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FAST TRACK COMMUNICATION

On phase transition and the critical size in spatially restricted systems

Artjom Vargunin, Teet Örd, Risto Tammelo and Niina Voropajeva

Institute of Physics, University of Tartu, 4 Tähe Street, 51010 Tartu, Estonia

E-mail: risto.tammelo@ut.ee

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Abstract
We study the finite-size effects on the critical temperature in spatially restricted systems with bulk second-order phase transition using the Fokker–Planck equation approach. It is established that the dependence of the transition temperature on system size is characterized by the competition of two length scales. The first scale is similar to the correlation length, determining the critical behavior in sufficiently large samples. The second scale appears as a consequence of the stochastic nature of the order parameter and controls the transitional features in small samples, particularly in the vicinity of the critical size. It is also found that the rate of the critical slowdown of relaxation of the order parameter fluctuations increases as the volume of the system decreases.

1. Introduction

The size effects on phase transition in ferroelectrics has been known since the 1950s [1, 2] but, due to their practical importance [3, 4], the interest in restricted condensed systems continues to be high nowadays as well. According to the phenomenological finite-size scaling theory [5–8], when the correlation length $\xi(T)$ attains, in the vicinity of the critical temperature T_c, a magnitude of the order of the characteristic size L of a finite system, the deviations from the genuine critical behavior will set in: the singularities in the thermodynamic functions become rounded extrema located in somewhat shifted positions. It is predicted that the finite-size effects on the critical phenomenon are controlled by the ratio L/ξ. This assertion determines the shift of the critical temperature of a finite-size system, particularly the lowering of T_c as the dimension decreases, until the critical size is reached at which the transition temperature vanishes. The critical size and size effect on the transition temperature in various ferroelectric systems, see e.g., [9–13], have recently been actively investigated.

In order to establish the size-induced features on confined condensed systems, we have proposed the complementarity between the deterministic behavior of the bulk sample and its stochastic nature in the finite volume case. When an external periodic field is also present, the complementarity leads to transformation of the phase transition anomaly in the bulk sample [14] to stochastic resonance [15–18] in a sufficiently small system [19]. The latter approach can be applied to the interpretation of the dielectric constant measurements in the ceramic and relaxor ferroelectrics [20–24], representing particularly the experimentally established fact that the system dimension decrease is attended by an increase in the diffuseness of the phase transition and lowering of the critical temperature [23–27].

In this paper we present a numerical analysis of the size-dependent evolution of the critical temperature which is associated with a critical slowdown of relaxation of the order parameter fluctuations in spatially restricted systems. We demonstrate that the Landau relaxation rates introduced in the conventional second-order phase transition theory have to be replaced in a finite sample by the first and third eigenvalues of the Fokker–Planck operator. We will derive the shift exponent and show that, despite the crucial role of correlations on the critical phenomenon in macroscopic systems, in the vicinity of the critical size the phase transition is driven by the thermal fluctuations, i.e. the stochastic nature of the order parameter dominates in sufficiently small samples. The increase of the slowdown rate in the transitional region is another feature of the relaxation mechanism established near the critical size.

2. Relaxation times

We start with the one-dimensional equation of overdamped motion for the order parameter φ, namely

$$\frac{\mathrm{d}\varphi(t)}{\mathrm{d}t} = -\frac{\partial U(\varphi; T)}{\partial \varphi} + A + \sqrt{\frac{T}{V}}\zeta(t), \tag{1}$$

where $\zeta(t)$ is the zero mean Gaussian white noise with the correlation function $\langle \zeta(t)\zeta(t')\rangle = 2\delta(t-t')$, T is temperature, V is the volume of the sample, A is an applied force term and a temperature-dependent soft potential is taken in the Landau form [14]

$$U(\varphi; T) = \tfrac{1}{2}a(T)\varphi^2 + \tfrac{1}{4}\varphi^4, \tag{2}$$

with $a(T) = \alpha(T - T_c^\infty)$, where the constant $\alpha > 0$ and T_c^∞ is the temperature of the bulk second-order phase transition. The potential $U(\varphi; T)$ is bistable if $T < T_c^\infty$ and monostable if $T > T_c^\infty$. The equilibrium of the system is described by the partition function

$$Z = \int_{-\infty}^{\infty} \exp\left\{-\frac{V}{T}\left[U(\varphi; T) - A\varphi\right]\right\} \mathrm{d}\varphi, \tag{3}$$

assuming here that $A = \text{const}$. The latter expression coincides with the partition function of a small particle of a system undergoing a second-order phase transition in the bulk limit (a so-called zero-dimensional system). Here the smallness of the particle implies that its dimensions are smaller than the correlation length of the order parameter fluctuations [28]. In (3), the function $F(\varphi) = V(U(\varphi; T) - A\varphi)$ is interpreted as reduced free energy, in which all degrees of freedom have been taken into account except those associated with the order parameter φ. Note also that the free energy density determined as $\Phi = -TV^{-1}\ln Z$ reduces in the limit $V \to \infty$ to the minimal (equilibrium) value of the homogeneous Landau free energy $F(\varphi)$ [14]. Furthermore, the infinite volume limit in the equation of motion (1) leaves us with the Landau–Khalatnikov equation describing the deterministic relaxation of the order parameter to its equilibrium position. On the other hand, it seems to be legitimate that, as the dimension decreases, the fluctuations of the order parameter will increase. So the Langevin equation (1) correctly describes, at least in qualitative terms, the evolution of the order parameter φ in the samples of bulk second-order phase transitions.

Note that in the present scheme the inhomogeneity of fluctuations is neglected. Another limiting case is the Gaussian approximation [29] which incorporates the spatial variance of fluctuations, but neglects, first of all, interwell motions in the potential (2). Both of these particular cases stem from the general Landau free energy expansion where the second-and fourth-order terms as well as the squared gradient of the order parameter are taken into account.

According to the scheme developed in [16], the stationary autocorrelation function of the order parameter in the asymptotic time limit can be expressed as

$$\langle \varphi(t)\varphi(0)\rangle = g_1 \mathrm{e}^{-\lambda_1 t} + g_3 \mathrm{e}^{-\lambda_3 t}, \tag{4}$$

where

$$g_1 = \langle \varphi^2\rangle_{\mathrm{st}} - g_3, \tag{5}$$

$$g_3 = \frac{[\lambda_1 - a(T)]\langle \varphi^2\rangle_{\mathrm{st}} - \langle \varphi^4\rangle_{\mathrm{st}}}{\lambda_1 - \lambda_3}. \tag{6}$$

Here $\langle \cdots \rangle_{\mathrm{st}} = \int_{-\infty}^{\infty} \cdots P_{\mathrm{st}}(\varphi)\,\mathrm{d}\varphi$, where $P_{\mathrm{st}}(\varphi)$ is the stationary probability distribution of the non-perturbed system and $\lambda_{1,3}$ are the first and third eigenvalues of the non-perturbed Fokker–Planck operator associated with the Langevin equation (1), i.e.

$$\hat{L}_{\mathrm{FP}}(\varphi) = \frac{\partial}{\partial \varphi}\frac{\partial U(\varphi; T)}{\partial \varphi} + \frac{T}{V}\frac{\partial^2}{\partial \varphi^2}. \tag{7}$$

Note also that only odd eigenvalues contribute to (4) in accordance with [30]. In (4), the term proportional to the coefficient g_1 describes the contribution from the interwell or hopping dynamics with the characteristic time $\tau_1 = \lambda_1^{-1}$, and the term proportional to the coefficient g_3 describes the contribution from the intrawell or local dynamics with corresponding characteristic time $\tau_3 = \lambda_3^{-1}$ to the correlation in the bistable regime [16]. As revealed by further analysis, a sufficiently large timescale separation between the interwell hopping and intrawell motion holds for a whole range of parameters under consideration. This is the only substantial restriction for the expansion (4).

In the bulk limit, the characteristic time τ_1 diverges below T_c^∞ and $g_1 \mathrm{e}^{-\lambda_1 t} \to -a(T)$, reflecting the fact that τ_3 governs the leading time dependence of the autocorrelation function (4) of a large system below T_c^∞. Above T_c^∞ this characteristic time represents only a subleading relaxation time [31]. The same consequence follows from the examination of the susceptibility which can be derived from the correlation function (4) by means of the fluctuation–dissipation relation [16]. Correspondingly, in the bulk limit we have

$$\chi(T, \Omega) = \frac{\lambda_{1,3} - \mathrm{i}\Omega}{\lambda_{1,3}^2 + \Omega^2}, \tag{8}$$

where Ω is the frequency of the applied periodic field $A(t)$. One must choose $\lambda_1 = a(T)$ if $T > T_c^\infty$ and $\lambda_3 = -2a(T)$ if $T < T_c^\infty$. Thus, in this limit the conventional Landau phase transition theory realizes with the anomaly of the susceptibility at the phase transition temperature T_c^∞. We also emphasize that the bulk transition temperature T_c^∞ itself may be derived as a point where the corresponding relaxation rates vanish. We suppose that this peculiarity also persists for the finite samples, allowing us to determine the critical temperature (more exactly, pseudocritical temperature [8]) in these systems.

3. Finite-size behavior of the eigenvalues

We calculate the eigenvalues $\lambda_{1,3}$, the inverse values of which give us the relaxation times $\tau_{1,3} = \lambda_{1,3}^{-1}$ numerically, solving the corresponding Schrödinger equation [32] by means of the symplectic method, see, e.g., [33]. The relevant Schrödinger operator has the form

$$\hat{L}_{\mathrm{S}}(\varphi) = \frac{T}{V}\frac{\partial^2}{\partial \varphi^2} - U_{\mathrm{S}}(\varphi; T) \tag{9}$$

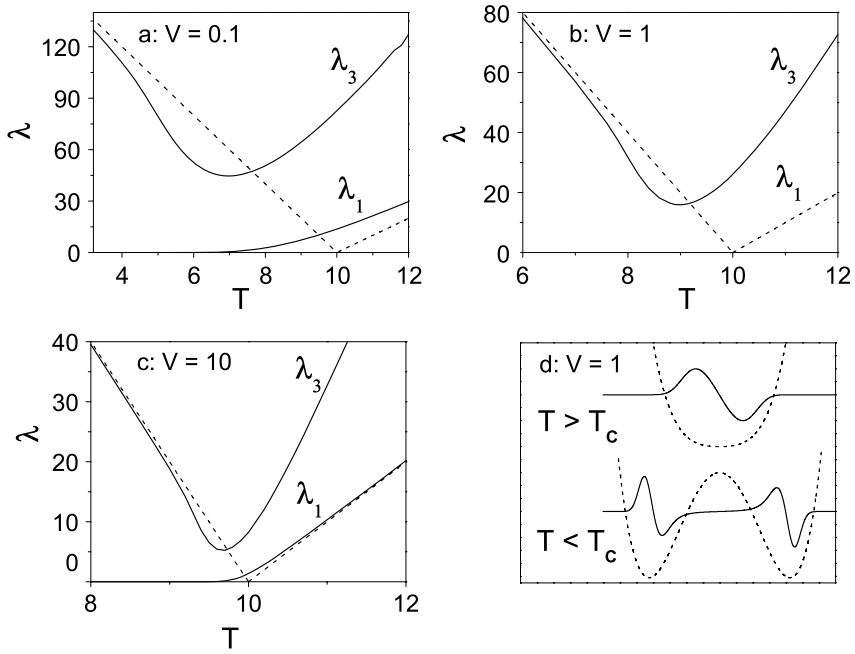

Figure 1. The plots of the eigenvalues $\lambda_{1,3}$ ((a), (b), (c): solid lines) versus temperature for various volumes $V = 0.1$ (a), $V = 1$ (b) and $V = 10$ (c). The dashed lines in ((a), (b), (c)) are defined as $2\alpha(T_c^\infty - T)$ for $T < T_c^\infty$ and $\alpha(T - T_c^\infty)$ for $T > T_c^\infty$. In (d) the sketch of the third eigenfunction below T_c^∞ and the first eigenfunction above T_c^∞ for $V = 1$ is given (solid lines) with the corresponding bistable and monostable behavior (dashed lines) of the Landau potential (2). Here we use $T_c^\infty = 10$ and $\alpha = 10$.

with the potential

$$U_S(\varphi; T) = \frac{V}{4T}\left(\frac{\partial U(\varphi; T)}{\partial \varphi}\right)^2 - \frac{1}{2}\frac{\partial^2 U(\varphi; T)}{\partial \varphi^2}. \quad (10)$$

Two eigenvalues $\lambda_{1,3}$ of the non-perturbed Fokker–Planck operator are shown in figure 1 as functions of temperature for various volumes of the system. As one can see, the first eigenvalue λ_1 is a monotonic function of temperature which, in the monostable region, asymptotically approaches $\alpha(T - T_c^\infty)$. In the bulk limit $\lambda_1 = 0$ for $T < T_c^\infty$, pointing at the spontaneous symmetry breaking phenomenon. In fact, the approximate assumption $\lambda_1 = 2r_K$ with the Kramers rate r_K cannot be adequate in the whole range of parameters T and V for $T < T_c^\infty$ [34]. A substantially better approximation of λ_1 is found in the context of the activated Brownian motion [35]. Unlike the monotonicity of the rate λ_1, the third eigenvalue λ_3 has a minimum in the bistable region which shifts to the critical temperature T_c^∞ and becomes deeper when the volume increases. In the bulk limit $\lambda_3 = 2\alpha(T_c^\infty - T)$ for $T < T_c^\infty$, in accordance with the Landau phase transition theory. We stress that, namely, the third eigenvalue has to be interpreted as the relaxation rate of the intrawell processes below T_c^∞, similar to the first eigenvalue which is a measure of the intrawell dynamics above T_c^∞. The same follows from the comparison of the corresponding eigenfunctions (see figure 1(d)). Moreover, from figure 1 one can conclude that symmetry is restored in finite samples as soon as the relaxation rate λ_1 becomes nonzero. However, this happens simultaneously with approaching the minimal value of λ_3 as temperature increases. The latter circumstance essentially indicates the transition point in spatially restricted systems.

From figure 1 it also follows that the slowdown phenomenon in the finite samples is accompanied by an increase in the slowdown rate near the transition point. The latter peculiarity develops as the volume of the sample decreases and seems to be crucial to the transition phenomenon in the vicinity of the critical size.

4. Critical temperature in finite samples

According to the phenomenological finite-size scaling theory [5–8], any thermodynamic property of M has its corresponding scaling form

$$M = L^{\gamma/\nu} M_0(\theta L^{1/\nu}), \quad (11)$$

where γ is the corresponding critical exponent, ν is the critical exponent of the correlation length, $\theta = T/T_c^\infty - 1$, and M_0 is the finite-size scaling function. Note also that the subsidiary scaling hypothesis $\xi_L \simeq LX(L/\xi)$, where ξ_L is the correlation length in the actual finite-size system, reconciles the role of the variable L/ξ_L with the original hypothesis of phenomenological finite-size scaling about the role of L/ξ [36].

The finite-size studies indicate that the structure of the finite-size scaling functions $M_0(x)$ is most interesting below the critical temperature T_c^∞ where they exhibit characteristic maxima [37–40]. The location of peaks in thermodynamic derivatives M can be used to determine the critical temperature of a finite system:

$$T_c = T_c^\infty - CL^{-\lambda}, \quad (12)$$

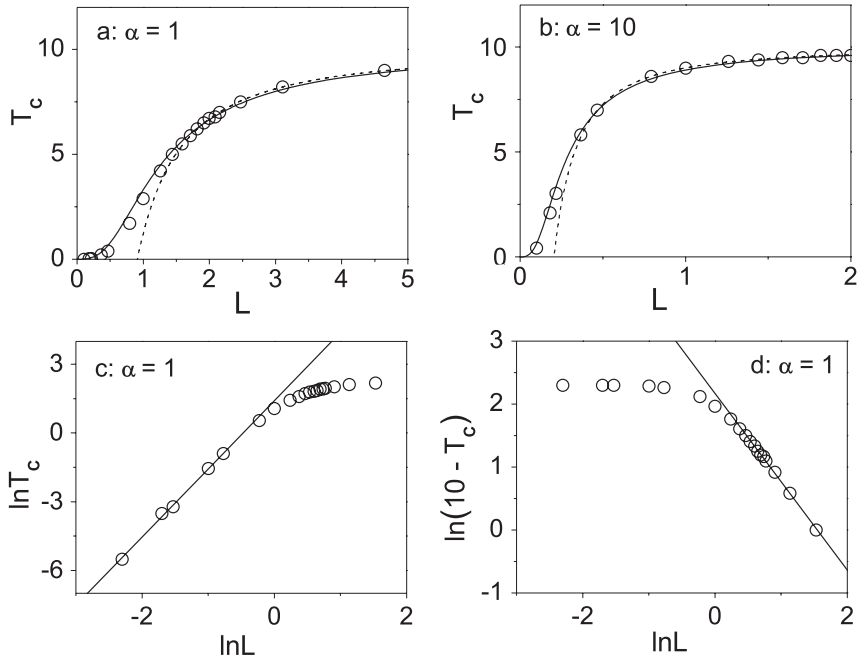

Figure 2. The plots of the critical temperature T_c (circles) versus the linear dimension of the system $L = V^{1/3}$ for $\alpha = 1$ ((a), (c), (d)) and $\alpha = 10$ (b). The bulk transition temperature is $T_c^{\infty} = 10$. In ((a), (b)) the dashed lines are determined by (12) and solid lines by (13) with the proportionality coefficient determined by means of a suitable fitting. In ((c), (d)) the appropriate logarithmic plots are present. See comments in the text.

where C is a non-universal positive constant and λ is a shift exponent [8]. As far as one accepts the assertion that the only criterion determining the finite-size scaling effects in the critical region is $\xi \sim L$, one can obtain $\lambda = 1/\nu$. For further analysis, we will be interested in the temperatures at which the relaxation time τ_3 takes its maximal value (or, equivalently, λ_3 takes its minimal value), reflecting in such a way a slowdown of the relaxation of order parameter fluctuations for the given dimension of the sample (see figure 1). We will also associate these temperatures with finite-sample critical temperatures. The dependences of the critical temperature on the linear size of the system are illustrated in figure 2(a) for $\alpha = 1$ and in figure 2(b) for $\alpha = 10$. As the volume of the sample decreases, the transition temperature decreases in accordance with (12). This allows us to determine the shift exponent λ which equals $\lambda = 1.405$ for $\alpha = 1$ (the slope of the solid line in figure 2(d) fixes this value) and $\lambda = 1.454$ for $\alpha = 10$. These estimates are close to $\frac{3}{2}$ which can be obtained as the approximate value of $1/\nu$ by using the hyperscaling relation $d\nu = 2 - \alpha$ with $\alpha \approx 0$ and $d = 3$ (three-dimensional case) [14]. Thus, in the present approach one can construct the quantity being an analogue of the correlation length ξ. This length scale determines the behavior of the critical temperature in sufficiently large samples. However, in small samples the shift equation (12) breaks down as shown in figure 2 and the critical size $L_{cr} = (T_c^{\infty}/C)^{-1/\lambda}$ does not appear. As follows from figure 2, this is caused by the appearance of another length scale in sufficiently small systems. In the present model, the critical temperature behaves in sufficiently small systems as $T_c \sim L^p$, where $p \sim 3$ (the slope in figure 2(c) determines the value p). This excludes the existence of a finite critical size of the sample and T_c remains nonzero for arbitrary finite sizes. Thus, one can find $L_{cr} = 0$. The latter result is not surprising because the present scheme does not take into account the main factors responsible for a finite critical size [41–43]. Nevertheless, it predicts suppression of ferroelectricity as the volume of the sample decreases, enacted solely by thermodynamics of the system and ignoring all boundary effects. Also it has to be noted that corrections [44, 45] to (12) do not predict the calculated dependence of the critical temperature on size.

The approximate solution for the transition temperature can be derived from the condition of competition between the activation energy and thermal energy $V\Delta U \sim T$, where $\Delta U = a(T)^2/4$ is the barrier height of the potential (2). This relation also follows from the analysis of the characteristic features of the potential (10) and is depicted in figures 2(a) and (b) with good agreement with numerically obtained points. The latter condition may also be interpreted as

$$L \sim \rho(T)\xi(T), \tag{13}$$

where $\xi \sim (-\theta)^{-2/3}$ has the meaning of correlation length and $\rho \sim T^{1/3}$. The phase transition in sufficiently large samples ($T \sim T_c^{\infty}$) is then determined by the condition $L \sim \xi$, but in smaller systems ($T \sim 0$) the critical behavior is driven by the thermal fluctuation and $L \sim \rho$, where the coefficient of proportionality depends on α in accordance with figures 2(a) and (b). This essentially reflects the competition between two characteristic length scales on the critical behavior in the spatially restricted system. At the same time the above criterion of the phase transition $V\Delta U \sim T$ takes into account all features of the conventional ideology, i.e. the growth of the fluctuations, the slowdown of the relaxation of the fluctuations

and the correlation of the fluctuations in the transitional region. The latter criterion also has the same structure as the Ginzburg condition (sufficiently far from the transition temperature T_c^∞) $Gi = (\frac{T_c^\infty}{4\Delta U V_c})^2 \ll 1$, where Gi is the Ginzburg number and $V_c = \xi^3$ is the correlation volume (see [14]). The correlation of the fluctuations implies that the correlation length should be the only significant length scale which, being finite even at zero temperature, leads to a finite value of the critical size. However, if $L \ll \xi(0)$, the correlation length loses its importance for the critical behavior. As follows from (13), in this case the length ρ, appearing as a consequence of the fluctuations, determines the leading length scale for the phase transition. Thus, we conclude that the crucial role of the correlation length in large systems has to be devolved to the length ρ in small samples. This result is a consequence of the increase in the slowdown rate near the critical point as the volume of the sample decreases.

One can also incorporate the critical size into the present model by taking into account the surface-affected layer [46, 47]. Assuming the passive surface layer [48] is connected successively with a homogeneous ferroelectric core, one can estimate the layer thickness as the extrapolation length δ appearing in the Landau–Devonshire theory with a surface term [49, 50]. The physical interpretation of δ depends on the nature of the layer [51]. This consideration leads to the formal transformation of the noise intensity in (1) $\frac{T}{V} \to \frac{T}{V-\delta^3}$ and guarantees a complete suppression of ferroelectricity below some critical dimension. However, in this case the condition (13) will take the form

$$(V - \delta^3) \sim \rho^3 \xi^3, \tag{14}$$

where V is the volume of the system. Thus, in the macroscopic case $V \gg \delta^3$ the phase transition occurs when $L \sim \xi$, but near the critical volume $V \sim \delta^3$ the transitional behavior is determined by the condition $(V - \delta^3) \sim \rho^3$, which implies the leading role of the length ρ on the transitional behavior in the vicinity of the critical size. Moreover, our approach predicts the enhancement of the susceptibility in small samples [19]. Thus, we believe that the present model may be of relevance for the description of the peculiarities of the critical temperature in ferroelectric particles (see [13, 52–54]), especially in sufficiently small ones.

5. Conclusion

We have examined the critical slowdown in the model with bulk second-order phase transition and demonstrated that this phenomenon is determined in spatially restricted systems by the eigenvalues of the Fokker–Planck operator. According to the evolution of the critical temperature in finite samples, we have established the simple criterion of the phase transition, which implies that the correlation length can play a substantial role only in a macroscopic system. In sufficiently small samples, particularly in the vicinity of the critical size, the slowdown rate increases and the critical behavior is driven by the thermal fluctuations, leading to suppression of ferroelectricity. We believe that these predictions will be useful for interpreting the experimental data about the evolution of transition temperature near the critical size in ferroelectric materials.

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