature branch.

The results of the calculations are presented in Figures 2-4. It is crucial to check the dependence of the results on the system size. Figure 2 presents the temperature dependence of X for sizes $15 \times 15 \times 15$ and $5 \times 5 \times 5$. It is clear, that change of the size of the slab affects practically only the fluctuation region near T_c. The value of T_c calculated from the fit of the dependence (see Figure 2) remains almost unchanged. This type of size dependence of the data is found for the whole range of a.

Figure 3 presents data for $\eta^2(T)$ obtained for the potential (6) for different values of the parameter a. Note that the Landau theory yields a linear temperature dependence for $\eta^2(T)$.

Values of T_c are extracted from the data presented in Figure 2. The plot for $T_c(a)$ is given in Figure 4 where a logarithmic scale for the a-axis is used. The monotonic dependence approaches known limit values with a good accuracy. The change in a is for which $T_c(a)$ varies significantly is about 2 orders of magnitude.

3. ANALYTICAL APPROACHES

Two standard decoupling schemes have been used in the literature to make the phase transition in the model tractable, usually referred to as mean field (or independent site) approximation and self-consistent phonon (or independent mode) approximation. In this section we first analyse the advantages and disadvantages of these standard approximations and then we propose a modified approximation scheme that combines advantages of both schemes.

3.1 Independent mode approximation

In the independent mode approximation (IMA), the deviations from the average value given by the order parameter

$$y_n = x_n - \eta \tag{8}$$

are represented by Fourier coordinates $Y_k = N^{-1/2} \sum_n y_n e^{ikn}$. Interaction between Fourier coordinates is simplified by assuming that each Fourier coordinate is influenced only by the average of its interactions with the other coordinates. This leads to an effective harmonic approximation. The order parameter in IMA is defined by the equation [2]

$$A\eta + B\eta^3 + 3B\eta I(T) = 0, \tag{9}$$

where the function $I(T) = N^{-1} \sum_k Y_k Y_{-k}$ is calculated from the phonon dispersion relation renormalized by the given value of the order parameter and the thermal fluctuations. In the vicinity of the phase transition point, $I(T)$ can be evaluated by assuming a "critical" phonon dispersion (with zero frequency of the zone-center mode):

$$I(T) \approx \frac{T}{4C(2\pi)^3} \int \frac{d^3k}{3 - \cos k_x - \cos k_y - \cos k_z} = \frac{T}{3C\kappa} \tag{10}$$

where $\kappa \approx 2.638$. Note that the stability limit $T_{\mathrm{c,IMA}} = -AC\kappa/B$ of the high temperature phase as obtained from (9) and (10), provides an exact prediction for T_c and $\eta(T)$ in the displacive limit. However, for the order-disorder limit, the IMA values differ considerably from the exact values.

3.2 Mean field approximation

In the mean-field approximation (MFA) for the system with a harmonic coupling, the behaviour of the original system is modelled by an auxiliary system in which all direct inter-site interactions are replaced by an effective external field E, but the on-site anharmonicity is kept without any approximation. Taking the on-site potential as given by (3), the ensemble averages in such an auxiliary system at fixed external field are given by

$$\eta = < x_n > = g_T(E) \equiv \frac{\int x \exp[-(v(x) - Ex)/T]dx}{\int \exp[-(v(x) - Ex)/T]dx}. \tag{11}$$

Since at finite temperatures the $g_T(E)$ is a monotonic function, it can be inverted and the self-consistent equation for the order parameter in the auxiliary system can be written as

$$E = g_T^{-1}(\eta). \tag{12}$$

The effective field E is defined as the force on x_n supplied by the interaction terms separated in (2), assuming that the displacement of the six nearest neighbouring sites (or at least their sum) is frozen at the equilibrium value η :

$$E = 12C\eta. \tag{13}$$

Self-consistent solution of equations (12,13) defines the order parameter $\eta_{\rm MFA}$ in MFA. The phase transition temperature $T_{\rm c,MFA}(a)$ at which $\eta_{\rm MFA}$ vanishes is shown in Figure 1. It was previously remarked by S. Aubry [1, 2] that the relative over-estimation of T_c by MFA is almost the same (about 30 percent) for both limit cases ($a \to +0, a \to +\infty$). Comparison of $T_{\rm c,MFA}(a)$ with our MC results shows that the discrepancy is really systematic for all intermediate cases. Although this error is rather large, its systematic character strongly suggests that the physics of the crossover is already well taken into account by the MFA.

Let us analyse the function $g_T(E)$ describing the auxiliary ensemble of the uncoupled on-site oscillators in more detail. Let us stress the following points:

1. The variation of T_c with a is within MFA entirely given by the slope of the function $g_T(\eta)$ at $\eta = 0$.

2. Unlike the on-site potential $v(x)$, the function $g_T(E)$ at finite temperature is a smooth monotonic odd function (see Figure 5) at any T, a [10]. Both $g_T(E)$ and its inverse $g_T^{-1}(\eta)$ can be expanded in Taylor series:

$$g_T(E) = \sum_{i=1}^{\infty} \chi_{2i-1}(T) E^{2i-1}, \quad g_T^{-1}(\eta) = \sum_{i=1}^{\infty} \xi_{2i-1}(T) \eta^{2i-1} \tag{14}$$

3. The function $g_T^{-1}(\eta)$ can be identified with the derivative of its free energy $F(\eta, T)$, which can thus be written in the form

$$F(\eta, T) = F(0, T) + \sum_{i=1}^{\infty} \frac{\xi_{2i-1}(T)}{(2i)} \eta^{2i} \tag{15}$$

4. Obviously, the Taylor expansion coefficients of $g_T(E)$ and $g_T^{-1}(\eta)$ are related ($\xi_1\chi_1 = 1$, $\xi_3\chi_1^3 + \chi_1\xi_3^3 = 0$, etc.) This allows to express $\xi_{2i-1}(T)$ in the limit case of the weak anharmonicity ($B << A'$) by expanding $g_T(E)$ in powers of B. With an accuracy $O(B^2)$ we obtain

$$\xi_1(T) = A' + \frac{3BT}{A'} \ , \quad \xi_3(T) = B \ . \tag{16}$$

   In the strongly anharmonic order-disorder limit ($A' < 0, T << A'^2/B$), expressing $g_T(E)$ via averages $< x^2 >, < x^4 >$ yields

$$\xi_1(T) = \frac{BT}{A'} \ , \quad \xi_3(T) = \frac{B^2}{3A'^2} \ , \quad ... \ . \tag{17}$$

5. Finally, let us note that in the weak anharmonicity case we can solve the inverse problem - express the parameters of the on-site potential via the first two free energy coefficients $\xi_1(T), \xi_3(T)$. With the same accuracy as (16)

$$A' = \xi_1(T) - \frac{3\xi_3(T)T}{\xi_1(T)} \ , \quad B = \xi_3(T) \ . \tag{18}$$

3.3 Combined scheme

We have seen that the IMA predicts well the phase transition temperature in the displacive limit, while MFA predicts rather well its variation with a. It would be desirable to have an approximate equation of state for the system (1) that combines the advantages of both above discussed approaches. The key idea of our approach is the assumption of the existence of an effective potential (with temperature dependent coefficients) for which the self-consistent phonon approximation gives correctly the order parameter. In determining the coefficients of such an effective potential, we use the properties of the free energy $F(\eta, T)$ (respectively its derivative $g_T^{-1}(\eta)$) of the auxiliary system of uncoupled anharmonic oscillators discussed above.

More precisely, the self-consistent equation for $\eta(T)$ is constructed in three steps, as follows:

1. We look for an effective on-site potential of the form

$$u(x) = \frac{\alpha'}{2}x^2 + \frac{\beta}{4}x^4 \tag{19}$$

where α' and β are defined by the expressions that appear in the above discussed inverse problem (18):

$$\alpha' = \xi_1 - \frac{3\xi_3 T}{\xi_1} \ , \quad \beta = \xi_3. \tag{20}$$

This potential obviously coincides with $v(x)$ in the weak anharmonic limit.

2. We introduce a function $\xi_{1,\mathrm{eff}}(T, \eta)$, which allows to write g_T^{-1} formally as a finite polynomial:

$$g_T^{-1}(\eta) \equiv \xi_{1,\mathrm{eff}}(T, \eta)\eta + \xi_3(T)\eta^3. \tag{21}$$

These functions $\xi_{i,\mathrm{eff}}(T)$ are used instead of $\xi_1(T)$ in the definitions (20), so that we have

$$\alpha' = \xi_{1,\mathrm{eff}}(T, \eta) - \frac{3\xi_3(T)T}{\xi_{1,\mathrm{eff}}(T, \eta)} \ , \quad \beta = \xi_3(T). \tag{22}$$

Note that the potential $u(x)$ still coincides with $v(x)$ in the weak anharmonic limit for small η, since $\xi_{1,\mathrm{eff}}(T, \eta)$ goes to $\xi_1(T)$ for $\eta \to 0$.

3. We consider eq. (2) and replace $v(x)$ with coefficients A' and B by an expression $u(x)$ with temperature-dependent coefficients α' and β defined in eq. (22). Then we apply IMA to this auxiliary system. The eq. (9) then becomes

$$\left[\xi_{1,\mathrm{eff}}(T,\eta) - 12C + \frac{\xi_3(T)T}{C\kappa} - \frac{3\xi_3(T)T}{\xi_{1,\mathrm{eff}}(T,\eta)}\right]\eta + \xi_3(T)\eta^3 = 0. \qquad (23)$$

This equation is to be solved together with formulae (21) and (11), defining $\xi_{1,\mathrm{eff}}$ and g_T, respectively. The value of $\xi_3(T)$, entering these equations, is given by the series (14).

For the calculation of the phase transition temperature only, the second step can be omitted. It is obvious from its construction that the suggested method provides the same (exact) result for the T_c in the displacive limit as the usual IMA. In the extreme order-disorder limit, the value of T_c defined by (23) can be obtained analytically using (17). The resulting value of T_c overestimates the known Ising value by less then 7%. The principal advantage of the modified approach is that it allows to calculate the T_c (and $\eta(T)$) with the above or better accuracy for all values of a, as it can be seen from the comparison with our MC data (Figure 6). The MC result for $\eta^2(T)$ is satisfactorily described as well (Figure 7).

4. DISCUSSION

Let us analyze the proposed model in comparison with the standard decoupling schemes. The latter treat the system as a gas of elementary excitations, which are supposed to interact weakly. The assumption of weak interaction allows to replace the interaction between the elementary excitations with an interaction with an average field. Choice of the elementary excitations as the plane waves or on-site oscillators yields IMA or MFA, respectively. It is clear, however, that the assumed weakness of the interaction is actually not realized for the general case, no matter what elementary excitations we choose.

The main advantage of our approach is that it virtually replaces the real strongly-correlated system (1) with an auxiliary one, which allows decoupling. It is also worth noting that the theory is carried out in terms of $g_T(\eta)$, which is always a smooth monotonic function. Moreover, $g_T(\eta)$ does not change drastically when a is varied from 0 to $+\infty$ - the calculation of parameters ξ_1 and ξ_3 at T_c shows that their dimensionless values lie within the relatively narrow ranges 9.7...12 and 0...4, respectively. Therefore the replacement procedure works uniformly well for all values of the parameters.

It would be interesting to investigate possible extensions to higher-order terms. A systematic extension of the present method should contain a larger

number of terms in the effective on-site potential (19) and in the expression for the function $g_T^{-1}(\eta)$ in (22), and solve the self-consistent equation for the auxiliary system more accurately than (23).

As a simplification we can consider a purely linear auxiliary system, *i.e.* neglect the β term in (19) and $\xi_3(T)$ in (22). We obtain $g_T^{-1}(\eta) \equiv \xi_{1,\mathrm{eff}}(T,\eta)\eta$ and (23) then reduces simply to the mean-field equation of state $g_T^{-1}(\eta) = 12C\eta$. Therefore, the scheme proposed here can also be considered as a generalization of the mean field approximation.

Our method can be applied to more complicated models for which the self-consistent phonon theory is exact in the weak anharmonic limit. This is particularly interesting for the analysis of the DIFFOUR model [12] in which the additional second neighbour harmonic coupling shows a phase transition to an incommensurate phase for which the MC calculations are much more difficult.

5. CONCLUSIONS

We have studied the crossover from a displacive to an order-disorder phase transition in the discrete ϕ^4 model with first-neighbour coupling.. The crossover is governed by the single parameter a. Quantitative information about $T_c(a)$ and $\eta(T,a)$ in this simple model may be helpful in elucidating the behaviour of some real crystals with phase transitions of a mixed displacive and order-disorder type.

In terms of the dimensionless parameter a we determined the change of the transition temperature by Monte-Carlo calculations. These show a crossover from the displacive to the order-disorder limit.

Monte Carlo calculations have shown an excellent agreement for T_c in the two limit cases in which exact results are known. We expect that the same precision is obtained for the intermediate region. Thus, the presented Monte Carlo results can be taken as quite reliable estimates of $T_c(a)$ with a precision of the order of 1% and we believe that a comparable precision was achieved for the temperature dependence of the order parameter (except in the critical region in the vicinity of the phase transition).

We have presented an analytical approach, which goes beyond the conventional decoupling schemes. For this, we introduce the auxiliary array of oscillators that (i) can be treated in the independent-mode approximation and (ii) yields approximately the same values of T_c and the order parameter, as the real system. The method combines the equation of state of the self-consistent phonon theory with the response function of the system of uncoupled anharmonic oscillators used in the the mean-field theory. It can be presented as a generalization of the mean-field scheme.

The analytical results for T_c agree with Monte-Carlo simulations with about 5% accuracy. Further improvement could possibly come from higher order terms in the expansion we have used. The formalism can be used to study incommensurate phase transitions as well.

6. ACKNOWLEDGEMENT

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Figure captions

Fig.1 The critical temperature vs. $\ln a$. The curve shows the mean-field result; thin horizontal lines show the asymptotic values of T_c. Results of previous Molecular-Dynamics [5, 3] and Monte-Carlo [4] calculations are plotted with filled and open circles, respectively.

Fig.2 The role of the finite size of the system studied numerically. Numerical data for the square of the order parameter plotted as a function of T. Filled circles: $5 \times 5 \times 5$ oscillators; open circles: $15 \times 15 \times 15$ oscillators. Both results are obtained for $a = 5$ in eq. (7) by averaging over 3000 realizations at each point. The solid line shows the interpolation used to obtain T_c.

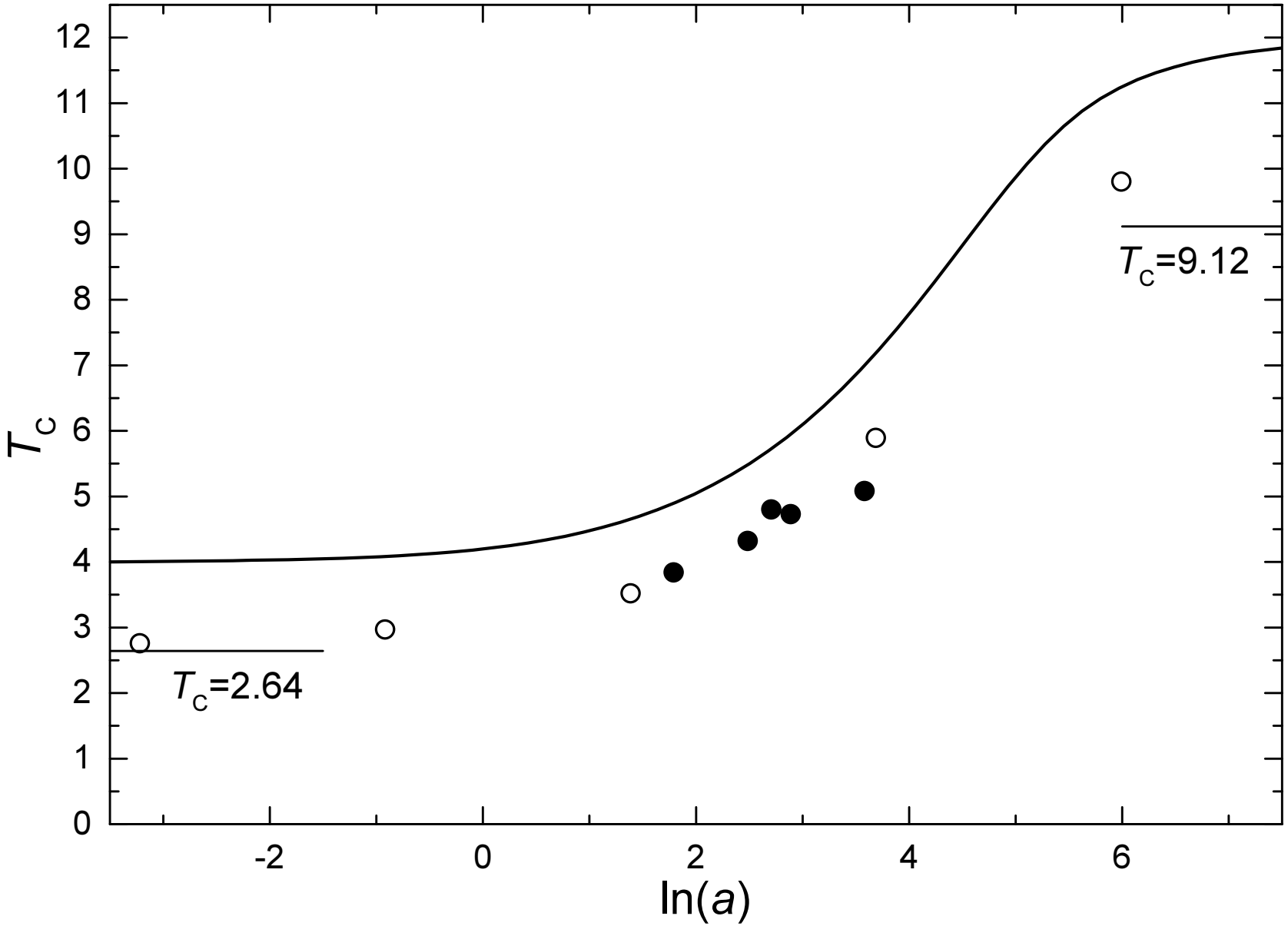
Fig.3 The temperature dependence of the square of the order parameter for values of a varying from 0.98 to 4000. There is a factor $\sqrt{2}$ between the a values for the neighbouring curves. The data are obtained using eq. (7) by averaging over 1000 realizations at each point; the relative amount of "magic" steps is 0.02.

Fig.4 Numerical results for the critical temperature T_c *vs.* $\ln a$. The values of T_c are extracted from the data presented in Fig.3. Thin horizontal lines show the asymptotic values of T_c.

Fig.5 Typical dependence of $g_T^{-1}(\eta)$ at small a (solid line) and large a (dashed line).The inset shows the on-site potential for both cases. (Calculated for (6)with $T = 5$ and $a = 1$ and 100, respectively.)

Fig.6 Numerical data for $T_c(\ln a)$ compared with results of calculations by equations (23,11,21) (the solid line). The mean-field approximation is given by the dashed line.

Fig.7 The temperature dependence of the square of the order parameter at several values of $a(= 0.98, 3.9, 15.6, 62.5, 250, 1000, 4000)$. T_c grows with increasing a: numerical data (points) and calculation from (23,11,21) (lines).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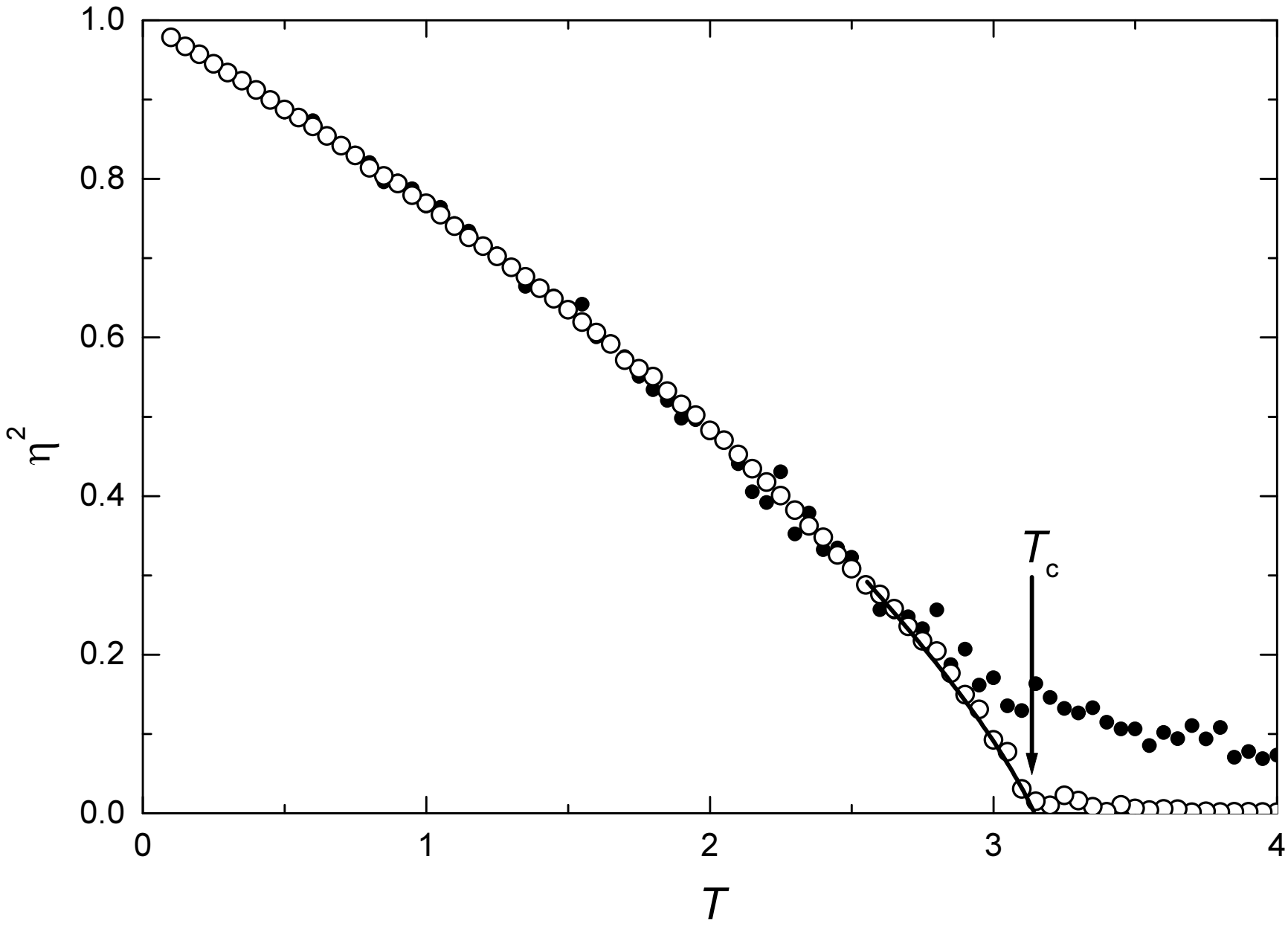
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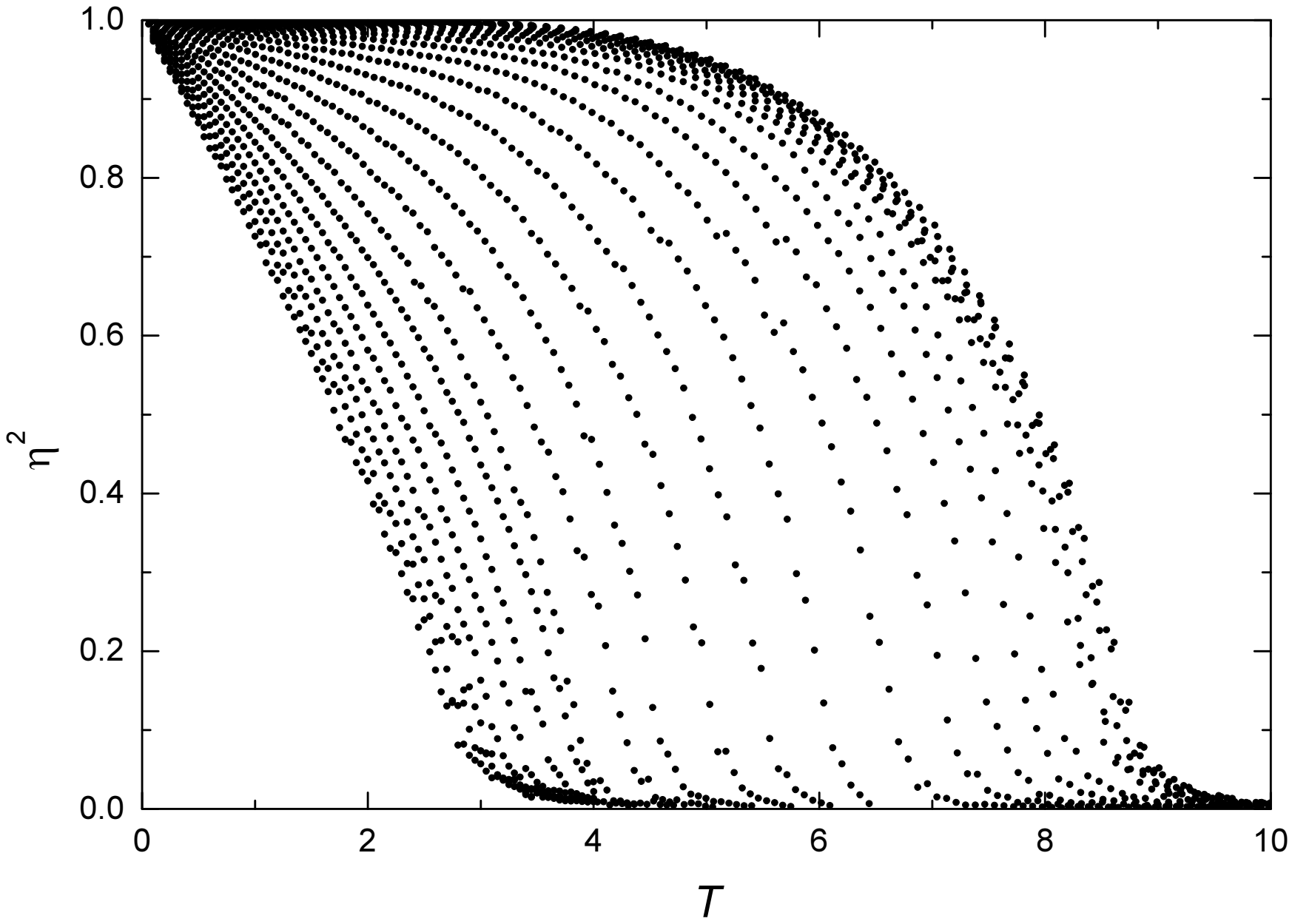
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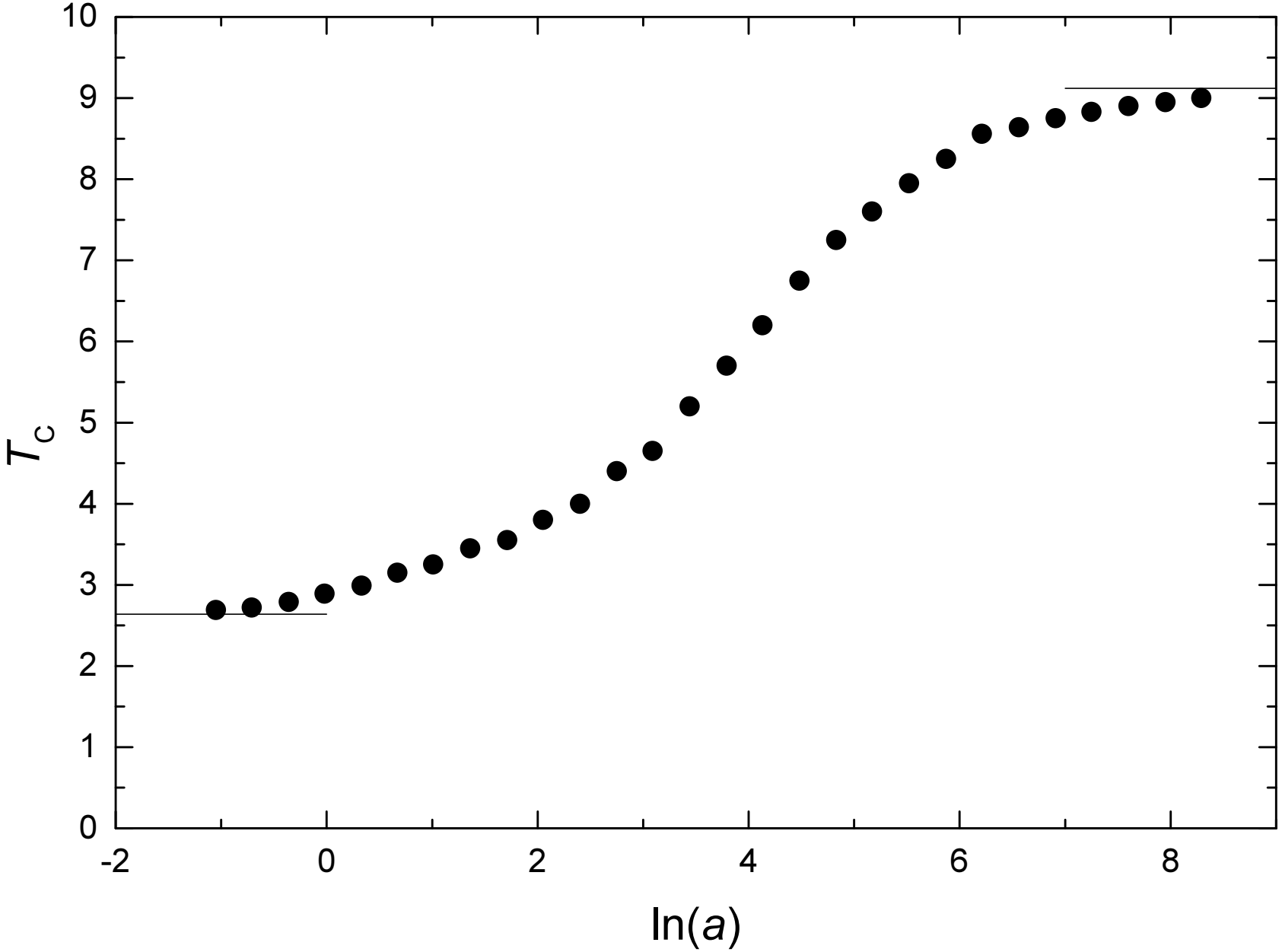
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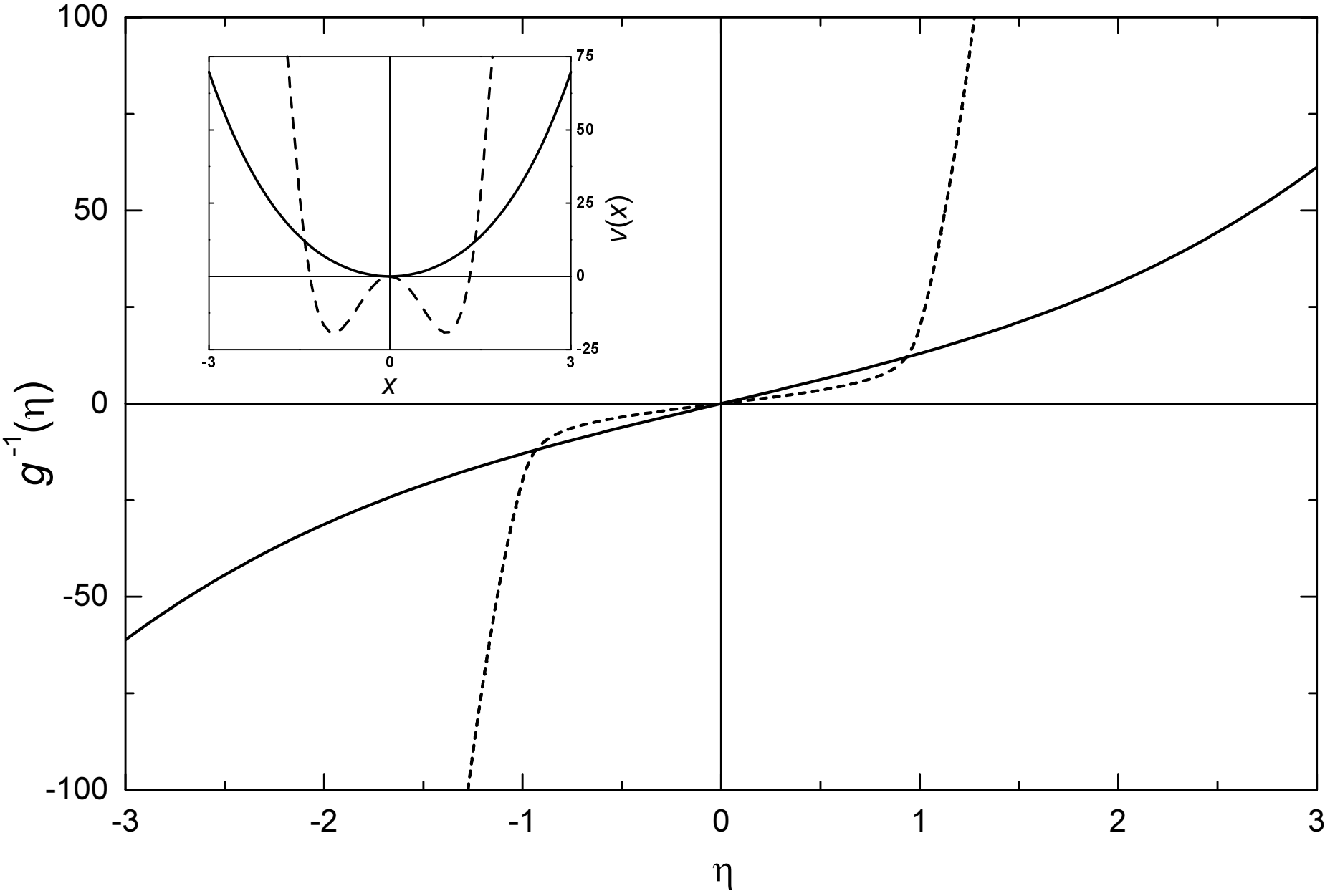
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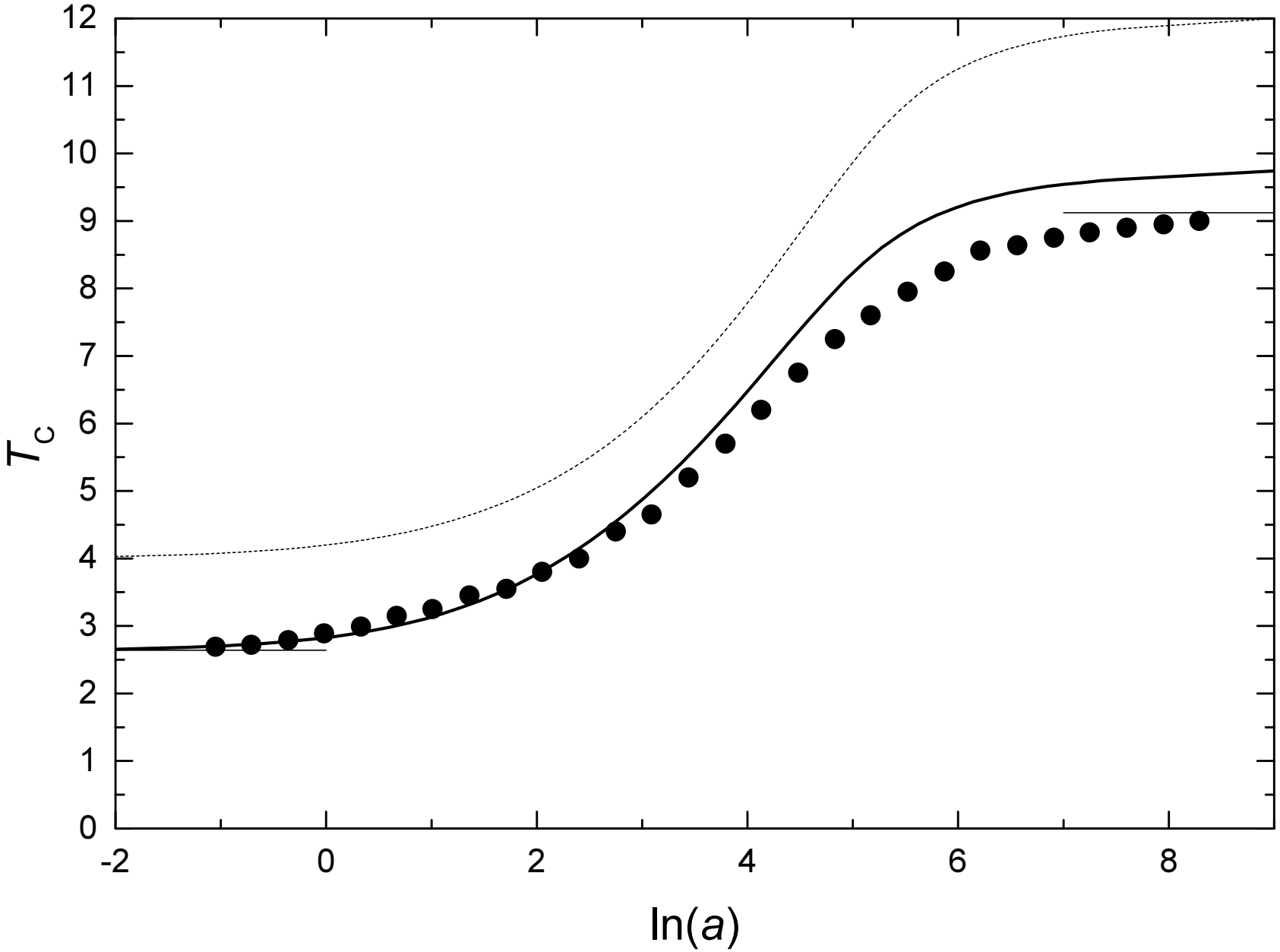
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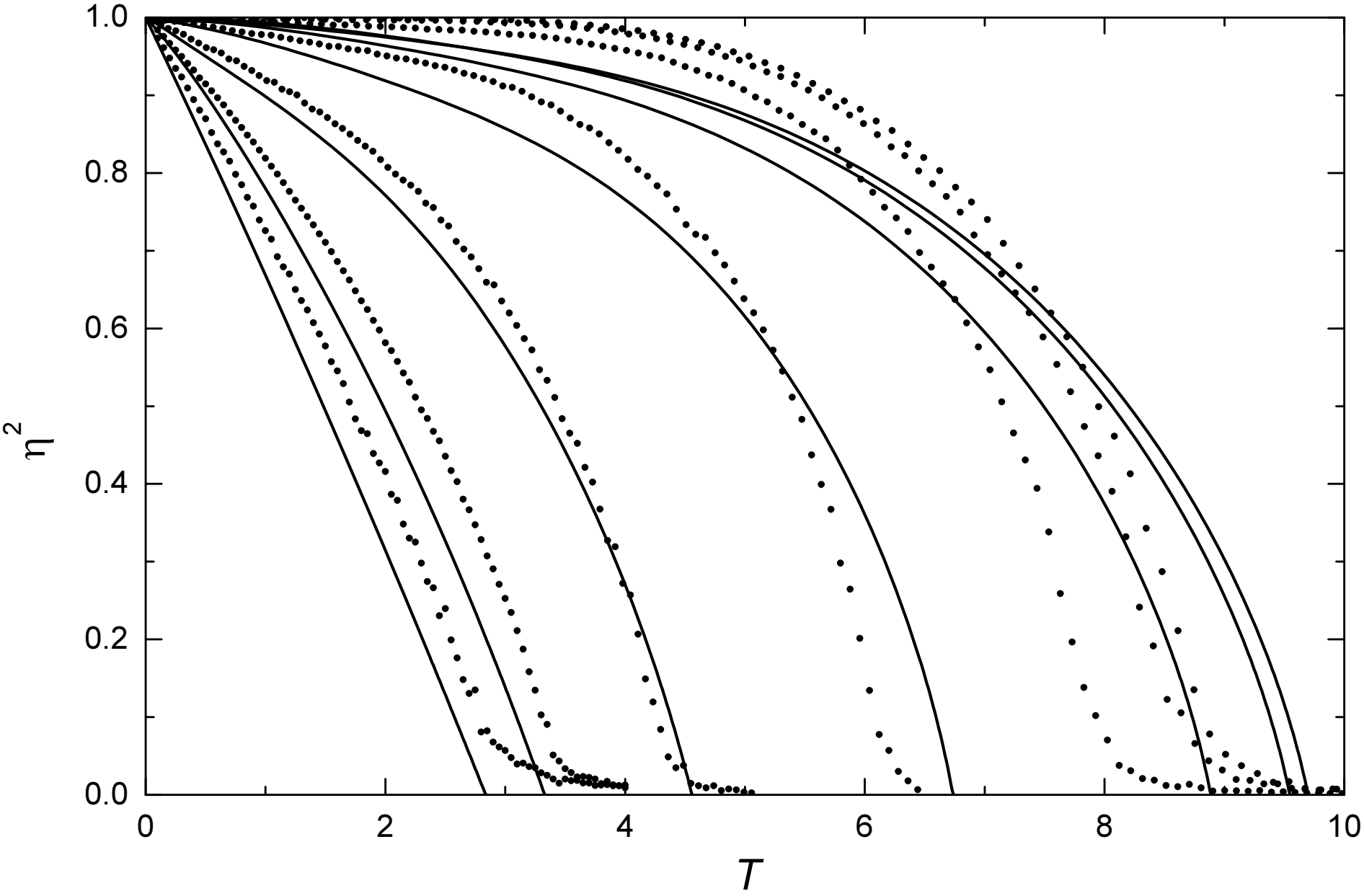
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