





# **ARTJOM VARGUNIN**

Stochastic and deterministic features  
of ordering in the systems with  
a phase transition



The study was carried out at the Institute of Physics, University of Tartu, Estonia.

The dissertation was admitted on June 18, 2010 in partial fulfilment of the requirements for the degree of Doctor of Philosophy (theoretical physics), and allowed for defence by the Council of the Institute of Physics, University of Tartu.

Supervisors: Prof. Teet Örd, University of Tartu, Estonia  
Prof. Risto Tammelo, University of Tartu, Estonia

Opponents: Prof. Grzegorz Litak, Technical University of Lublin, Poland  
Assoc. Prof. Ain Ainsaar, Tallinn University, Estonia

Defence: August 31, 2010 at University of Tartu, Estonia

The publication of the thesis is supported by Graduate School on Functional Materials and Technologies, University of Tartu and Tallinn University of Technology (ESF project 1.2.0401.09-0079).



Euroopa Liit  
Euroopa Sotsiaalfond



Eesti tuleviku heaks

ISSN 1406–0647

ISBN 978–9949–19–408–7 (trükis)

ISBN 978–9949–19–409–4 (PDF)

Autoriõigus: Artjom Vargunin, 2010

Tartu Ülikooli Kirjastus

[www.tyk.ee](http://www.tyk.ee)

Tellimus nr. 369

# Contents

<b>List of original publications</b>	<b>1</b>
<b>Introduction</b>	<b>3</b>
<b>1 Fundamentals</b>	<b>5</b>
1.1 Phase transition in the macroscopic systems . . . . .	5
1.1.1 Growth of the order parameter fluctuations . . . . .	7
1.1.2 Relaxation of the order parameter . . . . .	8
1.1.3 Correlations of the order parameter fluctuations . . . . .	9
1.2 Order parameter as stochastic variable . . . . .	10
<b>2 Methods and approaches</b>	<b>13</b>
2.1 Fluctuation-dissipation relation . . . . .	13
2.2 Fluctuation-dissipation theorem for heat capacity . . . . .	15
2.3 Eigenvalues of the Fokker-Planck operator . . . . .	18
2.4 Non-equilibrium free energy: microscopic consideration . . . . .	20
2.4.1 Bogolyubov inequality . . . . .	21
2.4.2 Hubbard-Stratonovich transformation . . . . .	23
<b>3 Results and discussion</b>	<b>27</b>
3.1 Relaxation rates in finite systems . . . . .	27
3.2 Dynamic susceptibility in finite systems . . . . .	31
3.3 Dynamic heat capacity in finite systems . . . . .	38
3.4 Relaxation channels in two-band superconductors . . . . .	42
3.5 Thermal fluctuations in two-band superconductors . . . . .	47
<b>Summary</b>	<b>51</b>
<b>Summary in Estonian</b>	<b>53</b>
<b>Acknowledgments</b>	<b>54</b>
<b>References</b>	<b>55</b>
<b>Attached original publications</b>	<b>67</b>



# List of original publications

The thesis is based on the following papers:

I. A. Vargunin, T. Örd, and R. Tammelo, *Complementarity of phase transition and stochastic resonance in spatially restricted systems*, Phys. Rev. E **77**, 061137 (2008).

II. A. Vargunin, T. Örd, R. Tammelo, and N. Voropajeva, *On phase transition and the critical size in spatially restricted systems*, J. Phys.: Condens. Matter **20**, 362202 (2008).

III. A. Vargunin, T. Örd, and R. Tammelo, *Deterministic and stochastic behavior in ferroelectric particles*, Phys. Lett. A **372**, 7187 (2008).

IV. A. Vargunin, *Dynamic heat capacity in spatially restricted systems with phase transition*, J. Phys.: Condens. Matter **21**, 382201 (2009).

V. T. Örd, K. Rågo, and A. Vargunin, *Relaxation of superconducting fluctuations in a two-component scenario with intra- and interband pairings*, J. Supercond. Nov. Magn. **22**, 85 (2009).

VI. T. Örd, K. Rågo, and A. Vargunin, *Critical and non-critical channel in the damping of superconducting fluctuations in two-band system*, in *Proceedings NATO ARW "Physical properties of nanosystems"*, edited by J. Bonca and S. Kruchinin, page 202, Springer, 2010 (in press).

VII. A. Vargunin, T. Örd, and K. Rågo, *Thermal fluctuations vs interband interaction in finite-size superconductors* (submitted to J. Phys.: Condens. Matter).

List of conference presentations:

1. T. Örd, K. Rågo, and A. Vargunin, *Relaxation of superconducting fluctuations in a two-component scenario with intra- and interband pairings*, Quantum Phenomena in Complex Matter, Erice, Italy, 2008.

2. A. Vargunin, T. Örd, and R. Tammelo, *Complementarity of phase transition and stochastic resonance in spatially restricted systems*, International Conference Stochastic Resonance, Perugia, Italy, 2008.

3. T. Örd, K. Rågo, and A. Vargunin, *Peculiarities of the relaxation of fluctuations in two-component superconductors*, Strong nonlinear vibronic and electronic interactions in solids, Cottbus, Germany, 2009.

4. T. Örd, K. Rågo, and A. Vargunin, *Critical and non-critical channel in the damping of superconducting fluctuations in two-band systems*, NATO ARW "Physical Properties of Nanosystems", Jalta, Ukraine, 2009.

5. A. Vargunin, T. Örd, and K. Răgo, *Effect of interband interaction on thermal fluctuations in two-band superconductors*, International Conference on Superconductivity and Magnetism, Antalya, Turkey, 2010.

Author's research has given the main contribution to the publications I-IV, VII: he has participated essentially in development of models and methods, performed analytical and numerical calculations; main person responsible for writing the papers. The calculations and analysis of the results in V, VI have been done as teamwork.

# Introduction

The diversity in the forms of matter has been apparent to humankind for millennia, and interrelations between various forms have been always an object of great interest. The scientific understanding of phase transformation has started to develop in the 1880s after van der Waals work on the liquid-gas phase transition [1]. Simplified description of ferromagnetic phase transition was given by Curie and Weiss [2, 3]. Only in 1937 the basic principles of phenomenological phase transition theory were formulated by Landau [4, 5]. A deep connection among different phase transition problems was established by revealing that each phase transition was a manifestation of a spontaneous symmetry breaking. The Landau approach has provided insight into the nature of various phenomena and contributed greatly to creation of many valuable concepts in physics. In 1950, in collaboration with Ginzburg, the phenomenological theory of superconductivity was published [6]. It was realized that the superconducting phase can be distinguished by long-range order (studied later by Yang [7]) and a cue to the electron pairing was given [8]. The electron attraction was indeed the microscopic origin of the superconducting state, and the connection between microscopic Bardeen-Cooper-Schrieffer theory [9] and phenomenological Ginzburg-Landau theory was given by Gorkov [10]. The phenomenological theory was also able to describe the instabilities of the normal phase known as superconducting vortices [11]. The universality of Landau approach has made it possible to understand ferroelectricity [12, 13] and led to the soft mode concept [14]. The applications to the superfluid matter [15] have essentially contributed to the formulation of Gross-Pitaevskii theory [16]. The birth of vortices in superfluid liquids [17] has attracted attention in connection with topological defects in cosmology [18]. Relativistic generalizations have applications in quantum field theory [19].

Landau phenomenological approach is based on free energy argument unifying various studies in different fields by means of a single mathematical apparatus. The phase distinctions are described by the order parameter. The latter characterizes a new physical property of the system which appears as a result of a phase transition from the initial phase where the corresponding property is absent. Polarization, energetic gap in the electron excitation spectrum or magnetic moment are some examples of the order parameter in corresponding materials. Nonlinearity of the Landau expansion is another essential property of the theory. The interest in applications of this scheme as well as in its generalizations is still high.

In the present Thesis we analyze the behavior of the order parameter driven by internal thermodynamic noise. Generally, the noise, via its interaction with nonlinearity of the system, can lead to very interesting physics: stochastic resonance [20], resonant activation [21], non-equilibrium phase transitions [22], and stochastic ratchets [23], to name but a few. An overview of the minimal theoretical scheme for the description of a phase transition is given in the first part of this work. The fluctuations of the order parameter are also discussed and the stochastic formalism is introduced. In the second part we present the mathematical approaches used, especially, the methods for microscopic evaluation of non-equilibrium free energy in two-gap superconducting systems. In the last part we study the effect of stochastic order parameter on the relaxation phenomenon, and investigate the size driven peculiarities of the critical temperature. We construct a description of

the response to the applied field and to the variation of the temperature, and analyze the size dependencies of the linear susceptibility and dynamic heat capacity. Afterwards, we consider the relaxation and fluctuations of the ordering in two-gap superconductor, especially, in connection with changes of interband interaction.

# 1 Fundamentals

## 1.1 Phase transition in the macroscopic systems

We start with the basics of phenomenological Landau phase transition theory. By introducing an abstract order parameter, we investigate the properties of a macroscopic system, taking into account the fluctuations of the order parameter and analyzing their behavior in the vicinity of the phase transition point.

Let us consider the system of  $N$  interacting particles with potential energy given by  $U(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)$ . The configuration of the system with values of  $\mathbf{r}_i$  belonging to  $\mathbf{r}_i \dots \mathbf{r}_i + d\mathbf{r}_i$  has the probability

$$dw = C e^{-\frac{U(\mathbf{r}_1, \dots, \mathbf{r}_N)}{k_B T}} d\mathbf{r}_1 \dots d\mathbf{r}_N. \quad (1.1)$$

Integration over all variables  $\mathbf{r}_i$  determines the constant  $C = Z^{-1}$ , where  $Z$  is the partition function and

$$Z = \int e^{-\frac{U(\mathbf{r}_1, \dots, \mathbf{r}_N)}{k_B T}} d\mathbf{r}_1 \dots d\mathbf{r}_N. \quad (1.2)$$

Equilibrium free energy related to the interaction  $U$  is defined as

$$F = -k_B T \ln Z, \quad (1.3)$$

and the probability (1.1) takes the form

$$dw = e^{-\frac{F - U(\mathbf{r}_1, \dots, \mathbf{r}_N)}{k_B T}} d\mathbf{r}_1 \dots d\mathbf{r}_N. \quad (1.4)$$

Let us now consider arbitrary spatial distribution of the real order parameter  $\eta(\mathbf{r})$  inside the system or, alternatively, a set of its Fourier components  $\eta_{\mathbf{k}}$

$$\eta(\mathbf{r}) = \sum_{\mathbf{k}} \eta_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}, \quad (1.5)$$

where  $\eta_{\mathbf{k}} = \eta'_{\mathbf{k}} + i\eta''_{\mathbf{k}}$ . For the given configuration of the system with probability (1.4) one can formally introduce the probability of the distribution  $\eta(\mathbf{r})$  in this configuration

$$\begin{aligned} dw[\eta(\mathbf{r})] &\equiv dw[\{\eta_{\mathbf{k}}\}^*] = e^{-\frac{F - U(\mathbf{r}_1, \dots, \mathbf{r}_N)}{k_B T}} d\mathbf{r}_1 \dots d\mathbf{r}_N \\ &\times \prod_{\mathbf{k}}^* \delta(\eta'_{\mathbf{k}} - \eta'_{\mathbf{k}}(\mathbf{r}_1, \dots, \mathbf{r}_N)) \delta(\eta''_{\mathbf{k}} - \eta''_{\mathbf{k}}(\mathbf{r}_1, \dots, \mathbf{r}_N)) d\eta'_{\mathbf{k}} d\eta''_{\mathbf{k}}. \end{aligned} \quad (1.6)$$

Here  $\eta'_{\mathbf{k}}(\mathbf{r}_1, \dots, \mathbf{r}_N)$  and  $\eta''_{\mathbf{k}}(\mathbf{r}_1, \dots, \mathbf{r}_N)$  are true values for Fourier components of the order parameter in the configuration given. Due to symmetry  $\eta_{\mathbf{k}} = \eta_{-\mathbf{k}}^*$ , we have put the star sign near multiplication in  $dw[\eta(\mathbf{r})]$ , having in mind only the part of  $\mathbf{k}$  space with independent variables  $\eta'_{\mathbf{k}}$  and  $\eta''_{\mathbf{k}}$ . Introducing non-equilibrium free energy in the form [24]

$$\begin{aligned} F[\eta(\mathbf{r})] &\equiv F[\{\eta_{\mathbf{k}}\}^*] = -k_B T \ln \int e^{-\frac{U(\mathbf{r}_1, \dots, \mathbf{r}_N)}{k_B T}} \\ &\times \prod_{\mathbf{k}}^* \delta(\eta'_{\mathbf{k}} - \eta'_{\mathbf{k}}(\mathbf{r}_1, \dots, \mathbf{r}_N)) \delta(\eta''_{\mathbf{k}} - \eta''_{\mathbf{k}}(\mathbf{r}_1, \dots, \mathbf{r}_N)) d\mathbf{r}_1 \dots d\mathbf{r}_N, \end{aligned} \quad (1.7)$$

we obtain after integration of Eq. (1.6)

$$Z = \int e^{-\frac{F[\eta(\mathbf{r})]}{k_B T}} \prod_{\mathbf{k}}^* d\eta'_{\mathbf{k}} d\eta''_{\mathbf{k}}. \quad (1.8)$$

By combining of Eqs. (1.6) and (1.7) we find that functional  $F[\eta]$  describes the probability density of  $\{\eta_{\mathbf{k}}\}^*$  and the most probable values of  $\{\eta_{\mathbf{k}}\}^*$  correspond to the minimum of  $F[\eta]$ . If one establishes from microscopic considerations the concrete form of the non-equilibrium free energy  $F[\eta]$  for the system considered, then all thermodynamic properties of the system become predefined.

The quantitative characteristics of the system undergoing phase transition, such as transition temperature  $T_c$ , are determined mostly by the atomic interactions in the short range scale. It has to be taken into account by the short-wave part of the series (1.5). On the other side, one can describe the phase transition phenomenologically by considering the long-wave part only. In this case the phase transition temperature has to be introduced manually.

In macroscopic (macroscopically large, but finite) system equilibrium value of the order parameter becomes non-zero in the vicinity of phase transition temperature  $T_c$ . Here one can expand non-equilibrium free energy  $F[\eta]$  in powers of non-equilibrium order parameter  $\eta$  as well as its derivatives. For the long-wave components of  $\eta$  in the vicinity of  $T_c$  one obtains [24]

$$F[\eta(\mathbf{r})] = F_n + \int \left( \frac{a}{2} \eta(\mathbf{r})^2 + \frac{b}{4} \eta(\mathbf{r})^4 + \frac{c}{2} (\nabla \eta(\mathbf{r}))^2 + \dots \right) dV, \quad (1.9)$$

where  $F_n = F[0]$ . The latter functional is also called effective Hamiltonian. In the homogeneous case with  $\eta = \eta_{\mathbf{k}=0}$  the corresponding non-equilibrium free energy density  $\tilde{F}(\eta) = F(\eta)/V$  reads as

$$\tilde{F}(\eta) = \tilde{F}_n + \frac{a}{2} \eta^2 + \frac{b}{4} \eta^4 + \dots \quad (1.10)$$

Here the coefficients before the odd powers are taken to be zero due to general requirements about phases and stability of transition state. Moreover, same requirements give  $a = 0$  and  $b > 0$  for  $T = T_c$ . Thus, one can consider the case

$$a = \alpha(T - T_c) \quad (1.11)$$

with positive constants  $\alpha$  and  $b$ . For the equilibrium free energy density of bulk ( $V \rightarrow \infty$ ) system we obtain from Eq. (1.3)

$$\frac{F}{V} = -\frac{k_B T}{V} \ln \int_{-\infty}^{\infty} e^{-\frac{V\tilde{F}(\eta)}{k_B T}} d\eta \xrightarrow{V \rightarrow \infty} \frac{\int_{-\infty}^{\infty} \tilde{F}(\eta) e^{-\frac{V\tilde{F}(\eta)}{k_B T}} d\eta}{\int_{-\infty}^{\infty} e^{-\frac{V\tilde{F}(\eta)}{k_B T}} d\eta} \xrightarrow{V \rightarrow \infty} \tilde{F}(\eta)_{\min}. \quad (1.12)$$

Thus, bulk equilibrium free energy density equals to the minimal value of non-equilibrium free energy density (1.10). The values of  $\eta$  which minimize  $\tilde{F}(\eta)$ , define the equilibrium values of order parameter  $\eta_{eq}$  in a bulk system

$$\eta_{eq}^2 = \begin{cases} 0, & T > T_c \\ -\frac{a}{b}, & T < T_c \end{cases}. \quad (1.13)$$

Therefore,

$$\frac{F}{V} = \begin{cases} \tilde{F}_n, & T > T_c \\ \tilde{F}_n - \frac{a^2}{4b}, & T < T_c \end{cases}. \quad (1.14)$$

From Eq. (1.14) we see that transition between disordered ( $\eta_{eq} = 0$ ) and ordered ( $\eta_{eq} \neq 0$ ) phases is energetically preferable.

According to the Ehrenfest classification, the non-equilibrium free energy (1.10) describes second-order phase transition because second-order derivatives of equilibrium free energy exhibit discontinuities at transition temperature  $T_c$ . For instance, the specific heat capacity reads

$$c = -\frac{T}{V} \frac{d^2 F}{dT^2} = \begin{cases} c_n, & T > T_c \\ c_n + \frac{\alpha^2 T}{2b}, & T < T_c \end{cases}, \quad (1.15)$$

where  $c_n = -T \frac{d^2 \tilde{F}_n}{dT^2}$ . The temperature behavior of specific heat capacity has jump  $\frac{\alpha^2 T_c}{2b}$  at transition temperature.

Introduction of the external field  $f$ , influencing the order parameter, requires an additional term  $-f\eta$  in Eq. (1.10). For the equilibrium states of a bulk system we then have an equation

$$a\eta_{eq} + b\eta_{eq}^3 = f. \quad (1.16)$$

The generalized susceptibility  $\chi = \frac{\partial \eta_{eq}}{\partial f}$  in the limit  $f \rightarrow 0$  reads

$$\chi = \frac{1}{a + 3b\eta_{eq}^2} = \begin{cases} \frac{1}{a}, & T > T_c \\ -\frac{1}{2a}, & T < T_c \end{cases}. \quad (1.17)$$

Found temperature behavior of susceptibility is known as Curie law. The divergence of  $\chi$  reflects the increase in flatness of non-equilibrium free energy as temperature moves to  $T_c$ . As a result, a weak perturbation is able to change equilibrium value of order parameter drastically. This behavior points to the dramatic properties of the order parameter fluctuations in the vicinity of the transition temperature in accordance with fluctuation-dissipation relation.

In the following we review three fundamental aspects of the phase transition in macroscopic system: growth of the order parameter fluctuations, their temporal relaxation and spatial correlation near the phase transition point.

### 1.1.1 Growth of the order parameter fluctuations

Far from origins of inhomogeneities in the macroscopic system the equilibrium value of order parameter can be approximated by Eq. (1.13). Let us consider the spatially dependent fluctuation of order parameter  $\Delta\eta(\mathbf{r}) = \eta(\mathbf{r}) - \eta_{eq}$ . For  $F[\eta]$  we obtain in the Gaussian approximation

$$F[\eta(\mathbf{r})] = F(\eta_{eq}) + \begin{cases} \int \left( \frac{a}{2} \Delta\eta(\mathbf{r})^2 + \frac{c}{2} (\nabla \Delta\eta(\mathbf{r}))^2 \right) dV, & T > T_c \\ \int \left( -a \Delta\eta(\mathbf{r})^2 + \frac{c}{2} (\nabla \Delta\eta(\mathbf{r}))^2 \right) dV, & T < T_c \end{cases}. \quad (1.18)$$

By introducing Fourier components<sup>1</sup> we get

$$F[\eta(\mathbf{r})] = F(\eta_{eq}) + \begin{cases} V \left( \frac{a}{2} \Delta\eta_0^2 + \sum_{\mathbf{k} \neq 0}^* (a + c\mathbf{k}^2) |\Delta\eta_{\mathbf{k}}|^2 \right), & T > T_c \\ V \left( -a \Delta\eta_0^2 + \sum_{\mathbf{k} \neq 0}^* (-2a + c\mathbf{k}^2) |\Delta\eta_{\mathbf{k}}|^2 \right), & T < T_c \end{cases}. \quad (1.19)$$

Taking into account  $\eta_{\mathbf{k}} = \eta_{eq} \delta_{\mathbf{k},0} + \Delta\eta_{\mathbf{k}}$  and  $d\eta'_{\mathbf{k}} = d\Delta\eta'_{\mathbf{k}}$ ,  $d\eta''_{\mathbf{k}} = d\Delta\eta''_{\mathbf{k}}$ , we calculate the mean values of  $\eta_{\mathbf{k}}$  by using the probability distribution (1.6) and non-equilibrium free energy (1.19)

$$\langle \eta_{\mathbf{k}} \rangle = \eta_{eq} \delta_{\mathbf{k},0}, \quad (1.20)$$

$$\langle |\eta_{\mathbf{k}}|^2 \rangle = \eta_{eq}^2 \delta_{\mathbf{k},0} + \langle |\Delta\eta_{\mathbf{k}}|^2 \rangle, \quad (1.21)$$

where

$$\langle |\Delta\eta_{\mathbf{k}}|^2 \rangle = \begin{cases} \frac{k_B T}{V(a + c\mathbf{k}^2)}, & T > T_c \\ \frac{k_B T}{V(-2a + c\mathbf{k}^2)}, & T < T_c \end{cases}. \quad (1.22)$$

The latter quantity determines the behavior of fluctuations in the equilibrium state and  $\frac{1}{V} \int \langle \Delta\eta(\mathbf{r})^2 \rangle dV = \sum_{\mathbf{k}} \langle |\Delta\eta_{\mathbf{k}}|^2 \rangle$ . We see that mean squared long-wave fluctuations of the order parameter increase drastically in a macroscopic system as temperature approaches  $T_c$ . Note also that factor  $1/V$  in Eq. (1.22) points to the absence of the mean squared equilibrium order parameter fluctuations in the bulk ( $V \rightarrow \infty$ ) system. The order parameter becomes deterministic in bulk limit.

### 1.1.2 Relaxation of the order parameter

In the bulk system the derivative of non-equilibrium free energy density or functional derivative of the effective Hamiltonian with respect to the non-equilibrium order parameter equals zero in the equilibrium. If the latter derivatives are non-zero, the relaxation process takes place where the non-equilibrium order parameter relaxes to its equilibrium value. According to the Landau-Khalatnikov equation [25], the relaxation rate is proportional to the discussed derivative and

$$\frac{d\eta(t)}{dt} = -\gamma \frac{\partial \tilde{F}(\eta)}{\partial \eta}, \quad (1.23)$$

where  $\gamma > 0$  is kinetic coefficient. In inhomogeneous case we have

$$\frac{d\eta(t)}{dt} = -\gamma(a\eta + b\eta^3 - c\nabla^2\eta). \quad (1.24)$$

In the asymptotic limit  $t \rightarrow \infty$  the equilibrium is reached. In this case the order parameter becomes time independent and the left-hand side of latter equations equals zero. Far from the origins of inhomogeneity the equilibrium value of bulk system is given in Eq. (1.13). If one considers the temporal relaxation of

---

<sup>1</sup>Note also  $\eta_{\mathbf{k}} = \frac{1}{V} \int \eta(\mathbf{r}) e^{-i\mathbf{k}\mathbf{r}} dV$ .

small spatially dependent deviation of order parameter from the equilibrium value  $\Delta\eta(\mathbf{r}, t) = \eta(\mathbf{r}, t) - \eta_{eq}$ , then the leading contribution to Eq. (1.24) reads as

$$\frac{d\Delta\eta(t)}{dt} = -\gamma((a + 3b\eta_{eq}^2)\Delta\eta - c\nabla^2\Delta\eta). \quad (1.25)$$

By using Fourier components we get

$$\frac{d\Delta\eta_{\mathbf{k}}(t)}{dt} = -\gamma(a + 3b\eta_{eq}^2 + c\mathbf{k}^2)\Delta\eta_{\mathbf{k}}. \quad (1.26)$$

We see that in bulk system the deviations of order parameter decrease in time approaching equilibrium value  $\Delta\eta_{\mathbf{k}}(t \rightarrow \infty) \rightarrow 0$  with corresponding relaxation rate

$$\lambda_{\mathbf{k}} = \gamma(a + 3b\eta_{eq}^2 + c\mathbf{k}^2) = \begin{cases} \gamma(a + c\mathbf{k}^2), & T > T_c \\ \gamma(-2a + c\mathbf{k}^2), & T < T_c \end{cases}. \quad (1.27)$$

In the long-wave limit the relaxation rate drops to zero as  $T \rightarrow T_c$ . This fundamental effect is called critical slowdown of the order parameter relaxation. The long-wave deviations relax in ordered phase with double rate compared to disordered phase. In the macroscopic system one obtains also the slowdown effect for the relaxation of the order parameter fluctuations.

### 1.1.3 Correlations of the order parameter fluctuations

The spatial correlations of the order parameter fluctuations  $\Delta\eta(\mathbf{r})$  in the equilibrium are characterized by the correlation function

$$\Gamma(\mathbf{r}, \mathbf{r}') = \langle \Delta\eta(\mathbf{r})\Delta\eta(\mathbf{r}') \rangle = \sum_{\mathbf{k}, \mathbf{k}'} \langle \Delta\eta_{\mathbf{k}}\Delta\eta_{\mathbf{k}'}^* \rangle e^{i\mathbf{k}\mathbf{r}} e^{-i\mathbf{k}'\mathbf{r}'}. \quad (1.28)$$

In case  $\langle \Delta\eta_{\mathbf{k}}\Delta\eta_{\mathbf{k}'}^* \rangle = \langle |\Delta\eta_{\mathbf{k}}|^2 \rangle \delta_{\mathbf{k}, \mathbf{k}'}$  the correlation function  $\Gamma$  depends on  $\mathbf{r} - \mathbf{r}'$ . Particularly, in Gaussian approximation (1.19) one has this type of behavior and

$$\Gamma(\mathbf{r} - \mathbf{r}') = \sum_{\mathbf{k}} \langle |\Delta\eta_{\mathbf{k}}|^2 \rangle e^{i\mathbf{k}(\mathbf{r} - \mathbf{r}')}, \quad (1.29)$$

where for macroscopic system  $\langle |\Delta\eta_{\mathbf{k}}|^2 \rangle$  is given in Eq. (1.22). The summation over  $\mathbf{k}$  gives the Ornstein-Zernike formula (see Ref. [24])

$$\Gamma(\mathbf{r} - \mathbf{r}') = \frac{k_B T}{4\pi c |\mathbf{r} - \mathbf{r}'|} e^{-\frac{|\mathbf{r} - \mathbf{r}'|}{r_c}}, \quad (1.30)$$

where correlation length for the order parameter fluctuations is given by

$$r_c = \begin{cases} \sqrt{\frac{c}{a}}, & T > T_c \\ \sqrt{-\frac{c}{2a}}, & T < T_c \end{cases}. \quad (1.31)$$

From Eq. (1.30) we see that the order parameter fluctuations in macroscopic system are significantly correlated at a distance of  $r_c$ . As temperature approaches  $T_c$ , the correlation length increases.

The phase transition theory based on the broken non-equilibrium free energy expansion in the form (1.9)-(1.11) can be applied to the case of small fluctuations and in the vicinity of transition temperature only. To get self-consistency the fluctuations in macroscopic system should not exceed the equilibrium value of the order parameter. In homogeneous case the fluctuations are maximal. Let us consider the homogeneous fluctuations in the volume  $V \sim r_c^3$  for ordered phase. The comparison of Eqs. (1.13) and (1.22) gives Ginzburg-Levanyuk criterion [26–28]

$$\text{Gi} \ll \frac{|T_c - T|}{T_c} \ll 1, \quad (1.32)$$

where  $\text{Gi} = \frac{k_B^2 T_c b^2}{\alpha c^3}$  is Ginzburg number. If the condition (1.32) is fulfilled, the phenomenological theory with expansions (1.9)-(1.11) has its application area in the temperature scale, otherwise does not. For instance, in superconductors  $\text{Gi}$  is sufficiently small and fluctuational region near  $T_c$  is narrow in macroscopic sample.

## 1.2 Order parameter as stochastic variable

In the following we consider the finite system with spatially homogeneous fluctuations. This approach is exhaustive for a zero-dimensional system [29], i.e. for the spatially restricted sample whose dimensions are less than correlation length of the ordering fluctuations. In this case uniform spatial mode  $\eta = \eta_{\mathbf{k}=0}$  dominates. In the equilibrium the fluctuation (stochastic) properties of the order parameter  $\eta$  are defined by the probability density

$$P_{eq}(\eta) = \frac{e^{-\frac{V\tilde{F}(\eta)}{k_B T}}}{\int e^{-\frac{V\tilde{F}(\eta)}{k_B T}} d\eta}. \quad (1.33)$$

To describe the relaxation of the non-equilibrium order parameter in a finite system we use the following modification of the Landau-Khalatnikov equation [30]

$$\frac{d\eta(t)}{dt} = -\gamma \frac{\partial \tilde{F}(\eta)}{\partial \eta} + \sqrt{\frac{\gamma k_B T}{V}} \xi(t). \quad (1.34)$$

Here the additional correction term can be interpreted as a random force and it takes into account possible stochastic nature of the order parameter if  $V \neq \infty$ . We assume that  $\xi$  represents the Gaussian white noise with zero mean value

$$\langle \xi(t) \rangle = 0, \quad (1.35)$$

and correlation function

$$\langle \xi(t)\xi(t') \rangle = 2\delta(t - t'). \quad (1.36)$$

As a result we have Langevin equation [31, 32] which was originally introduced together with Einstein [33, 34] and Smoluchowski [35] approaches for the description of Brownian motion. Equation (1.34) can be also considered as formal Newton equation of motion for variable  $\eta$  in the potential  $\tilde{F}$  with additional random force  $\xi$  in the overdamped regime [36]. Another widely used description of stochastic

variables is offered by the Fokker-Planck equation for the time evolution of the probability density [37]

$$\frac{\partial P(\eta, t)}{\partial t} = L_{FP}P(\eta, t), \quad (1.37)$$

where in connection with Eq. (1.34) the Fokker-Planck operator reads as

$$L_{FP} = \gamma \frac{\partial}{\partial \eta} \frac{\partial \tilde{F}(\eta)}{\partial \eta} + \frac{\gamma k_B T}{V} \frac{\partial^2}{\partial \eta^2}. \quad (1.38)$$

If the probability density is time independent, one can easily solve the Fokker-Planck equation assuming natural or reflecting boundary conditions. The time independent solution corresponds to the stationary distribution (1.33) and this explains why the intensity of the Langevin source in Eq. (1.34) is taken in the form  $\sim \sqrt{\frac{T}{V}}$ .

According to the proposed Langevin or, alternatively, Fokker-Planck equations one gets instead of Eq. (1.23)

$$\frac{d\langle \eta(t) \rangle}{dt} = -\gamma \left\langle \frac{\partial \tilde{F}(\eta)}{\partial \eta} \right\rangle. \quad (1.39)$$

In the bulk ( $V \rightarrow \infty$ ) system the order parameter is deterministic, and the latter equation transforms into Eq. (1.34) where random force  $\xi$  is omitted. In this case the relaxation of the order parameter to its equilibrium value exhibits critical slowdown. However, for finite samples the nature of the order parameter becomes stochastic. The temporal evolution of the order parameter fluctuations  $\Delta\eta(t) = \eta(t) - \langle \eta(t) \rangle$  close to the equilibrium is approximately described in the macroscopic system by Eq. (1.26) for  $\mathbf{k} = 0$  with additional noise term

$$\frac{d\Delta\eta(t)}{dt} = -\gamma(a + 3b\eta_{eq}^2)\Delta\eta + \sqrt{\frac{\gamma k_B T}{V}}\xi(t). \quad (1.40)$$

Note that the first term in right-hand side follows also from the derivative of non-equilibrium free energy (1.19). In Eq. (1.40) the mean square fluctuations relax to the non-zero equilibrium value (see Ref. [37]) in agreement with Eq. (1.22) for  $V \neq \infty$ . Moreover, the relaxation of the order parameter fluctuations slows down in macroscopic system near transition temperature. Therefore, the approach based on the Langevin equation (1.34) enables us to analyze in more consistent manner the interplay between the stochastic behavior of spatially restricted system and corresponding deterministic contribution of the bulk sample and examine the evolution of the phase transition as system dimension decreases.

Certain behavior of the order parameter fluctuations is the main origin of the phase transition. These fluctuations are described by the probability densities for  $\{\eta_{\mathbf{k}}\}^*$ , and in order to investigate the phase transition one needs statistical methods. However, it is clear that the main factor affecting the fluctuations is the volume  $V$ . In a bulk ( $V \rightarrow \infty$ ) system the behavior of the order parameter is purely deterministic without any fluctuations and  $\eta_{eq}^2 = 0$  for temperature  $T_c + \frac{\delta T}{2}$ . If one considers the state with temperature  $T_c - \frac{\delta T}{2}$ , then the relaxation process to the corresponding equilibrium value  $\eta_{eq}^2 \neq 0$  from initial state  $\eta^2 = 0$  slows

critically down as  $\delta T \rightarrow 0$ . It implies that observable value of the order parameter below  $T_c$  is practically zero, and the phase transition can not develop. However, for a macroscopic system the order parameter becomes stochastic. For temperature  $T_c + \frac{\delta T}{2}$  in the equilibrium  $\langle \eta^2 \rangle = \langle \Delta \eta^2 \rangle$  and the latter value increases as  $\delta T \rightarrow 0$ . In the state  $T_c - \frac{\delta T}{2}$  the relaxation of the mean square order parameter from the initial value  $\langle \Delta \eta^2 \rangle \neq 0$  exhibits critical slowdown as  $\delta T \rightarrow 0$ . As a result, the observable value of the order parameter below  $T_c$  is non-zero. Due to strong correlations of the order parameter fluctuations near  $T_c$ , the transition between states with zero and non-zero value of the equilibrium order parameter happens in all points of the system similarly. In accordance with this rough picture, the phase transition develops as a result of the growth, slowdown for the relaxation, and correlations of the order parameter fluctuations. At the same time the growth of the fluctuations makes the expansion (1.9) unacceptable very close to the temperature  $T_c$  and one has to deal with criterion (1.32).

## 2 Methods and approaches

### 2.1 Fluctuation-dissipation relation

Fluctuation-dissipation relation predicts non-equilibrium behavior of the system, such as the irreversible dissipation of energy into heat, from its reversible fluctuations in thermal equilibrium. It offers the general relationship between the response of a given system to an external perturbation and the internal fluctuation in the absence of the perturbation. Such a reaction is characterized by a response function and the internal fluctuation is characterized by a correlation function of relevant physical quantity fluctuating in thermal equilibrium. Although the proportionality between diffusion constant and the mobility of Brownian particle was found in 1905 by Einstein [33], the fluctuation-dissipation theorem was originally formulated by Nyquist [38] and Onsager [39] and was first proved by Callen and Welton [40]. Remarkable examples of fluctuation-dissipation relation are known as Green-Kubo formulas [41, 42].

The derivation of the fluctuation-dissipation theorem proceeds in the following way [43]. We consider the situation with a real external field  $f(\mathbf{r}) = \sum f_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}$  which is applied for a long time until the system reaches equilibrium, and the field is then switched off at the moment  $t = 0$ . In the presence of the field at time  $t = 0$  the equilibrium probability density for the Fourier components  $\{\eta_{\mathbf{k}}\}^*$  reads as

$$P_{eq}(\{\eta_{\mathbf{k}}\}^*)_{t=0} = \frac{\exp\left(-\frac{1}{k_B T} (F[\eta(\mathbf{r})] - \int f(\mathbf{r})\eta(\mathbf{r})dV)\right)}{\int \exp\left(-\frac{1}{k_B T} (F[\eta(\mathbf{r})] - \int f(\mathbf{r})\eta(\mathbf{r})dV)\right) \prod_{\mathbf{k}'}^* d\eta'_{\mathbf{k}'} d\eta''_{\mathbf{k}'}}. \quad (2.1)$$

This distribution contains  $\int f(\mathbf{r})\eta(\mathbf{r})dV = V \sum f_{\mathbf{k}}^* \eta_{\mathbf{k}}$ , and in the linear approximation with respect to  $f_{\mathbf{k}}^*$  we get

$$P_{eq}(\{\eta_{\mathbf{k}}\}^*)_{t=0} = P_{eq}^0(\{\eta_{\mathbf{k}}\}^*) + \frac{V}{k_B T} \sum_{\mathbf{k}''} f_{\mathbf{k}''}^* \left( \frac{\eta_{\mathbf{k}''} \exp\left(-\frac{F[\eta(\mathbf{r})]}{k_B T}\right)}{\int \exp\left(-\frac{F[\eta(\mathbf{r})]}{k_B T}\right) \prod_{\mathbf{k}'}^* d\eta'_{\mathbf{k}'} d\eta''_{\mathbf{k}'}} \right. \\ \left. - P_{eq}^0(\{\eta_{\mathbf{k}}\}^*) \frac{\int \eta_{\mathbf{k}''} \exp\left(-\frac{F[\eta(\mathbf{r})]}{k_B T}\right) \prod_{\mathbf{k}'}^* d\eta'_{\mathbf{k}'} d\eta''_{\mathbf{k}'}}{\int \exp\left(-\frac{F[\eta(\mathbf{r})]}{k_B T}\right) \prod_{\mathbf{k}'}^* d\eta'_{\mathbf{k}'} d\eta''_{\mathbf{k}'}} \right), \quad (2.2)$$

where  $P_{eq}^0(\{\eta_{\mathbf{k}}\}^*)$  is the probability density in the absence of the field. Since there is no external field for  $t > 0$ , the probability density  $P_{eq}(\{\eta_{\mathbf{k}}\}^*)_t$  is related to  $P_{eq}(\{\eta_{\mathbf{k}}\}^*)_{t=0}$  by the transition probability  $T^0$  in the absence of the field

$$P_{eq}(\{\eta_{\mathbf{k}}\}^*)_t = \int T^0(\{\eta_{\mathbf{k}}\}^*, t | \{\tilde{\eta}_{\mathbf{k}'}\}^*, 0) P_{eq}(\{\tilde{\eta}_{\mathbf{k}'}\}^*)_{t=0} \prod_{\mathbf{k}'}^* d\tilde{\eta}'_{\mathbf{k}'} d\tilde{\eta}''_{\mathbf{k}'}. \quad (2.3)$$

Using the stationary property of the equilibrium state

$$P_{eq}^0(\{\eta_{\mathbf{k}}\}^*) = \int T^0(\{\eta_{\mathbf{k}}\}^*, t | \{\tilde{\eta}_{\mathbf{k}'}\}^*, 0) P_{eq}^0(\{\tilde{\eta}_{\mathbf{k}'}\}^*) \prod_{\mathbf{k}'}^* d\tilde{\eta}'_{\mathbf{k}'} d\tilde{\eta}''_{\mathbf{k}'}, \quad (2.4)$$

one obtains for the mean value of  $\eta_{\mathbf{k}}$  at the moment  $t$

$$\begin{aligned}\langle \eta_{\mathbf{k}}(t) \rangle &= \int \eta_{\mathbf{k}} P_{eq}(\{\eta_{\mathbf{k}'}\}^*)_t \prod_{\mathbf{k}'}^* d\eta'_{\mathbf{k}'} d\eta''_{\mathbf{k}'} \\ &= \langle \eta_{\mathbf{k}} \rangle_0 + \frac{V}{k_B T} \sum_{\mathbf{k}''} f_{\mathbf{k}''}^* (\langle \eta_{\mathbf{k}}(t) \eta_{\mathbf{k}''}(0) \rangle_0 - \langle \eta_{\mathbf{k}} \rangle_0 \langle \eta_{\mathbf{k}''} \rangle_0).\end{aligned}\quad (2.5)$$

Here  $\langle \dots \rangle_0$  denotes the equilibrium mean value in the absence of the field. Multiplying the latter equation by  $e^{i\mathbf{k}\mathbf{r}}$  and taking sum we have

$$\delta\eta(\mathbf{r}, t) = \frac{V}{k_B T} \sum_{\mathbf{k}, \mathbf{k}'} f_{\mathbf{k}'}^* (\langle \eta_{\mathbf{k}}(t) \eta_{\mathbf{k}'}(0) \rangle_0 - \langle \eta_{\mathbf{k}} \rangle_0 \langle \eta_{\mathbf{k}'} \rangle_0) e^{i\mathbf{k}\mathbf{r}}, \quad (2.6)$$

where  $\delta\eta(\mathbf{r}, t) = \sum (\langle \eta_{\mathbf{k}}(t) \rangle - \langle \eta_{\mathbf{k}} \rangle_0) e^{i\mathbf{k}\mathbf{r}}$ . According to the general definition of the autocorrelation function

$$\begin{aligned}K(\mathbf{r}, \mathbf{r}', t) &= \langle \eta(\mathbf{r}, t) \eta(\mathbf{r}', 0) \rangle - \langle \eta(\mathbf{r}, t) \rangle \langle \eta(\mathbf{r}', 0) \rangle \\ &= \sum_{\mathbf{k}, \mathbf{k}'} (\langle \eta_{\mathbf{k}}(t) \eta_{\mathbf{k}'}(0) \rangle - \langle \eta_{\mathbf{k}}(t) \rangle \langle \eta_{\mathbf{k}'}(0) \rangle) e^{i\mathbf{k}\mathbf{r}} e^{i\mathbf{k}'\mathbf{r}'},\end{aligned}\quad (2.7)$$

this quantity becomes dependent on  $\mathbf{r} - \mathbf{r}'$  if

$$\langle \eta_{\mathbf{k}}(t) \eta_{\mathbf{k}'}(0) \rangle - \langle \eta_{\mathbf{k}}(t) \rangle \langle \eta_{\mathbf{k}'}(0) \rangle = \delta_{\mathbf{k}, -\mathbf{k}'} K_{\mathbf{k}}(t). \quad (2.8)$$

In this situation Eq. (2.6) gives

$$\delta\eta(\mathbf{r}, t) = \frac{V}{k_B T} \sum_{\mathbf{k}} f_{\mathbf{k}} K_{\mathbf{k}}(t) e^{i\mathbf{k}\mathbf{r}}. \quad (2.9)$$

Using the general definition of the response function  $\chi(\mathbf{r}, t)$  [44]

$$\delta\eta(\mathbf{r}, t) = \frac{1}{V} \int_0^\infty d\tau \int dV' \chi(\mathbf{r} - \mathbf{r}', \tau) f(\mathbf{r}', t - \tau), \quad (2.10)$$

which provides<sup>2</sup>  $\delta\eta_{\mathbf{k}}(\omega) = \chi_{\mathbf{k}}(\omega) f_{\mathbf{k}}(\omega)$  and

$$\chi_{\mathbf{k}}(\omega) = \int_0^\infty \chi_{\mathbf{k}}(\tau) e^{-i\omega\tau} d\tau, \quad (2.11)$$

we get for the field  $f(\mathbf{r})$  which switches off at  $t = 0$

$$\delta\eta(\mathbf{r}, t) = \frac{1}{V} \int_t^\infty d\tau \int dV' \chi(\mathbf{r} - \mathbf{r}', \tau) f(\mathbf{r}'). \quad (2.12)$$

By introducing Fourier components and comparing with Eq. (2.9) we obtain

$$\int_t^\infty d\tau \chi_{\mathbf{k}}(\tau) = \frac{V}{k_B T} K_{\mathbf{k}}(t), \quad (2.13)$$

---

<sup>2</sup>We use  $\eta(\mathbf{r}, t) = \frac{1}{2\pi} \int_{-\infty}^\infty \eta(\mathbf{r}, \omega) e^{i\omega t} d\omega$ .

or after differentiating

$$\chi_{\mathbf{k}}(t) = -\frac{V}{k_B T} \frac{dK_{\mathbf{k}}(t)}{dt}. \quad (2.14)$$

This is essentially the fluctuation-dissipation relation which shows how equilibrium fluctuations in the absence of the field define the response of the system to the small perturbation. Let us derive more convenient form of the fluctuation-dissipation relation. From Eqs. (2.14) and (2.11) we have

$$\chi_{\mathbf{k}}(\omega) = -\frac{V}{k_B T} \left( -K_{\mathbf{k}}(t=0) + i\omega \int_0^{\infty} K_{\mathbf{k}}(t) e^{-i\omega t} dt \right), \quad (2.15)$$

where  $K_{\mathbf{k}}(t = \infty) = 0$  is used. Considering the Fourier transform of  $K_{\mathbf{k}}(t)$  one gets

$$\chi_{\mathbf{k}}(\omega) = -\frac{V}{k_B T} \left( -K_{\mathbf{k}}(t=0) + \frac{i\omega}{2\pi} \int_{-\infty}^{\infty} K_{\mathbf{k}}(\omega') A(\omega' - \omega) d\omega' \right), \quad (2.16)$$

where

$$A(\omega' - \omega) = \int_0^{\infty} e^{it(\omega' - \omega)} dt, \quad (2.17)$$

and  $A(\omega' - \omega) + A(\omega' - \omega)^* = 2\pi\delta(\omega' - \omega)$ . The dispersion of real order parameter is real and, consequently,  $K_{\mathbf{k}}(\omega) = K_{\mathbf{k}}(\omega)^*$  and  $K_{\mathbf{k}}(t=0) = K_{\mathbf{k}}(t=0)^*$ . Evaluation of imaginary part of the susceptibility  $\chi_{\mathbf{k}}(\omega) - \chi_{\mathbf{k}}(\omega)^* = 2i\chi_{\mathbf{k}}(\omega)''$  gives

$$K_{\mathbf{k}}(\omega) = -\frac{2k_B T}{\omega V} \chi_{\mathbf{k}}(\omega)''. \quad (2.18)$$

This result represents the classical limit of the fluctuation-dissipation relation.

## 2.2 Fluctuation-dissipation theorem for heat capacity

Statistical physics predicts for small fluctuations the proportionality between the dispersion of the internal energy  $\langle \varepsilon \rangle$  and the heat capacity  $C$  in case of fixed volume [24]

$$C = \frac{1}{k_B T^2} (\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2). \quad (2.19)$$

This formula can be interpreted as the fluctuation-dissipation theorem, i.e. the equilibrium fluctuations of the internal energy define the response of the system to the small perturbation of the temperature. If one considers periodic temperature oscillations around some nominal value, then the latter equation has to be generalized and, particularly, the heat capacity becomes frequency dependent.

The first notion of frequency dependent complex heat capacity appears in literature at the beginning of the 20th century in scientific works concerning the propagation of sound in various media [45]. Anomalous ultrasonic attenuations in polyatomic gases [46] and the critical attenuation of ultrasound near critical point [47] have been explained in terms of the dynamic heat capacity. The first measurements using specific heat spectroscopy were made on glycerol near the glass

transition [48, 49]. It was shown that the frequency dependent specific heat of supercooled liquids is directly related to a frequency dependent longitudinal viscosity [50]. Dynamic calorimetry was recently successfully applied to ferroelectric and ferromagnetic systems [51–56].

Several theoretical approaches for the formulation of the dynamic specific heat were suggested, e.g., generalized hydrodynamics [57], the fluctuation-dissipation theorem [58], projection operator formalism [59], generalized constitutive equation [60], framework of free energy landscape [61], or non-equilibrium considerations [62]. Simulations have been able to reproduce various qualitative features [59, 63]. Nowadays, the dynamic heat capacity continues to be explored from both experimental and theoretical perspectives in anticipation that dynamic calorimetry would provide an insight into the energy landscape dynamics.

Following Refs. [43, 58], we formulate the fluctuation-dissipation theorem for frequency dependent heat capacity if the volume of the system is kept constant. We consider the situation when the equilibrium between the system and thermal bath with the temperature  $T + \delta T$  is reached till the moment  $t = 0$  and then the temperature changes to the value  $T$ . The internal energy for the temperature  $T$  equals

$$E = \frac{k_B T^2}{Z} \frac{\partial Z}{\partial T} = \langle \varepsilon[\eta(\mathbf{r})] \rangle_0, \quad (2.20)$$

where the partition function  $Z$  is given in Eq. (1.8) and

$$\varepsilon[\eta(\mathbf{r})] = F[\eta(\mathbf{r})] - T \frac{\partial}{\partial T} F[\eta(\mathbf{r})]. \quad (2.21)$$

In the latter equation we suppose that functional  $F[\eta(\mathbf{r})]$  depends on temperature  $T$ , and for evaluation of mean value  $\langle \varepsilon[\eta(\mathbf{r})] \rangle_0$  we use the probability density

$$P_{eq}^0(\{\eta_{\mathbf{k}}\}^*) = \frac{\exp\left(-\frac{F[\eta(\mathbf{r})]}{k_B T}\right)}{\int \exp\left(-\frac{F[\eta(\mathbf{r})]}{k_B T}\right) \prod_{\mathbf{k}'}^* d\eta'_{\mathbf{k}'} d\eta''_{\mathbf{k}'}}. \quad (2.22)$$

At the moment  $t = 0$  (temperature equals to  $T + \delta T$ ) the probability density and the quantity  $\varepsilon$  are given in the linear approximation with respect to  $\delta T$  by

$$P_{eq}(\{\eta_{\mathbf{k}}\}^*)_{t=0} = P_{eq}^0(\{\eta_{\mathbf{k}}\}^*) + \frac{\delta T}{k_B T^2} \left( \frac{\Delta \varepsilon[\eta(\mathbf{r})] \exp\left(-\frac{F[\eta(\mathbf{r})]}{k_B T}\right)}{\int \exp\left(-\frac{F[\eta(\mathbf{r})]}{k_B T}\right) \prod_{\mathbf{k}'}^* d\eta'_{\mathbf{k}'} d\eta''_{\mathbf{k}'}} - P_{eq}^0(\{\eta_{\mathbf{k}}\}^*) \langle \Delta \varepsilon[\eta(\mathbf{r})] \rangle_0 \right). \quad (2.23)$$

$$\Delta \varepsilon[\eta(\mathbf{r})]_{t=0} = \Delta \varepsilon[\eta(\mathbf{r})] - T \delta T \frac{\partial^2}{\partial T^2} \Delta F[\eta(\mathbf{r})]. \quad (2.24)$$

Here  $P_{eq}^0(\{\eta_{\mathbf{k}}\}^*)$  is the probability density in the absence of the temperature perturbation (see Eq. (2.22)), and  $\Delta$  denotes the difference between corresponding quantities in phases with  $\eta(\mathbf{r}) \neq 0$  and  $\eta(\mathbf{r}) = 0$ , e.g.  $\Delta F[\eta(\mathbf{r})] = F[\eta(\mathbf{r})] - F_n$ .

In Eq. (2.24) the last term vanishes, because  $\Delta F[\eta(\mathbf{r})]$  depends on temperature linearly in the Landau theory, and for  $t = 0$  one has

$$\begin{aligned}\langle \Delta\varepsilon[\eta(\mathbf{r})]_{t=0} \rangle &= \int \Delta\varepsilon[\eta(\mathbf{r})]_{t=0} P_{eq}(\{\eta_{\mathbf{k}}\}^*)_{t=0} \prod_{\mathbf{k}}^* d\eta'_{\mathbf{k}} d\eta''_{\mathbf{k}} \\ &= \langle \Delta\varepsilon[\eta(\mathbf{r})] \rangle_0 + \frac{\delta T}{k_B T^2} (\langle \Delta\varepsilon[\eta(\mathbf{r})]^2 \rangle_0 - \langle \Delta\varepsilon[\eta(\mathbf{r})] \rangle_0^2).\end{aligned}\quad (2.25)$$

Since there is no temperature perturbation for  $t > 0$ , the probability density  $P_{eq}(\{\eta_{\mathbf{k}}\}^*)_t$  is related to  $P_{eq}(\{\eta_{\mathbf{k}}\}^*)_{t=0}$  by the transition probability in the absence of the perturbation

$$P_{eq}(\{\eta_{\mathbf{k}}\}^*)_t = \int T^0(\{\eta_{\mathbf{k}}\}^*, t | \{\tilde{\eta}_{\mathbf{k}'}\}^*, 0) P_{eq}(\{\tilde{\eta}_{\mathbf{k}'}\}^*)_{t=0} \prod_{\mathbf{k}'}^* d\tilde{\eta}'_{\mathbf{k}'} d\tilde{\eta}''_{\mathbf{k}'}. \quad (2.26)$$

For  $t > 0$  one, consequently, has

$$\begin{aligned}\langle \Delta\varepsilon[\eta(\mathbf{r})]_t \rangle &= \int \Delta\varepsilon[\eta(\mathbf{r})]_t P_{eq}(\{\eta_{\mathbf{k}}\}^*)_t \prod_{\mathbf{k}}^* d\eta'_{\mathbf{k}} d\eta''_{\mathbf{k}} \\ &= \langle \Delta\varepsilon[\eta(\mathbf{r})] \rangle_0 + \frac{\delta T}{k_B T^2} K_{\Delta\varepsilon}(t),\end{aligned}\quad (2.27)$$

where the autocorrelation function for quantity  $\Delta\varepsilon$  is defined as

$$K_{\Delta\varepsilon}(t) = \langle \Delta\varepsilon[\eta(\mathbf{r})]_t \Delta\varepsilon[\eta(\mathbf{r})] \rangle_0 - \langle \Delta\varepsilon[\eta(\mathbf{r})] \rangle_0^2. \quad (2.28)$$

Note that the quantity  $\Delta\varepsilon[\eta(\mathbf{r})]$  depends on the set of  $\{\eta_{\mathbf{k}}\}^*$  and has explicit dependence on the temperature. Thus, if time dependent temperature perturbation happens, the temporal dependence in  $\langle \Delta\varepsilon[\eta(\mathbf{r})]_t \rangle$  appears due to time dependent probability density (2.26) related to the variables  $\{\eta_{\mathbf{k}}\}^*$  and due to explicit dependence of  $\Delta\varepsilon[\eta(\mathbf{r})]$  on the temperature perturbation. In the Landau theory the quantity  $\Delta\varepsilon[\eta(\mathbf{r})]$  is temperature independent, and  $\langle \Delta\varepsilon[\eta(\mathbf{r})]_t \rangle$  gets its time dependence via probability density for  $\{\eta_{\mathbf{k}}\}^*$  only.

Now we introduce the response function  $\Delta C(t)$  to the perturbation  $\delta T$  for the case considered

$$\delta \Delta\varepsilon(t) = \int_t^\infty d\tau \Delta C(\tau) \delta T, \quad (2.29)$$

where  $\delta \Delta\varepsilon(t) = \langle \Delta\varepsilon[\eta(\mathbf{r})]_t \rangle - \langle \Delta\varepsilon[\eta(\mathbf{r})] \rangle_0$ . By combining with Eq. (2.27) one obtains

$$\Delta C(t) = -\frac{1}{k_B T^2} \frac{dK_{\Delta\varepsilon}(t)}{dt}. \quad (2.30)$$

Using the definition of generalized susceptibility

$$\Delta C(\omega) = \int_0^\infty \Delta C(t) e^{-i\omega t} dt, \quad (2.31)$$

we get frequency dependent heat capacity difference

$$\Delta C(\omega) = -\frac{1}{k_B T^2} \left( -K_{\Delta\varepsilon}(t=0) + i\omega \int_0^\infty K_{\Delta\varepsilon}(t) e^{-i\omega t} dt \right). \quad (2.32)$$

In static case  $\omega \rightarrow 0$  the latter expression gets the form of Eq. (2.19). Using the line of reasoning which starts from Eq. (2.15), we obtain fluctuation-dissipation relation for frequency dependent heat capacity difference

$$K_{\Delta\varepsilon}(\omega) = -\frac{2k_B T^2}{\omega} \Delta C(\omega)''. \quad (2.33)$$

The real and imaginary parts of the frequency dependent complex heat capacity difference have to be related to each other by the Kramers-Kronig relations as a result of causality and linearity.

Usually, one associates the imaginary part of a linear susceptibility with the dissipation of the perturbation energy into heat. However, in the case of the generalized calorimetric susceptibility the perturbation parameter is already heat. There is no net exchange of energy between the sample and the surrounding heat bath during a complete cycle of a frequency-domain specific heat experiment. However, the entropy does change during a complete cycle. When a particular internal degree of freedom is suddenly perturbed by a temperature variation, it relaxes following a characteristic relaxation time constant. If heat is supplied in a shorter time interval than this relaxation time constant, the corresponding internal degree of freedom does not contribute entirely to the equilibrium value of the measured heat capacity under the time scale of observation because it is still relaxing. In this situation, the measured heat capacity varies in time and becomes dynamic quantity. Thus, the frequency dependent complex heat capacity is the consequence of particular physical irreversible process in the vicinity of thermodynamic equilibrium. The relaxation of internal degree of freedom is accompanied by a definite positive entropy production which, when it is averaged over the time scale of the experiment, is directly connected to the imaginary part of the complex heat capacity [64, 65].

### 2.3 Eigenvalues of the Fokker-Planck operator

Let us consider the Fokker-Planck equation (1.37) which can be rewritten for transition probability  $T(\eta, t|\tilde{\eta}, 0)$  as

$$\frac{\partial T(\eta, t|\tilde{\eta}, 0)}{\partial t} = L_{FP}(\eta) T(\eta, t|\tilde{\eta}, 0). \quad (2.34)$$

The formal solution of this equation with initial value  $T(\eta, 0|\tilde{\eta}, 0) = \delta(\eta - \tilde{\eta})$  is

$$T(\eta, t|\tilde{\eta}, 0) = e^{L_{FP}(\eta)t} \delta(\eta - \tilde{\eta}). \quad (2.35)$$

If one looks for non-stationary solutions of the original Fokker-Planck equation (1.37), it is convenient to use a separation ansatz for  $P(\eta, t)$

$$P(\eta, t) \sim \psi_n(\eta) e^{-\lambda_n t}, \quad (2.36)$$

which leads to

$$L_{FP}(\eta)\psi_n(\eta) = -\lambda_n\psi_n(\eta), \quad (2.37)$$

i.e.  $\lambda_n$  and  $\psi_n(\eta)$  are the eigenvalues and the eigenfunctions of the Fokker-Planck operator. The latter operator (1.38), which may be written in the form

$$L_{FP}(\eta) = \frac{\gamma k_B T}{V} \frac{\partial}{\partial \eta} e^{-\frac{V\tilde{F}(\eta)}{k_B T}} \frac{\partial}{\partial \eta} e^{\frac{V\tilde{F}(\eta)}{k_B T}}, \quad (2.38)$$

is not a Hermitian operator [37]. The adjoint Fokker-Planck operator

$$L_{FP}^\dagger(\eta) = \frac{\gamma k_B T}{V} e^{\frac{V\tilde{F}(\eta)}{k_B T}} \frac{\partial}{\partial \eta} e^{-\frac{V\tilde{F}(\eta)}{k_B T}} \frac{\partial}{\partial \eta} = e^{\frac{V\tilde{F}(\eta)}{k_B T}} L_{FP} e^{-\frac{V\tilde{F}(\eta)}{k_B T}} \quad (2.39)$$

has the same eigenvalues  $\lambda_n$  and the eigenfunctions

$$\varphi_n(\eta) = e^{\frac{V\tilde{F}(\eta)}{k_B T}} \psi_n(\eta). \quad (2.40)$$

At the same time, the operator  $e^{\frac{V\tilde{F}}{k_B T}} L_{FP}$  as well as

$$L(\eta) = e^{\frac{V\tilde{F}(\eta)}{2k_B T}} L_{FP}(\eta) e^{-\frac{V\tilde{F}(\eta)}{2k_B T}} \quad (2.41)$$

is an Hermitian operator. The functions

$$\phi_n(\eta) = e^{\frac{V\tilde{F}(\eta)}{2k_B T}} \psi_n(\eta) \quad (2.42)$$

are eigenfunctions of the operator  $L$  with the same eigenvalues  $\lambda_n$

$$L(\eta)\phi_n(\eta) = -\lambda_n\phi_n(\eta). \quad (2.43)$$

Because  $L$  is an Hermitian operator, the eigenvalues  $\lambda_n$  are real and two eigenfunctions  $\phi_1$  and  $\phi_2$  with different eigenvalues  $\lambda_1 \neq \lambda_2$  must be orthogonal. For natural or reflecting boundary conditions  $\lambda_0 = 0$  corresponds to the stationary solution  $\psi_0(\eta) = P_{eq}(\eta)$  (see Eq. (1.33)), and all other eigenvalues  $\lambda_n$  ( $n \geq 1$ ) must be larger than zero [37].

Eigenfunctions of Hermitian operators usually form a complete set. The completeness relation for  $\phi_n$  may be expressed by

$$\delta(\eta - \tilde{\eta}) = \sum_n \phi_n(\eta)\phi_n(\tilde{\eta}) = e^{\frac{V\tilde{F}(\tilde{\eta})}{k_B T}} \sum_n \psi_n(\eta)\psi_n(\tilde{\eta}) = \sum_n \psi_n(\eta)\varphi_n(\tilde{\eta}). \quad (2.44)$$

We also require orthonormality of the eigenfunctions

$$\int \psi_n(\eta)\varphi_{n'}(\eta)d\eta = \delta_{n,n'}. \quad (2.45)$$

If the eigenvalue  $\lambda_0 = 0$  exists, then  $\varphi_0(\eta) = 1$  and

$$\int \psi_{n \neq 0}(\eta)d\eta = 0, \quad \int \varphi_{n \neq 0}(\eta)P_{eq}(\eta)d\eta = 0. \quad (2.46)$$

The first eigenfunction  $\psi_0$  has no zeros, the next eigenfunction has one zero and so on. Using the expression (2.44) we get for the transition probability (2.35)

$$\begin{aligned} T(\eta, t|\tilde{\eta}, 0) &= \sum_n e^{L_{FP}(\eta)t} \psi_n(\eta) \varphi_n(\tilde{\eta}) \\ &= \sum_n \psi_n(\eta) \varphi_n(\tilde{\eta}) e^{-\lambda_n t}. \end{aligned} \quad (2.47)$$

Thus, in the steady state one gets for the correlation function of two variables  $x(\eta)$  and  $y(\eta)$  [66]

$$\begin{aligned} K(t) &= \langle x(\eta(t))y(\eta(0)) \rangle - \langle x(\eta(t)) \rangle \langle y(\eta(0)) \rangle \\ &= \sum_{n \geq 0} x_n y_n e^{-\lambda_n t} - x_0 y_0 = \sum_{n \geq 1} x_n y_n e^{-\lambda_n t}, \end{aligned} \quad (2.48)$$

where

$$x_n = \int x(\eta) \psi_n(\eta) d\eta, \quad (2.49)$$

$$y_n = \int y(\eta) \varphi_n(\eta) P_{eq}(\eta) d\eta. \quad (2.50)$$

The expression (2.48) together with fluctuation-dissipation relation allows one to calculate the susceptibilities if the eigenvalues of the Fokker-Plank operator are known. For these eigenvalues one can use the operator (2.41) which has the form

$$L(\eta) = \frac{\gamma k_B T}{V} \frac{\partial^2}{\partial \eta^2} - V_S(\eta), \quad (2.51)$$

where

$$V_S(\eta) = \frac{\gamma V}{4k_B T} \left( \frac{\partial \tilde{F}}{\partial \eta} \right)^2 - \frac{\gamma}{2} \frac{\partial^2 \tilde{F}}{\partial \eta^2}. \quad (2.52)$$

Thus, the equation (2.43) is formally the Schrödinger equation for stationary states. Various numerical methods (e.g., difference method, Numerov method, and eigenfunction expansion method) have been developed to solve time independent Schrödinger equation. Recently, the symplectic schemes have been used for the computation of the quantum systems [67]. For the numerical calculation of the eigenvalues  $\lambda_n$  we have used symplectic scheme-shooting method [68, 69], which can be also extended for the two-dimensional case [70].

## 2.4 Non-equilibrium free energy: microscopic consideration

In this section we demonstrate how the non-equilibrium free energy itself can be carried out from the microscopic theory. For this aim we consider two methods based on the Bogolyubov inequality [71] and on the Hubbard-Stratonovich transformation [72], and apply them to the two-band superconducting system. Historically, the first models of two-band superconductivity [73, 74] were suggested as the natural developments of the Bardeen-Cooper-Schrieffer theory by introducing

effective interband attraction of electron-phonon nature between electrons near the Fermi level. Afterwards, Kondo showed [75] that interband electron-electron repulsion induces the superconducting ordering. For the presence, the various multi-component theoretical schemes have been applied for a number of superconducting materials (see Ref. [76] and references therein). In particular, the research activity in this direction have been stimulated by the general acceptance of multi-band superconductivity in MgB<sub>2</sub> [77], cuprates [78] and iron-arsenic compounds [79].

In the following, we consider the two-band Hamiltonian with intra- and interband pair transfer interactions,

$$H = \sum_{\alpha\mathbf{k}\sigma} \tilde{\epsilon}_\alpha(\mathbf{k}) a_{\alpha\mathbf{k}\sigma}^+ a_{\alpha\mathbf{k}\sigma} - \frac{1}{V} \sum_{\alpha\alpha'} \sum_{\mathbf{k}\mathbf{k}'} W_{\alpha\alpha'}(\mathbf{k}, \mathbf{k}') a_{\alpha\mathbf{k}\sigma}^+ a_{\alpha-\mathbf{k}-\sigma}^+ a_{\alpha'-\mathbf{k}'-\sigma} a_{\alpha'\mathbf{k}'\sigma}, \quad (2.53)$$

where  $\tilde{\epsilon}_\alpha = \epsilon_\alpha - \mu$  is the electron energy in the bands  $\alpha = 1, 2$ ;  $\mu$  is the chemical potential;  $V$  is the volume of superconductor and  $W_{\alpha\alpha'}(\vec{k}, \vec{k}')$  are the matrix elements of intraband or interband interaction, if  $\alpha = \alpha'$  or  $\alpha \neq \alpha'$ , respectively. It is supposed that the chemical potential is located in the region of the bands overlapping. We assume that effective electron-electron interactions are nonzero only in the layer  $\mu \pm \hbar\omega_c$  and that the interaction constants are independent on electron wave vector in this layer. Intraband interactions are supposed to be of attractive nature.

### 2.4.1 Bogolyubov inequality

According to Bogolyubov, we formally rewrite the Hamiltonian (2.53) in the form

$$H = H_0 + H_1, \quad (2.54)$$

where

$$H_0 = \sum_{\alpha\mathbf{k}\sigma} \tilde{\epsilon}_\alpha(\mathbf{k}) a_{\alpha\mathbf{k}\sigma}^+ a_{\alpha\mathbf{k}\sigma} + \sum_{\alpha\mathbf{k}} (\eta_{\alpha\mathbf{k}} a_{\alpha\mathbf{k}\sigma}^+ a_{\alpha-\mathbf{k}-\sigma}^+ + h.c.), \quad (2.55)$$

$$H_1 = - \sum_{\alpha\mathbf{k}} (\eta_{\alpha\mathbf{k}} a_{\alpha\mathbf{k}\sigma}^+ a_{\alpha-\mathbf{k}-\sigma}^+ + h.c.) - \frac{1}{V} \sum_{\alpha\alpha'} \sum_{\mathbf{k}\mathbf{k}'} W_{\alpha\alpha'} a_{\alpha\mathbf{k}\sigma}^+ a_{\alpha-\mathbf{k}-\sigma}^+ a_{\alpha'-\mathbf{k}'-\sigma} a_{\alpha'\mathbf{k}'\sigma}, \quad (2.56)$$

and  $\eta_{\alpha\mathbf{k}}$  are non-equilibrium superconducting order parameters. The Bogolyubov inequality  $F \leq F(H_0) + \langle H_1 \rangle_{H_0}$  determines the model free energy of a two-band superconductor

$$F(H) = F(H_0) + \langle H_1 \rangle_{H_0}, \quad (2.57)$$

where  $F(H_0)$  is free energy with respect to the Hamiltonian  $H_0$ . To find this quantity we use the Bogolyubov-Valatin transformation

$$\begin{aligned} a_{\alpha\mathbf{k}\sigma} &= u_{\alpha\mathbf{k}} A_{\alpha\mathbf{k}\sigma} + \text{sgn}(\sigma) v_{\alpha\mathbf{k}}^* A_{\alpha-\mathbf{k}-\sigma}^+, \\ a_{\alpha\mathbf{k}\sigma}^+ &= u_{\alpha\mathbf{k}} A_{\alpha\mathbf{k}\sigma}^+ + \text{sgn}(\sigma) v_{\alpha\mathbf{k}} A_{\alpha-\mathbf{k}-\sigma}. \end{aligned} \quad (2.58)$$

Here  $u_{\alpha\mathbf{k}}^2 + |v_{\alpha\mathbf{k}}|^2 = 1$  and  $u_{\alpha\mathbf{k}} = u_{\alpha-\mathbf{k}}$ ,  $v_{\alpha\mathbf{k}} = v_{\alpha-\mathbf{k}}$  guarantee that new operators  $A_{\alpha\mathbf{k}\sigma}$  are Fermi operators. Note that in this transformation the coefficients  $u_{\alpha\mathbf{k}}$

and  $v_{\alpha\mathbf{k}}$  are not determined uniquely, and one can define them by requiring the diagonalization of the Hamiltonian  $H_0$

$$H_0 = \sum_{\alpha\mathbf{k}\sigma} E_{\alpha\mathbf{k}} A_{\alpha\mathbf{k}\sigma}^+ A_{\alpha\mathbf{k}\sigma} + E_0, \quad (2.59)$$

where

$$E_{\alpha\mathbf{k}} = \sqrt{\tilde{\epsilon}_\alpha(\mathbf{k})^2 + |\eta_{\alpha\mathbf{k}}|^2}, \quad (2.60)$$

$$E_0 = \sum_{\alpha\mathbf{k}} (\tilde{\epsilon}_\alpha(\mathbf{k}) - E_{\alpha\mathbf{k}}). \quad (2.61)$$

Thus, we obtain

$$\begin{aligned} F(H_0) &= -k_B T \ln \text{Sp} \left( e^{-\frac{H_0}{k_B T}} \right) \\ &= \sum_{\alpha\mathbf{k}} \left( \tilde{\epsilon}_\alpha(\mathbf{k}) - 2k_B T \ln \left( 2 \cosh \frac{E_{\alpha\mathbf{k}}}{2k_B T} \right) \right). \end{aligned} \quad (2.62)$$

In order to find  $\langle H_1 \rangle_{H_0}$  we consider the following approximation

$$\begin{aligned} \langle H_1 \rangle_{H_0} &= - \sum_{\alpha\mathbf{k}} \left( \eta_{\alpha\mathbf{k}} \langle a_{\alpha\mathbf{k}\sigma}^+ a_{\alpha-\mathbf{k}-\sigma}^+ \rangle_{H_0} + \eta_{\alpha\mathbf{k}}^* \langle a_{\alpha-\mathbf{k}-\sigma} a_{\alpha\mathbf{k}\sigma} \rangle_{H_0} \right) \\ &\quad - \frac{1}{V} \sum_{\alpha\alpha'} \sum_{\mathbf{k}\mathbf{k}'} W_{\alpha\alpha'} \langle a_{\alpha\mathbf{k}\sigma}^+ a_{\alpha-\mathbf{k}-\sigma}^+ \rangle_{H_0} \langle a_{\alpha'\mathbf{k}'-\sigma} a_{\alpha'\mathbf{k}'\sigma} \rangle_{H_0}. \end{aligned} \quad (2.63)$$

Since

$$\langle A_{\alpha\mathbf{k}\sigma}^+ A_{\alpha'\mathbf{k}\sigma} \rangle_{H_0} = \frac{\delta_{\alpha\alpha'}}{1 + \exp \frac{E_{\alpha\mathbf{k}}}{k_B T}} \quad (2.64)$$

and  $\langle A_{\alpha\mathbf{k}\sigma}^+ A_{\alpha'\mathbf{k}'\sigma'} \rangle_{H_0} = \langle A_{\alpha\mathbf{k}\sigma} A_{\alpha'\mathbf{k}'\sigma'} \rangle_{H_0} = 0$ , we obtain the model free energy in the form

$$F(H) = \sum_{\alpha} J_{\alpha}(\eta_{\alpha}) + \sum_{\alpha} \eta_{\alpha}^2 I_{\alpha}(\eta_{\alpha}) - \frac{1}{4V} \sum_{\alpha\alpha'} W_{\alpha\alpha'} \eta_{\alpha} \eta_{\alpha'} I_{\alpha}(\eta_{\alpha}) I_{\alpha'}(\eta_{\alpha'}), \quad (2.65)$$

where the non-equilibrium order parameters  $\eta_{\alpha}$  are taken real and  $\mathbf{k}$  independent, and

$$J_{\alpha} = \sum_{\mathbf{k}} \left( \tilde{\epsilon}_\alpha(\mathbf{k}) - 2k_B T \ln \left( 2 \cosh \frac{E_{\alpha\mathbf{k}}}{2k_B T} \right) \right), \quad (2.66)$$

$$I_{\alpha} = \sum_{\mathbf{k}} \frac{1}{E_{\alpha\mathbf{k}}} \tanh \frac{E_{\alpha\mathbf{k}}}{2k_B T}. \quad (2.67)$$

By replacing the summation over wave vector  $\mathbf{k}$  with the integration over energy, the model free energy density  $\tilde{F} = F/V$  can be written as

$$\tilde{F}(\eta_1, \eta_2) = \tilde{F}_n + \sum_{\alpha} \rho_{\alpha} \tilde{J}_{\alpha}(\eta_{\alpha}) + \sum_{\alpha} \eta_{\alpha}^2 \rho_{\alpha} \tilde{I}_{\alpha}(\eta_{\alpha}) - \frac{1}{4} \sum_{\alpha\alpha'} W_{\alpha\alpha'} \eta_{\alpha} \eta_{\alpha'} \rho_{\alpha} \rho_{\alpha'} \tilde{I}(\eta_{\alpha}) \tilde{I}(\eta_{\alpha'}), \quad (2.68)$$

where we assume  $W_{12} = W_{21}$ ,  $\rho_\alpha$  are the densities of electron states at the Fermi level, and

$$\tilde{J}_\alpha(\eta_\alpha) = -4k_B T \int_0^{\hbar\omega_c} \ln \left( \frac{\cosh \frac{E_\alpha(\tilde{\epsilon}_\alpha, \eta_\alpha)}{2k_B T}}{\cosh \frac{E_\alpha(\tilde{\epsilon}_\alpha, 0)}{2k_B T}} \right) d\tilde{\epsilon}_\alpha, \quad (2.69)$$

$$\tilde{I}_\alpha(\eta_\alpha) = 2 \int_0^{\hbar\omega_c} \frac{1}{E_\alpha(\tilde{\epsilon}_\alpha, \eta_\alpha)} \tanh \frac{E_\alpha(\tilde{\epsilon}_\alpha, \eta_\alpha)}{2k_B T} d\tilde{\epsilon}_\alpha, \quad (2.70)$$

$$E_\alpha(\tilde{\epsilon}_\alpha, \eta_\alpha) = \sqrt{\tilde{\epsilon}_\alpha^2 + \eta_\alpha^2}. \quad (2.71)$$

The stationary points of the non-equilibrium free energy density (2.68) determine equilibrium gaps, which vanish as temperature moves to the transition point. Corresponding minimal value of the model free energy density  $\tilde{F}$  equals to the equilibrium mean-field free energy density. The deviations from this value are treated in the present scheme as an effect of the order parameter fluctuations. As compared to the Landau expansion, the non-equilibrium free energy density (2.68) can describe the system far from the transition point, however, it permits again only small gap fluctuations.

#### 2.4.2 Hubbard-Stratonovich transformation

The description of superconductivity in the framework of mean-field approximation does not take into account the order parameter fluctuations. It is approximately justified for macroscopic samples, however, the thermal and quantum fluctuations become decisively important in small systems [29, 80, 81]. Static thermal fluctuations reflect the deviation of a finite system from its most probable state. Quantum fluctuations are associated with the tunneling in the free energy landscape. In addition, one has to take into account the discreteness of the electron spectrum and the parity of the number of electrons in small samples, especially at low temperatures [82–84].

To describe the fluctuation corrections in superconductors it is convenient to regard the functional integral representation of the partition function based on the Hubbard-Stratonovich transformation [85–87]. In this approach the saddle-point evaluation of the functional integral gives the standard mean-field results, in the static approximation one includes thermodynamic fluctuations, and in higher order contributions one can involve some of the quantum fluctuations. The scheme has been exploited mainly in the case of one-band superconductors [29, 82, 88–92]. However, recently the study of the Leggett mode in a two-band superconductor MgB<sub>2</sub> [93] and the fluctuation conductivity of pnictides in a four-band model [94] have been carried out using the Hubbard-Stratonovich fields.

To apply the Hubbard-Stratonovich transformation, we first rewrite the Hamiltonian (2.53) using the pseudospin formalism

$$H = H' - \sum_{\alpha\alpha'} \frac{W_{\alpha\alpha'}}{V} (X_\alpha X_{\alpha'} + Y_\alpha Y_{\alpha'}), \quad (2.72)$$

where

$$H' = \sum_{\alpha\mathbf{k}s} \tilde{\epsilon}_\alpha(\mathbf{k}) a_{\alpha\mathbf{k}s}^+ a_{\alpha\mathbf{k}s} + \sum_{\alpha\mathbf{k}s} \frac{W_{\alpha\alpha}}{2V} \left( \frac{1}{2} - a_{\alpha\mathbf{k}s}^+ a_{\alpha\mathbf{k}s} \right), \quad (2.73)$$

and

$$X_\alpha = \frac{1}{2} \sum_{\mathbf{k}} (a_{\alpha-\mathbf{k}-\sigma} a_{\alpha\mathbf{k}\sigma} + a_{\alpha\mathbf{k}\sigma}^+ a_{\alpha-\mathbf{k}-\sigma}^+), \quad (2.74)$$

$$Y_\alpha = \frac{i}{2} \sum_{\mathbf{k}} (a_{\alpha-\mathbf{k}-\sigma} a_{\alpha\mathbf{k}\sigma} - a_{\alpha\mathbf{k}\sigma}^+ a_{\alpha-\mathbf{k}-\sigma}^+). \quad (2.75)$$

Due to commutation rules for Fermi operators  $[a_{\alpha\mathbf{k}s}, a_{\alpha'\mathbf{k}'s'}^+]_+ = \delta_{\alpha,\alpha'} \delta_{\mathbf{k},\mathbf{k}'} \delta_{s,s'}$  and  $[a_{\alpha\mathbf{k}s}^+, a_{\alpha'\mathbf{k}'s'}^+]_+ = [a_{\alpha\mathbf{k}s}, a_{\alpha'\mathbf{k}'s'}]_+ = 0$ , operators  $X_1$  and  $Y_1$  commute with  $X_2$  and  $Y_2$ , respectively. We also assume  $W_{12} = W_{21}$ . Next, we use diagonal presentation of the quadratic forms in  $H$ , e.g. in connection with  $X_\alpha$  operators,

$$\sum_{\alpha\alpha'} W_{\alpha\alpha'} X_\alpha X_{\alpha'} = \sum_{\mu=1}^2 \tilde{W}_\mu \tilde{X}_\mu^2 \quad (2.76)$$

by utilizing the orthogonal transformation  $\tilde{X}_\mu = \sum_\alpha \vartheta_{\mu\alpha} X_\alpha$  with

$$\vartheta = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} \quad (2.77)$$

and

$$\tilde{W}_{1,2} = \frac{1}{2} \left( W_{11} + W_{22} \pm \sqrt{(W_{11} - W_{22})^2 + 4W_{12}^2} \right), \quad (2.78)$$

$$\tan \theta = \frac{W_{11} - \tilde{W}_1}{W_{12}} = \frac{\tilde{W}_2 - W_{22}}{W_{12}}. \quad (2.79)$$

To calculate the partition function  $Z = \text{Sp} \exp(-\frac{H}{k_B T})$  we apply the Hubbard-Stratonovich transformation

$$e^{\tilde{a}\tilde{X}^2} = \int_{-\infty}^{\infty} e^{-\pi x^2 - 2\sqrt{\pi\tilde{a}x}\tilde{X}} dx. \quad (2.80)$$

Here, by introducing the integration variable, one achieves a linearization of the exponent. As the operators in  $H$  do not commute, one has to use the Feynman ordering technique [95], and therefore

$$e^{-\frac{H}{k_B T}} = \lim_{M \rightarrow \infty} \int_{-\infty}^{\infty} \prod_{\mu=1}^2 \prod_{j=1}^M dx_{\mu j} dy_{\mu j} \exp \left( -\pi \sum_{\mu=1}^2 \sum_{j=1}^M (x_{\mu j}^2 + y_{\mu j}^2) - \frac{1}{k_B T M} \sum_{j=1}^M (H'_j + 2 \sum_{\mu=1}^2 \sqrt{\pi k_B T M \frac{\tilde{W}_\mu}{V}} (\tilde{X}_{\mu j} x_{\mu j} + \tilde{Y}_{\mu j} y_{\mu j})) \right). \quad (2.81)$$

Let us use discrete Fourier transform, e.g. in connection with variables  $x_{\mu j}$ ,

$$x_{\mu j} = \sum_{p=-\frac{M-1}{2}}^{\frac{M-1}{2}} \eta_{\mu p}^x e^{-\frac{2\pi i}{M} p j} \quad (2.82)$$

and consider new complex variables  $\eta_{\mu p}^x$ . In the static path approximation,

$$\tilde{X}_{\mu j} x_{\mu j} + \tilde{Y}_{\mu j} y_{\mu j} = \tilde{X}_{\mu j} \eta_{\mu 0}^x + \tilde{Y}_{\mu j} \eta_{\mu 0}^y, \quad (2.83)$$

one gets

$$e^{-\frac{H}{k_B T}} = \lim_{M \rightarrow \infty} \int_{-\infty}^{\infty} M^2 \prod_{\mu=1}^2 d\eta_{\mu 0}^x d\eta_{\mu 0}^y \exp\left(-\pi M \sum_{\mu=1}^2 (\eta_{\mu 0}^{x2} + \eta_{\mu 0}^{y2}) - \frac{1}{k_B T M} \sum_{j=1}^M \left( H'_j + 2 \sum_{\mu=1}^2 \sqrt{\pi k_B T M \frac{\tilde{W}_{\mu}}{V}} (\tilde{X}_{\mu j} \eta_{\mu 0}^x + \tilde{Y}_{\mu j} \eta_{\mu 0}^y) \right)\right). \quad (2.84)$$

By using new notations  $\sqrt{M} \eta_{\mu 0}^x = \eta_{\mu}^x$ , we obtain for  $M \rightarrow \infty$

$$e^{-\frac{H}{k_B T}} = \int_{-\infty}^{\infty} \prod_{\mu=1}^2 d\eta_{\mu}^x d\eta_{\mu}^y \exp\left(-\pi \sum_{\mu=1}^2 (\eta_{\mu}^{x2} + \eta_{\mu}^{y2}) - \frac{H'}{k_B T} - 2 \sum_{\mu=1}^2 \sqrt{\frac{\pi \tilde{W}_{\mu}}{k_B T V}} (\tilde{X}_{\mu} \eta_{\mu}^x + \tilde{Y}_{\mu} \eta_{\mu}^y)\right). \quad (2.85)$$

In the case of small interband interaction,  $W_{12} < W_{11} W_{22}$ , one can diagonalize the operator inside the exponent in Eq. (2.85) by means of Bogolyubov-Valatin transformation (2.58)

$$e^{-\frac{H}{k_B T}} = \int_{-\infty}^{\infty} \prod_{\mu=1}^2 d\eta_{\mu}^x d\eta_{\mu}^y \exp\left(-\pi \sum_{\mu=1}^2 (\eta_{\mu}^{x2} + \eta_{\mu}^{y2}) - \frac{H_0(\eta_1, \eta_2)}{k_B T}\right), \quad (2.86)$$

where  $H_0$  is given by Eqs. (2.59) and (2.61) with

$$E_{\alpha \mathbf{k}} = \sqrt{\left(\tilde{\epsilon}_{\alpha}(\mathbf{k}) - \frac{W_{\alpha\alpha}}{2V}\right)^2 + |\eta_{\alpha}|^2}, \quad (2.87)$$

$$\eta_{\alpha} = \sum_{\mu=1}^2 \sqrt{\pi k_B T \frac{\tilde{W}_{\mu}}{V}} \vartheta_{\mu\alpha} (\eta_{\mu}^x - i\eta_{\mu}^y). \quad (2.88)$$

After transformation of the integration variables we finally have

$$e^{-\frac{H}{k_B T}} = \frac{V^2}{(\pi k_B T)^2 \tilde{W}_1 \tilde{W}_2} \int_{-\infty}^{\infty} d\eta'_1 d\eta'_2 d\eta''_1 d\eta''_2 \exp\left(-\frac{V \Xi(\eta_1, \eta_2)}{k_B T} - \frac{H_0(\eta_1, \eta_2)}{k_B T}\right), \quad (2.89)$$

where

$$\Xi(\eta_1, \eta_2) = \frac{1}{\tilde{W}_1 \tilde{W}_2} (W_{11} |\eta_2|^2 + W_{22} |\eta_1|^2 - 2W_{12} (\eta'_1 \eta'_2 + \eta''_1 \eta''_2)). \quad (2.90)$$

For the partition function of two-band superconductor one obtains after replacing the summation over wave vector  $\mathbf{k}$  with the integration over energy

$$Z = \int_{-\infty}^{\infty} d\eta'_1 d\eta'_2 d\eta''_1 d\eta''_2 \exp\left(-\frac{V \tilde{F}(\eta_1, \eta_2)}{k_B T}\right). \quad (2.91)$$

Here non-equilibrium free energy density  $\tilde{F} = F/V$  reads as

$$\tilde{F}(\eta_1, \eta_2) = \tilde{F}_n + \sum_{\alpha} \rho_{\alpha} \tilde{J}_{\alpha}(\eta_{\alpha}) + \Xi(\eta_1, \eta_2), \quad (2.92)$$

where the function  $\tilde{J}_{\alpha}(\eta_{\alpha})$  is given by Eq. (2.69) with notation (2.87) and  $\tilde{F}_n = \tilde{F}(0)$ . In the limit  $W_{12} \rightarrow 0$  the partition function factorizes and one gets two autonomous one-band contributions. Note that bulk equilibrium free energy densities as well as the equations for corresponding equilibrium order parameters coincide in the approaches based on the Bogolyubov inequality and on the Hubbard-Stratonovich transformation.

### 3 Results and discussion

In the next three sections we consider spatially restricted homogeneous system with the second-order phase transition. We will investigate its behavior by use of the model non-equilibrium free energy density (1.10) and study the finite-size effects by means of the Fokker-Planck equation approach (see section 1.2). We calculate the eigenvalues of the Fokker-Planck operator and analyze the behavior of the dynamic susceptibility and dynamic heat capacity. For our calculations we use the following set of parameters:  $T_c = 10$ ,  $\alpha = 10$  (if other value is not specified),  $b = 1$ , and  $k_B = \gamma = 1$ .

Afterwards, we will study the properties of the superconducting ordering and investigate the relaxation and homogeneous gap order parameter fluctuations in two-band system. In the latter case no artificial constraints for the physical constants are assumed.

#### 3.1 Relaxation rates in finite systems

The size effects on phase transition in ferroelectrics has been known since the 1950s [96, 97] but, due to their practical importance [98, 99], the interest in restricted condensed systems continues to be high nowadays as well. According to the phenomenological finite size scaling theory [100–103], when the correlation length  $r_c(T)$  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  $L/r_c$ . This assertion determines the shift of the critical temperature of a finite-size system, particularly, the lowering of transition temperature 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. [104–108], have recently been actively investigated.

In order to establish finite-size behavior of the eigenvalues of the Fokker-Planck operator, we calculate them numerically, solving the corresponding Schrödinger equation by means of the symplectic method (see section 2.3). The first four eigenvalues  $\lambda_{1-4}$  of the Fokker-Planck operator  $L_{FP}$  are shown in Fig. 1 as functions of temperature for various volumes of the system. As one can see, the first eigenvalue  $\lambda_1$  is a monotonous function of temperature which in the monostable region  $T > T_c$  asymptotically approaches  $\alpha(T - T_c)$  (compare with Eq. (1.27)). Thus, above  $T_c$  this eigenvalue is a measure of intrawell dynamics. In the bulk limit  $\lambda_1 = 0$  for  $T < T_c$ , pointing at the spontaneous symmetry breaking phenomenon. For finite system the rate  $\lambda_1$  determines below  $T_c$  the relaxation for the interwell dynamics. It may be approximately described by the Arrhenius-like formula [109] in the appropriate temperature range below  $T_c$ . To be adequate in the whole range of parameters, a substantially better approximation of  $\lambda_1$  is found in the context of the activated Brownian motion [110]. Unlike the monotonicity of  $\lambda_1$ , the higher eigenvalues  $\lambda_{2-4}$  have a minimum in the bistable region which shifts to the critical temperature  $T_c$  and becomes deeper when the volume increases. It is the consequence of the volume dependent noise. In the bulk limit  $\lambda_3 = 2\alpha(T_c - T)$

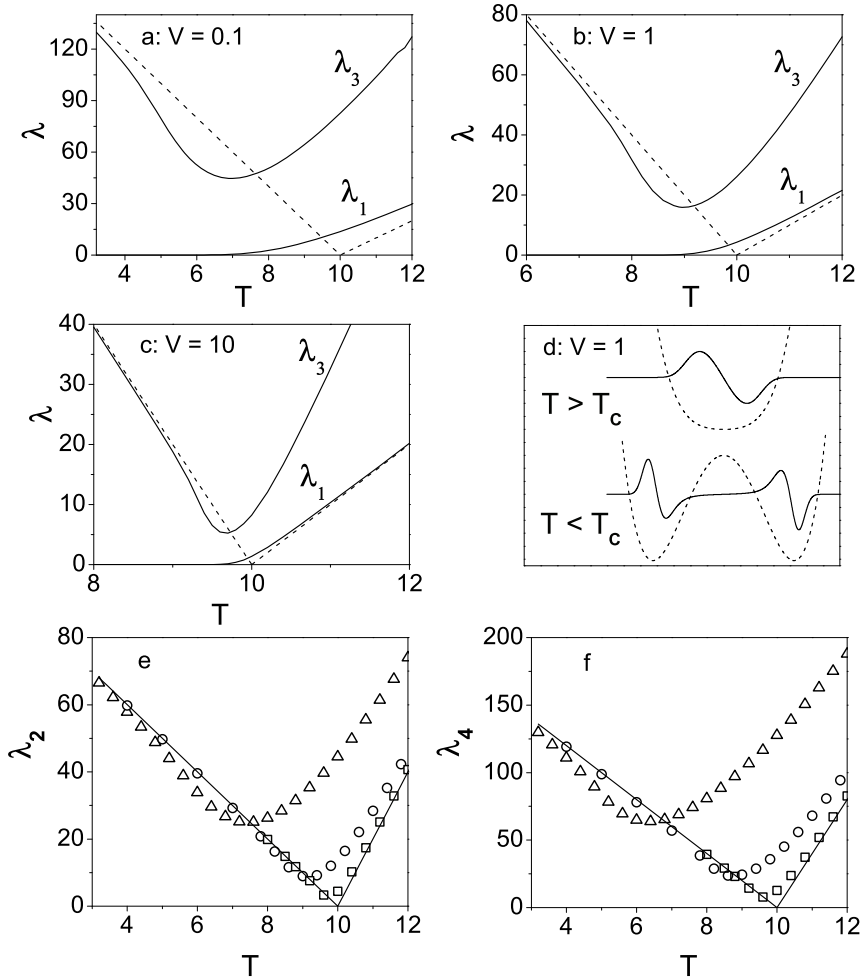


Figure 1: (a, b, c) The plots of the eigenvalues  $\lambda_{1,3}$  (solid lines) vs temperature for various volumes  $V = 0.1$  (a),  $V = 1$  (b), and  $V = 10$  (c). The dashed lines are defined as  $2\alpha(T_c - T)$  for  $T < T_c$  and  $\alpha(T - T_c)$  for  $T > T_c$ . In (d) the sketch of the 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 (1.10). (e, f) The plots of the eigenvalues  $\lambda_2$  and  $\lambda_4$  vs temperature for various volumes  $V = 0.1$  (triangles),  $V = 1$  (circles),  $V = 10$  (squares) and bulk limit  $V \rightarrow \infty$  (solid curve).

for  $T < T_c$ , in accordance with the Landau phase transition theory (1.27). Thus, the third eigenvalue has to be interpreted at low temperatures as the relaxation rate of the intrawell processes. The same follows from the comparison of the corresponding eigenfunctions (see Figure 1d). For the even eigenvalues one obtains in the bulk limit for  $T < T_c$

$$\lambda_2 \rightarrow \alpha(T_c - T), \quad \lambda_4 \rightarrow 2\alpha(T_c - T), \quad (3.1)$$

and for  $T > T_c$

$$\lambda_2 \rightarrow 2\alpha(T - T_c), \quad \lambda_4 \rightarrow 4\alpha(T - T_c). \quad (3.2)$$

Non-monotone change of  $\lambda_{2-4}$  appears also in the volume scale as temperature is kept fixed: for  $T < T_c$  eigenvalues have minimum for finite sample which shifts to larger volumes and becomes deeper when  $T \rightarrow T_c$ .

The behavior of eigenvalues in finite systems has another interesting property. At critical temperature  $T_c$  we obtain the universal volume independent ratios

$$R_\chi = \frac{\lambda_3}{\lambda_1} \simeq 6.04, \quad (3.3)$$

$$R_C = \frac{\lambda_4}{\lambda_2} \simeq 2.86. \quad (3.4)$$

In fact, for glasses the close values were found for  $\alpha$ - and  $\beta$ -relaxation [111].

According to the phenomenological finite size scaling theory [100–103], any thermodynamic property of  $M$  has its scaling form at fixed system size  $L$

$$M_L(T) = L^{\gamma_M/\nu} M_0\left(\frac{T - T_c}{T_c} L^{1/\nu}\right), \quad (3.5)$$

where  $\gamma_M$  is the corresponding critical exponent,  $\nu$  is the critical exponent of the correlation length, and  $M_0$  is the finite-size scaling function. Note also that the subsidiary scaling hypothesis  $r_{cL} \simeq LX(L/r_c)$ , where  $r_{cL}$  is the correlation length in the actual finite-size system, reconciles the role of the variable  $L/r_{cL}$  with the original hypothesis of phenomenological finite-size scaling about the role of  $L/r_c$  [112].

The finite-size studies indicate that the structure of the finite-size scaling functions  $M_0$  is most interesting below the critical temperature  $T_c$  where these functions have characteristic maxima [113–116]. The location of peaks in quantity  $M_L$  can be used to determine the critical temperature of a finite system  $T_{cL}$ . As far as one accepts the assertion that the only criterion determining the finite-size scaling effects in the critical region is  $r_c \sim L$ , one obtains

$$T_{cL} = T_c - BL^{-\frac{1}{\nu}}, \quad (3.6)$$

where  $B$  is a non-universal positive constant. Following Fig. 1 one can conclude that symmetry is restored in finite samples as soon as the relaxation rate  $\lambda_1$  becomes nonzero. However, this happens simultaneously with approaching the minimal value of  $\lambda_{2-4}$  (maximal value of relaxation time  $1/\lambda_{2-4}$ ) as temperature increases. The latter circumstance essentially indicates the transition point in spatially restricted system. We will be interested in the temperatures at which the relaxation rates  $\lambda_{2-4}$  take their minimal value, reflecting in such a way a slow-down effect for the given dimension of the sample. We will also associate these temperatures with finite-sample (pseudo)critical temperatures  $T_{cL}$ . The typical dependence of the temperature  $T_{cL}$  on the linear size of the system  $L = V^{1/3}$  is illustrated in Fig. 2. As the volume of the sample decreases, the transition temperature decreases. This allows us to estimate the exponent  $\nu \approx \frac{2}{3}$ . The latter can be also obtained by using hyperscaling relation in three dimensional case [24]. In fact, in the Gaussian approximation which incorporates the spatial variance of fluctuations, but neglects interwell motions in the non-equilibrium free energy landscape, one has  $\nu = \frac{1}{2}$  (see Eq. (1.31)). Thus, in the present approach one can construct the quantity being an analog of the correlation length  $r_c$ . This length

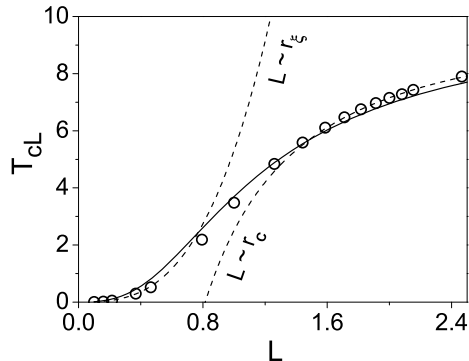


Figure 2: The plot of the (pseudo)critical temperature  $T_{cL}$  vs the linear dimension of the system  $L = V^{1/3}$  for  $\alpha = 1$  (points). The bulk transition temperature is  $T_c = 10$ . The left dashed line is determined by the condition  $L \sim r_{\xi}(T_{cL})$ , the right dashed line by the condition  $L \sim r_c(T_{cL})$ , i.e. by Eq. (3.6). The solid line corresponds to Eq. (3.8).

scale determines the behavior of the temperature  $T_{cL}$  in the sufficiently large samples. However, in small samples the shift equation (3.6) breaks down as shown in Fig. 2 and the critical size  $(T_c/B)^{-\nu}$  does not appear. This is caused by the appearance of another length scale  $r_{\xi}$  in sufficiently small systems. In the present model, the critical temperature behaves in sufficiently small systems as  $T_{cL} \sim L^3$ . This excludes the existence of a finite critical size of the sample and  $T_{cL}$  remains non-zero for arbitrary finite sizes. The latter result is not surprising because the present scheme does not take into account the main factors responsible for a finite critical size [12, 14]. Nevertheless, it predicts suppression of the ordering as the volume of the sample decreases enacted solely by thermodynamics of the system and ignoring all boundary effects. It has to be noted that corrections [117, 118] to Eq. (3.6) do not predict the calculated dependence of the critical temperature  $T_{cL}$  on size  $L$ .

The approximate solution for the transition temperature  $T_{cL}$  can be derived from the condition of competition between activation energy and thermal energy

$$\tilde{F}(0) - \tilde{F}(\eta)_{\min} \sim \frac{T}{V}, \quad (3.7)$$

where  $\tilde{F}(0) - \tilde{F}(\eta)_{\min} = a^2/4$  is the barrier height of non-equilibrium free energy density (1.10) below  $T_c$ . This relation also follows from the analysis of the characteristic features for the potential (2.52), and is depicted in Fig. 2. One can see good agreement with numerically obtained points. At the same time the above criterion has the same structure as the Ginzburg-Levanyuk criterion (1.32) and it simply states that behavior similar to phase transition occurs in finite system when stationary probability density redistributes between essential bi- and monostable structures. This redistribution appears as a result of the order parameter fluctuations which increase with temperature. The condition (3.7) may also be interpreted as

$$L \sim r_{\xi}(T_{cL})r_c(T_{cL}), \quad (3.8)$$

where  $r_c(T) \sim (T_c - T)^{-2/3}$  has the meaning of the correlation length in the ordered phase and  $r_{\xi}(T) \sim T^{1/3}$ . The phase transition in sufficiently large samples ( $T_{cL} \sim$

$T_c$ ) is then determined by the condition  $L \sim r_\xi(T_c)r_c(T_{cL}) \sim r_c(T_{cL})$ . However, in smaller systems ( $T_{cL} \sim 0$ ) the critical behavior is driven by the thermal fluctuations and  $L \sim r_\xi(T_{cL})r_c(0) \sim r_\xi(T_{cL})$ . This essentially reflects the competition between two characteristic length scales on the critical behavior in the spatially restricted samples. The crucial role of the correlation length  $r_c$  in large systems has to be devolved to the length  $r_\xi$  in small samples. The latter length scale appears as a consequence of the stochastic nature of the order parameter in small systems.

One can also incorporate the critical size to the present model by taking into account the surface-affected layer [119, 120]. Assuming the passive surface layer [121] is connected with a homogenous core, one can estimate the layer thickness, for instance, as the extrapolation length  $r_{\partial V}$  appearing in the Landau-Devonshire theory with surface term [122, 123]. The physical interpretation of  $r_{\partial V}$  depends on the nature of the layer. This consideration leads to the formal transformation of the noise intensity  $\frac{T}{V} \rightarrow \frac{T}{V-r_{\partial V}^3}$  and guarantees a complete suppression of the ordering below some critical dimension. In this case the condition (3.8) takes the form

$$(V - r_{\partial V}^3) \sim r_\xi^3 r_c^3, \quad (3.9)$$

where  $V$  is the volume of the system (core and surface layer). Thus, in the macroscopic sample  $V \gg r_{\partial V}^3$  the phase transition occurs when  $L \sim r_c$ , but in the vicinity of critical size  $V \sim r_{\partial V}^3$  the transitional behavior is determined by the condition  $(V - r_{\partial V}^3) \sim r_\xi^3$ , i.e. by the length  $r_\xi$ . We believe that present model may be of relevance for the description of the size dependent peculiarities of the critical temperature, for instance, in ferroelectric particles [106–108, 124].

### 3.2 Dynamic susceptibility in finite systems

The response of the bulk order parameter to the applied field exhibits well-known anomalous behavior in the vicinity of the phase transition temperature (see Eq. (1.17)). At the same time, the internal noise in the finite sample, which leads to the stochastic behavior of the order parameter, can interact with nonlinearity of the system. The phenomenon of stochastic resonance [20, 125–127] is the consequence of this interaction: the response of the non-linear system to the weak external field can be considerably enhanced by the increase of the noise intensity and it reaches the maximum at optimal noise level. We will demonstrate that the anomaly of susceptibility at the phase transition point described by the Landau phase transition theory transforms into maximal response caused by stochastic resonance if the volume of the system decreases. This crossover reflects the size dependent competition between intrawell relaxation and interwell hopping dynamics of the order parameter under applied weak force.

We start with non-equilibrium free energy density (1.10) which determines the stationary probability density (1.33) for the order parameter  $\eta$ . In accordance with Eq. (2.48), the correlation function for  $\eta(t)$  reads in steady state as

$$K(t) = \langle \eta(t)\eta(0) \rangle \simeq g_1 e^{-\lambda_1 t} + g_3 e^{-\lambda_3 t}, \quad (3.10)$$

where  $\lambda_{1,3}$  are the first and third eigenvalues of the Fokker-Planck operator (1.38). The coefficients  $g_{1,3}$  are generally defined in Eqs. (2.49)-(2.50). Due to the symmetry of  $\tilde{F}(\eta)$  the zeroth eigenfunction of the Fokker-Planck operator  $\psi_0(\eta) = P_{eq}(\eta)$

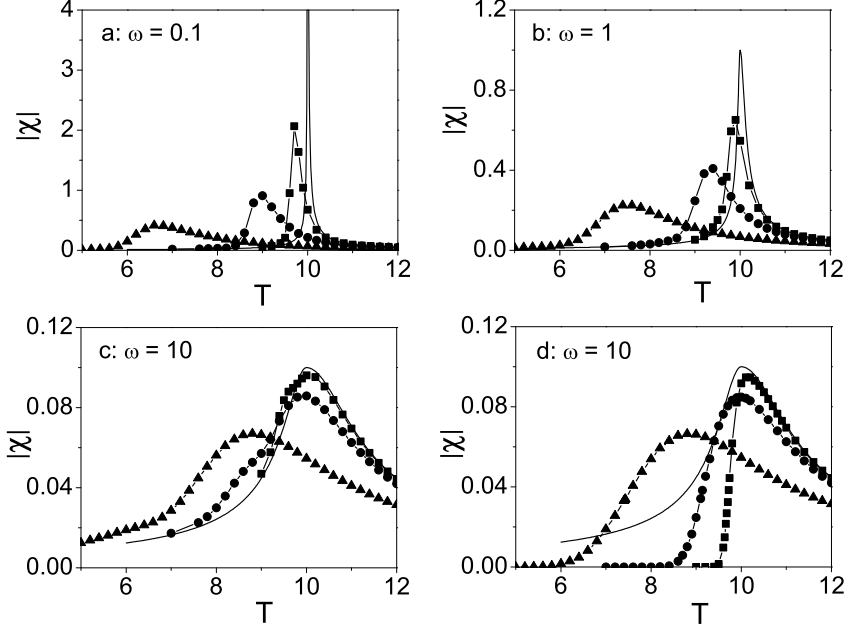


Figure 3: The plots of the modulus of susceptibility vs temperature at frequencies  $\omega = 0.1$  (a),  $\omega = 1$  (b),  $\omega = 10$  (c, d) for various volumes  $V = 0.1$  (triangles),  $V = 1$  (circles),  $V = 10$  (squares) and the bulk limit (solid lines without symbols). In Fig. (d) only interwell dynamics is taken into account for finite systems.

is even function, the first eigenfunction  $\psi_1(\eta)$  is odd and so on. It implies that only terms with odd eigenvalues contribute to the correlation function (3.10). The same eigenvalues define the order parameter relaxation, see Eq. (2.9). Following Ref. [125], the coefficients  $g_{1,3}$  can be obtained from the correlation function and its derivative at  $t = 0$ . By using Eq. (2.35) we get

$$K(t=0) = \int_{-\infty}^{\infty} \eta e^{L_{FP} t} \eta P_{eq}(\eta) d\eta = \langle \eta^2 \rangle \equiv g_1 + g_3, \quad (3.11)$$

$$\begin{aligned} \dot{K}(t=0) &= \int_{-\infty}^{\infty} (L_{FP}^\dagger \eta) e^{L_{FP} t} \eta P_{eq}(\eta) d\eta = -a(T) \langle \eta^2 \rangle - \langle \eta^4 \rangle \\ &\equiv -\lambda_1 g_1 - \lambda_3 g_3. \end{aligned} \quad (3.12)$$

Therefore,

$$g_3 = \frac{(\lambda_1 - a(T)) \langle \eta^2 \rangle - \langle \eta^4 \rangle}{\lambda_1 - \lambda_3}, \quad (3.13)$$

$$g_1 = \langle \eta^2 \rangle - g_3. \quad (3.14)$$

Using fluctuation-dissipation relation (2.14) we find the expression for the complex susceptibility in finite system

$$\chi(\omega) = \chi(0) \left( \frac{g_1}{g_1 + g_3} \frac{\lambda_1}{\lambda_1 + i\omega} + \frac{g_3}{g_1 + g_3} \frac{\lambda_3}{\lambda_3 + i\omega} \right), \quad (3.15)$$

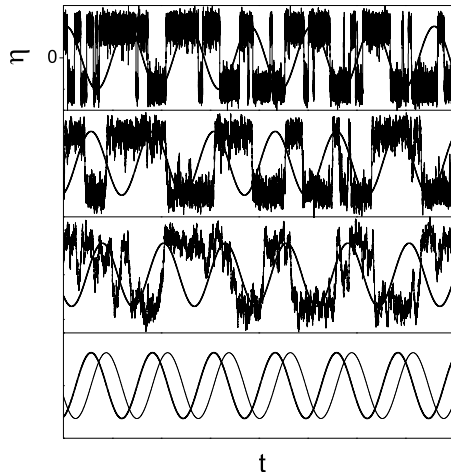


Figure 4: The temporal realization of the order parameter for various volumes (from top to bottom)  $V = 0.1$ ,  $V = 10$ ,  $V = 200$ , and  $V = \infty$  (bulk limit). For each volume the temperature is taken to produce the maximal response (maximal value of the modulus of the susceptibility) to the small external field (thick periodic curves) with  $\omega = 0.1$ . For convenience of the data presentation the field amplitude is appropriately renormalized.

where  $\chi(0) = \frac{V}{T}(g_1 + g_3)$  and  $\omega$  is the frequency of the applied periodic field influencing the order parameter. In finite system the term proportional to the coefficient  $g_1$  describes the contribution from the interwell or hopping dynamics with the characteristic rate  $\lambda_1$ , and the term proportional to the coefficient  $g_3$  describes the contribution from the intrawell or local dynamics with the corresponding characteristic rate  $\lambda_3$  in the bistable regime. In the bulk limit, the characteristic time  $\lambda_1^{-1}$  diverges below  $T_c$ , reflecting the fact that  $\lambda_3^{-1}$  governs the leading time dependence of the autocorrelation function (3.10) in large system below  $T_c$ . Above  $T_c$  this characteristic time represents only a subleading relaxation channel. The relaxation times exhibit substantial changes as the volume of the system decreases, however, the minimum of  $\lambda_3$ , appearing as soon as the relaxation rate  $\lambda_1$  becomes nonzero, remains an essential feature of the relaxation phenomena in finite samples (see Fig. 1).

The dependence of susceptibility (3.15) on temperature for various volumes and frequencies is displayed in Fig. 3. As one can see, the resonant maximum of  $|\chi(\omega)|$  shifts to higher temperatures if the volume increases, approaching asymptotically the response anomaly at the phase transition point  $T_c$  in the infinite volume limit. According to the Landau theory, in the latter limit the temperature and frequency dependencies of  $\chi$  are given by the following relations

$$\chi(\omega) = \begin{cases} \frac{1}{\lambda_1 + i\omega}, & T > T_c \\ \frac{1}{\lambda_3 + i\omega}, & T < T_c \end{cases}, \quad (3.16)$$

where one must choose  $\lambda_1 = \alpha(T - T_c)$  if  $T > T_c$ , and  $\lambda_3 = 2\alpha(T_c - T)$  if  $T < T_c$ . To obtain this expressions from Eq. (3.15) one has to compute the weak noise limit, evaluating the moments  $\langle \eta^n \rangle$  by means of parabolic cylinder

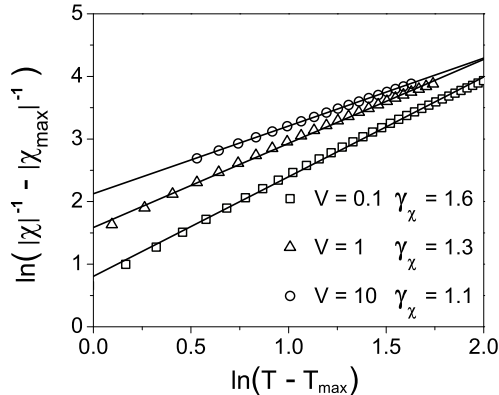


Figure 5: The logarithmic plot of the reciprocal susceptibility  $|\chi(\omega, T)|^{-1} - |\chi(\omega, T_{\max})|^{-1}$  measured at frequency  $\omega = 1$  as a function of  $T - T_{\max}$  for various volumes  $V = 0.1$  (squares),  $V = 1$  (triangles), and  $V = 10$  (circles) with fitted to the Eq. (3.17) solid lines. The slope determines the critical exponent  $\gamma_\chi$ .

functions [128]. The transformation of the response maximum with volume is caused by the competition between the interwell and intrawell processes. This competition is observable from the comparison of cases (c) and (d) in Fig. 3. The main contribution to the response maximum for larger systems (lower noise intensity) stems from the intrawell relaxation, but for smaller volumes (higher noise intensity) the interwell dynamics dominates. As a result, in smaller systems the phenomenon of stochastic resonance takes place where the order parameter hopping processes become synchronized with weak periodic field (Fig. 4). An increase in the frequency leads to the lowering and broadening of the maxima of susceptibility together with the rise of the resonant temperature.

Thus, there is a crossover from the stochastic resonance in a small sample to the usual second-order phase transition anomaly in a macroscopic system. These phenomena, both characterized by enhanced sensitivity to the external field, are complementary to each other in the present model.

Stochastic resonance with an external source of noise was experimentally observed in ferroelectrics, for example, triglycine sulfate [129, 130]. However, let us look at the relaxor [131] and ceramic [132–136] ferroelectrics. In these materials the ferroelectric transition becomes increasingly diffuse with a decrease in grain size. A diffuse phase transition is usually characterized by the following features: a broadening in the maxima of the  $\chi$ - $T$  curves, relatively large separation in temperature scale between the real and imaginary parts of the susceptibility maxima, a deviation from the Curie-Weiss law in the vicinity of the transition temperature, frequency dispersion of the susceptibility and some others. All these signatures are realized in the present model if one considers the finite sample. The quantitative measure of the diffuseness of the phase transition can be estimated using the following equation for  $T > T_{\max}$  ( $T_{\max}$  corresponds to the peak in  $|\chi(\omega)|$ ) [134–139]

$$|\chi(\omega, T)|^{-1} - |\chi(\omega, T_{\max})|^{-1} = D(T - T_{\max})^{\gamma_\chi}, \quad (3.17)$$

where  $D$  is a constant and the critical exponent  $\gamma_\chi = 1$  for a classical Curie-Weiss ferroelectric,  $\gamma_\chi = 2$  for the system with a completely diffuse phase transition, and

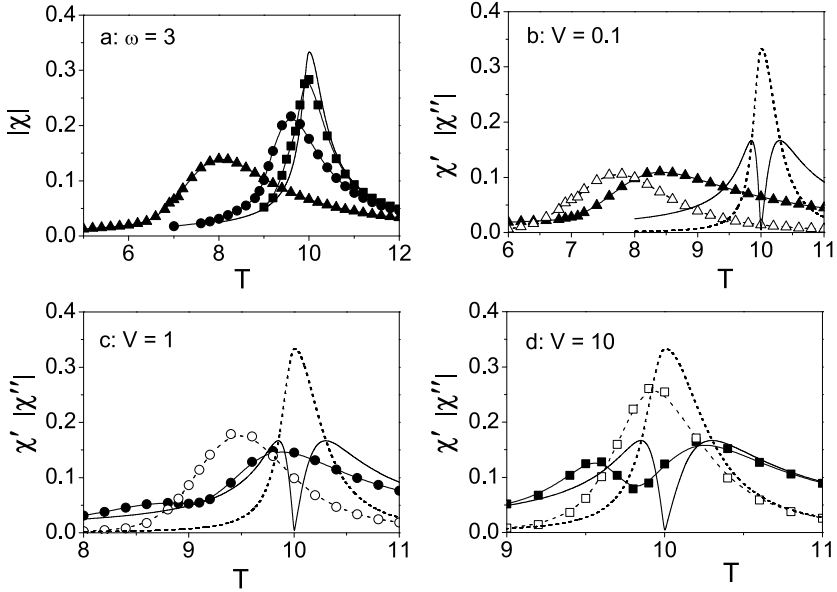


Figure 6: The plots of the susceptibility vs temperature at frequency  $\omega = 3$  for various volumes  $V = 0.1$  (a, b: triangles),  $V = 1$  (a, c: circles),  $V = 10$  (a, d: squares) and the bulk limit (a-d: curves without points). In Figs. (a-d) the modulus of the susceptibility (a), its real part (b-d: solid curves and filled points) and imaginary part (b-d: dashed curves and empty points) are displayed.

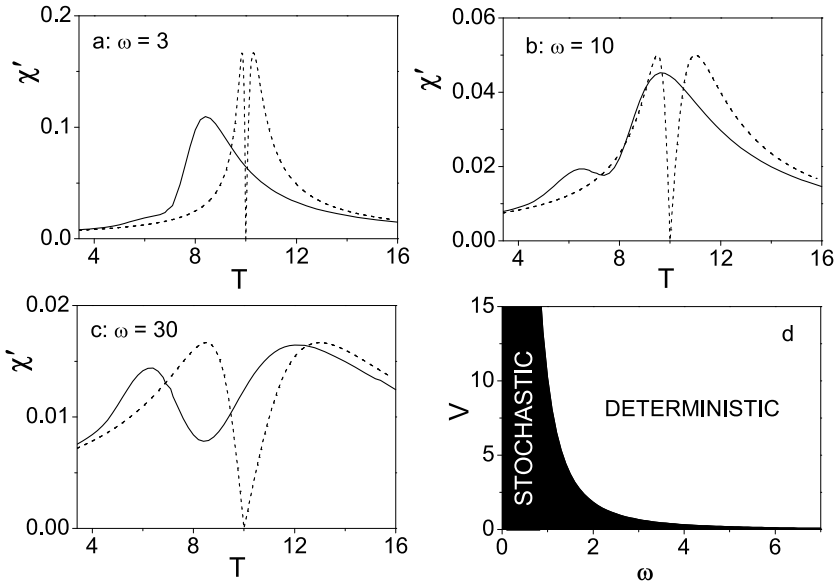


Figure 7: The plots of real part of the susceptibility vs temperature at various frequencies  $\omega = 3$  (a: solid curve),  $\omega = 10$  (b: solid curve) and  $\omega = 30$  (c: solid curve) for the sample with  $V = 0.1$ . In Figs. (a-c) the bulk limit is depicted by dashed curves. In Fig. (d) the borderline between stochastic and deterministic behavior is plotted in  $V$ - $\omega$  space.

for systems with intermediate degrees of diffuseness  $1 < \gamma_\chi < 2$ . As follows from Fig. 5, the critical exponent  $\gamma_\chi$  decreases in our model with dimension increase pointing to the well-known experimental fact that a sharp phase transition can occur only in the thermodynamical limit, getting smeared in the finite system. Thus, we believe that stochastic resonance may be of relevance for the dielectric constants measurements in these types of materials reproducing the observed diffuseness of the phase transition. Moreover, these experiments may be thought to evidence that in small samples the order parameter becomes unavoidably a stochastic variable.

The size induced crossover from stochastic to deterministic response is clearly seen also in the behavior of real and imaginary parts of susceptibility (Fig. 6). In the region of pure stochastic response the real part of the susceptibility has only one maximum. However, three extrema of the real part appear as the volume increases. Real and imaginary parts of the susceptibility approach in the bulk limit their deterministic values predicted by the Landau theory. Similar behavior is stated also in the frequency space for fixed volume of the system. Thus, the borderline between pure stochastic and deterministic-like response of the finite system appears in the  $V$ - $\omega$  diagram (Fig. 7).

The discussed above crossover of the response behavior in the spatially restricted sample may also be illustrated in terms of relaxation characteristics. One can rewrite expression (3.15) in the Debye form

$$\chi(\omega) = \frac{d(\omega)}{\lambda(\omega) + i\omega}, \quad (3.18)$$

where  $d(\omega) = -\omega(\chi'{}^2 + \chi''{}^2)/\chi''$  and  $\lambda(\omega) = -\omega\chi'/\chi''$  are temperature and frequency dependent quantities determined by the real  $\chi'$  and imaginary  $\chi''$  parts of the susceptibility (3.15). The frequency dependence appears due to multiple relaxation mechanism with rates  $\lambda_1$  and  $\lambda_3$ . In the high frequency limit  $d \rightarrow 1$  and the relaxation rate  $\lambda$  takes the form

$$\lambda_\infty = \frac{g_1\lambda_1^2 + g_3\lambda_3^2}{g_1\lambda_1 + g_3\lambda_3}. \quad (3.19)$$

According to this equation, the high frequency relaxation rate has the minimum near the phase transition temperature  $T_c$  (Fig. 8). This relaxation rate takes into account only fast intrawell processes. Thus, in the high frequency limit Eq. (3.18) generates essentially the deterministic-like response. The deviation from Eq. (3.16) is mainly due to finite size effect on the relaxation rate. Similar peculiarities of the high frequency relaxation were recently established in various ceramic ferroelectrics, see, for instance, [140–146].

In the low frequency limit the response of finite system has stochastic nature. In this situation the relaxation rate  $\lambda$  passes through a broad frequency dependent minimum in the temperature scale (Fig. 8), and the coefficient  $d$  exhibits non-monotone temperature behavior. While the eigenvalue  $\lambda_1$  is non-zero, the low frequency relaxation rate coincides with  $\lambda_1$ . This feature reflects the essential role of the interwell processes in the corresponding temperature and frequency domain, and enhanced sensitivity to the external field is caused here by the phenomenon of stochastic resonance. However, at low temperatures, where  $\lambda_1 = 0$ , the relaxation

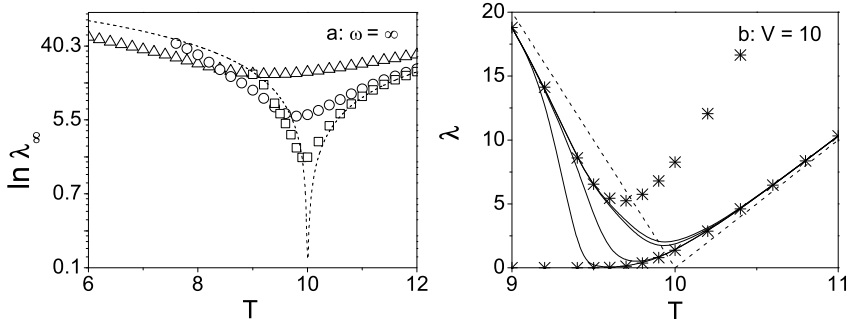


Figure 8: (a) The logarithmic plots of the high frequency relaxation rate  $\lambda_\infty$  vs temperature for  $V = 0.1$  (triangles),  $V = 1$  (circles) and  $V = 10$  (squares). The dashed curve corresponds to the macroscopic limit. (b) The plots of the frequency dependent relaxation rate  $\lambda$  vs temperature at various frequencies  $\omega = 0.1$ ,  $\omega = 1$ ,  $\omega = 10$  and  $\omega = \infty$  (solid curves: from bottom to top) for the system with  $V = 10$ . The dashed curve represents the macroscopic limit. Points correspond to the eigenvalues  $\lambda_1$  and  $\lambda_3$  ( $\lambda_3 > \lambda_1$ ).

rate  $\lambda$  approaches the value  $\lambda_3$ . This leads to the remarkable change in slope of  $\lambda$  near the corresponding (pseudo)critical region as compared with its high frequency or bulk limit. Similar peculiarities were also experimentally established in ceramic ferroelectrics [144–146].

It is interesting to note, that at  $T_c$  the ratio of the high frequency and low frequency relaxation rates in finite systems is also volume independent

$$R = \frac{\lambda_\infty}{\lambda_1} \simeq 1.46. \quad (3.20)$$

The latter relation may be checked in the relaxation experiments.

Finally, in addition to the resonance of the response driven by temperature, the existence of the system size resonance in the present scheme is illustrated in Fig. 9. As one can see, the dynamic susceptibility behaves resonantly when the dimension increases. A similar phenomenon was recently established in various ferroelectric systems both experimentally and theoretically, e.g., see Refs. [147–152] and references therein. However, in the present scheme the sharp maximum of the susceptibility in the low-volume region is the consequence of the size stochastic resonance [147, 153–155], relating the latter phenomenon to the existence of the critical dimension below which the ordering vanishes. In this region, the susceptibility is very sensitive to the frequency of the applied field and an effect of the size stochastic resonance is supported by its smaller values. As temperature increases the maximum of the susceptibility moves to larger volumes and broadens. In the large-volume region the role of the interwell dynamics and size stochastic resonance are suppressed. The main cost to the susceptibility stems from the intrawell processes (Fig. 9), and the asymptotic behavior is given by Eq. (3.16). As frequency increases, the response becomes indistinguishable from deterministic one, once more suggesting the crossover between stochastic and deterministic behavior.

The susceptibility analysis presented here shows that one can separate both temperature and volume scales into three zones. There are the intrawell vibrations,

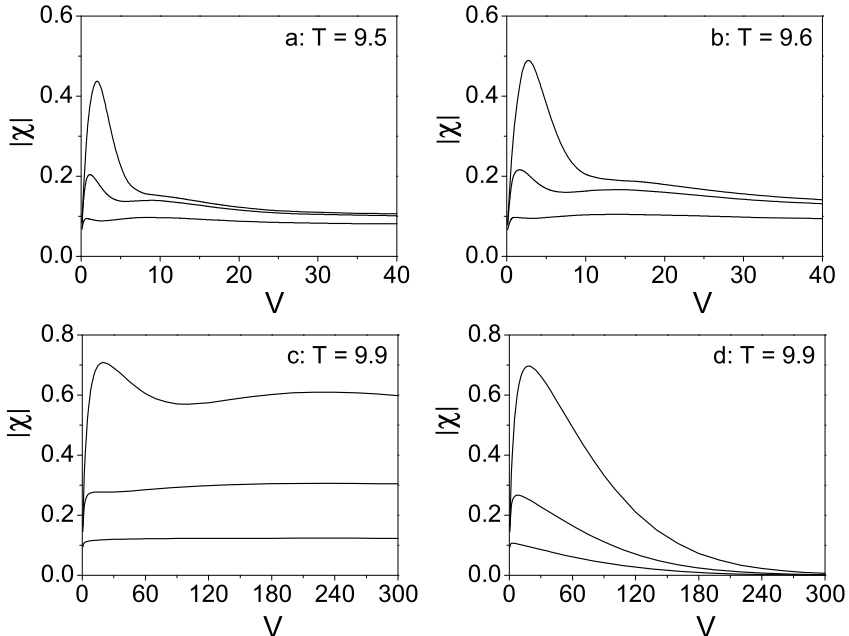


Figure 9: The plots of the modulus of susceptibility vs the volumes at fixed temperatures  $T = 9.5$  (a),  $T = 9.6$  (b),  $T = 9.9$  (c, d) for various frequencies  $\omega = 1$ ,  $\omega = 3$ ,  $\omega = 8$  (from top to bottom on each figure). In Fig. (d) only interwell dynamics is taken into account.

interwell transitions, and "one-well" response (these terms are taken from Ref. [156]). The left-hand side of the maximum in Fig. 9a corresponds to the "one-well" response. In this region, a bistable system behaves effectively as a monostable one and the susceptibility is governed mostly by its real part. The interwell transitions manifest themselves in the right-hand side of the maximum. The resonant behavior of the imaginary part is responsible for the formation of susceptibility in this region, relating it to the maximal usage of the external field energy. The plateau of the response is related to the intrawell vibrations, because for sufficiently large volumes the wells in the bistable potential do not "sense" each other. In this case, the susceptibility is governed by its real part. Similar scale separation holds also for the temperature dependent response (see, for instance, Fig. 3), but only in the reverse order.

### 3.3 Dynamic heat capacity in finite systems

In this section we study the peculiarities of the dynamic heat capacity associated with the order parameter distributed in the potential (1.10). We assume that temperature is homogeneous in all parts of the sample considered.

The equilibrium properties of the system are determined by the partition function (1.8) and the internal energy difference  $\Delta E = \langle \Delta \varepsilon \rangle$  is given by

$$\Delta \varepsilon = V \left( -\frac{1}{2} \alpha T_c \eta^2 + \frac{1}{4} \eta^4 \right) \quad (3.21)$$

with  $\langle \dots \rangle = \int_{-\infty}^{\infty} \dots P_{eq}(\eta) d\eta$ . For the static heat capacity difference  $\Delta C(\omega = 0)$  we correspondingly have

$$\Delta C(0) = \frac{\partial}{\partial T} \Delta E = \frac{1}{T^2} (\langle \Delta \varepsilon^2 \rangle - \langle \Delta \varepsilon \rangle^2). \quad (3.22)$$

The latter expression defines the well-known proportionality between heat capacity in the constant volume case and dispersion of the internal energy.

To obtain the frequency dependent heat capacity given by Eq. (2.32), we have to find the appropriate correlation functions for  $\eta^n$  with  $n = 2, 4$  by using Eq. (2.48). Again, due to symmetry of  $\tilde{F}(\eta)$  the stationary probability density  $P_{eq}(\eta) = \psi_0(\eta)$  is an even function of  $\eta$  and the parity of  $\psi_i(\eta)$  alternates. As a result, odd terms do not contribute to expansion (2.48) and we have

$$K_{2n,2m}(t) \equiv \langle \eta^{2n}(t) \eta^{2m}(0) \rangle - \langle \eta^{2n} \rangle \langle \eta^{2m} \rangle \simeq g_{n,m} e^{-\lambda_2 t} + h_{n,m} e^{-\lambda_4 t}. \quad (3.23)$$

Note that the expansion (2.48) stops after certain term, strictly speaking, only for harmonic potential. By using relations similar to Eqs. (3.11) and (3.12), one obtains

$$K_{2n,2m}(t=0) = \langle \eta^{2n+2m} \rangle - \langle \eta^{2n} \rangle \langle \eta^{2m} \rangle \equiv g_{n,m} + h_{n,m}, \quad (3.24)$$

$$\begin{aligned} \dot{K}_{2n,2m}(t=0) &= -2n \left\langle \frac{\partial \tilde{F}(\eta)}{\partial \eta} \eta^{2n+2m-1} \right\rangle + \frac{T}{V} 2n(2n-1) \langle \eta^{2n+2m-2} \rangle \\ &\equiv -\lambda_2 g_{n,m} - \lambda_4 h_{n,m}. \end{aligned} \quad (3.25)$$

Therefore,

$$g_{n,m} = \langle \eta^{2n+2m} \rangle - \langle \eta^{2n} \rangle \langle \eta^{2m} \rangle - h_{n,m}, \quad (3.26)$$

$$h_{n,m} = \frac{\dot{K}_{2n,2m}(t=0) + \lambda_2 (\langle \eta^{2n+2m} \rangle - \langle \eta^{2n} \rangle \langle \eta^{2m} \rangle)}{\lambda_2 - \lambda_4}. \quad (3.27)$$

Using above equations, we obtain the frequency dependent heat capacity difference by means of the fluctuation-dissipation theorem (2.30), namely,

$$\Delta C(\omega) = \Delta C(0) \left( \frac{g_2}{g_2 + g_4} \frac{\lambda_2}{\lambda_2 + i\omega} + \frac{g_4}{g_2 + g_4} \frac{\lambda_4}{\lambda_4 + i\omega} \right), \quad (3.28)$$

where

$$g_2 = \alpha^2 T_c^2 \frac{g_{1,1}}{4} - \alpha T_c \frac{g_{1,2} + g_{2,1}}{8} + \frac{g_{2,2}}{16}, \quad (3.29)$$

$$g_4 = \alpha^2 T_c^2 \frac{h_{1,1}}{4} - \alpha T_c \frac{h_{1,2} + h_{2,1}}{8} + \frac{h_{2,2}}{16}. \quad (3.30)$$

The static heat capacity difference may be expressed in terms of  $g_2$  and  $g_4$  as  $\Delta C(0) = \frac{V^2}{T^2} (g_2 + g_4)$ .

The frequency dependent heat capacity (3.28) indicates that generally for the symmetric (even) potential the time scales of the energy relaxation are defined by the even eigenvalues of the Fokker-Planck operator. For harmonic potential only the second eigenvalue of the appropriate Fokker-Planck operator contributes to the relaxation process [58]. For the asymmetric (odd) potential the non-zero time

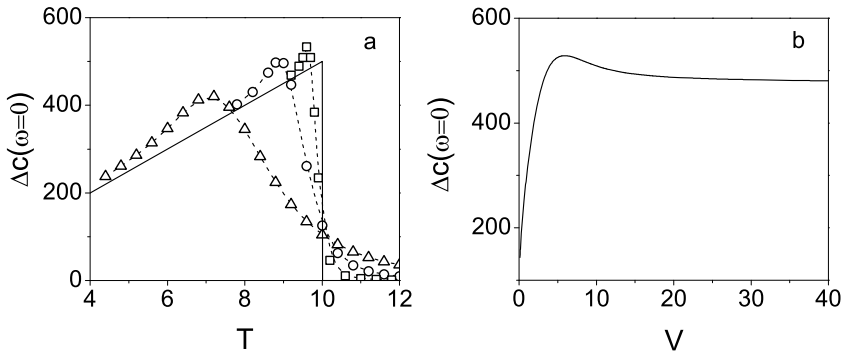


Figure 10: The plots of the static specific heat capacity difference  $\Delta c(0)$  vs temperature  $T$  (a) for various volumes  $V = 0.1$  (triangles),  $V = 1$  (circles),  $V = 10$  (squares),  $V \rightarrow \infty$  (solid curve) and vs volume  $V$  (b) for fixed temperature  $T = 9.5$ .

correlations  $K_{2n+1,m}(t)$  appear. This implies that the odd part of the spectrum  $\{\lambda_i\}$  will be also involved to the energy relaxation. Thus, the frequency dependent heat capacity provides an insight into the symmetry of the reduced free energy  $\tilde{F}$  and internal energy  $\varepsilon$ . In contrary to the prediction our model makes on the energy relaxation, it is rather the dominance of the lowest odd eigenvalues (e.g.,  $\lambda_1, \lambda_3$ ) that has been obtained for the order parameter relaxation. While the order of glass transition is still under discussions (see, for instance, Refs. [48, 157–159]), very similar suggestions were recently made for glassy dynamics described by the two-level model [160, 161]. Namely, if one visualizes the  $\beta$ -processes originating from activated dynamics within a metabasin, while escape from one metabasin to another is taken to describe an  $\alpha$ -process, then for a symmetric double well only the  $\beta$ -peak appears in the frequency spectrum of the imaginary part of the dynamic heat capacity. However, it is rather the predominance of the  $\alpha$ -peak that has been observed for the dielectric relaxation.

Let us analyze the volume dependent peculiarities of the internal energy relaxation and the dynamic heat capacity. In Fig. 10 the static specific heat capacity difference  $\Delta c(0) = C(0)/V$  is illustrated. In the temperature scale this quantity has a volume dependent maximum. As the volume increases,  $\Delta c(0)$  approaches its bulk limit known from the conventional Landau phase transition theory, namely  $\alpha^2 T/2$  for  $T < T_c$  and 0 for  $T > T_c$ . This values follow also from Eq. (3.22). As the temperature is fixed, one can get the enhancement of the static specific heat capacity compared with its bulk value by changing the volume of the system. For temperatures below  $T_c$  the maximum of  $\Delta c(0)$  appears for finite sample. As temperature increases, this maximum shifts to larger volumes approaching the bulk value for  $T = T_c$ . This behavior can be also related to the existence of the critical dimension.

The latter deviations from the Landau-like behavior are essentially stochastic effects. One can relate the (pseudo)critical region with the temperature region where the static specific heat capacity  $\Delta c(0)$  approaches its maximal value. While the internal energy difference itself increases with temperature in ordered phase, its dispersion approaches the maximal value at the corresponding (pseudo)critical temperature. The decrease of the volume leads to the noise driven redistribution

of the probability density (between essentially bi- and monostable structure) at slightly lower temperatures. As a result, one observes the lowering of the critical temperature with volume decrease. The phase transition becomes diffused due to the fluctuational corrections to the Landau-like behavior. Similar effects were revealed also experimentally in ferroelectrics. Here the temperature of the specific heat jump appears to be dependent on the film thickness or particle size and there was a distribution of these temperatures: the width became larger with temperature decrease [162–164]. This size driven behavior is typical for the spatially restricted systems under consideration. Appropriate analysis of the static specific heat in small superconducting particles was also made for the complex order parameter in Ref. [29].

The behavior of the dynamic heat capacity difference (3.28) is determined by the relaxation rates  $\lambda_{2,4}$ . Their bulk values are given by Eqs. (3.1) and (3.2). At the same time, the linearization of  $\Delta\tilde{F}$  above  $T_c$  leads to the harmonic (therefore, symmetric) potential with the second and the fourth eigenvalue given by Eq. (3.2). For the harmonic potential only the second eigenvalue contributes to the dynamic heat capacity, i.e., above  $T_c$  in the bulk limit  $g_2 \neq 0$  and  $g_4 = 0$  in Eq. (3.28). However, the linearization below  $T_c$  leads to the shifted harmonic (asymmetric) potential with the first eigenvalue  $2\alpha(T_c - T)$ . Due to asymmetry the latter governs the leading time dependence in the correlation of the internal energy difference. Thus, below  $T_c$  in the bulk limit  $g_2 = 0$  and  $g_4 \neq 0$  in Eq. (3.28). The computation of the weak noise limit leads to the same results. Therefore, for the bulk dynamic heat capacity the leading time scale is given by  $2\alpha|T_c - T|$  above and below  $T_c$ . In case of bulk susceptibility corresponding time scales are different above and below  $T_c$ , namely,  $2\alpha(T_c - T)$  for  $T < T_c$  and  $\alpha(T - T_c)$  for  $T > T_c$  (see Eq. (3.16)). Consequently, the "law of two" is valid for the order parameter relaxation, but is violated for the energy relaxation.

As the volume increases, the heat capacity contains a contribution (Fig. 1) which relaxes increasingly slowly near the transition temperature leading to longer waiting time for the energy to attain its equilibrium value ( $\omega > \lambda_{2,4}$ ). Therefore, in real measurements the energy response shows a time delay, and one can expect that the complex heat capacity difference contains the information about this slow dynamics. On the other hand, when the relaxation occurs at a rate faster than the probing frequencies  $\omega < \lambda_{2,4}$ , the energy relaxes faster to its equilibrium value and the dynamic heat capacity difference coincides with its usual static value. In this case the modulus of the heat capacity is determined mostly by the real part and its imaginary part is small. Unlike the bulk limit, in finite sample the dynamic heat capacity difference becomes frequency independent at low frequencies  $\omega < \lambda_{2,4}$  due to  $\min \lambda_{2,4} \neq 0$  (Fig. 11). Particularly, it means that in finite sample the energy relaxes faster than the order parameter. As the frequency increases ( $\omega > \min \lambda_2$ ), the (pseudo)critical region of the finite sample contributes to the dynamic capacity. As a result, its imaginary part rapidly increases, while real part tends to decrease. The peak of modulus gets smaller in height and more rounded (see also Refs. [51, 165]). For frequencies  $\min \lambda_2 < \omega < \min \lambda_4$  the overlapping between real and imaginary parts occurs. Further increase in frequencies ( $\omega > \min \lambda_4$ ) leads to the monotone decrease of both parts. The dynamic heat capacity difference for the restricted system becomes almost undistinguishable from its bulk value at high

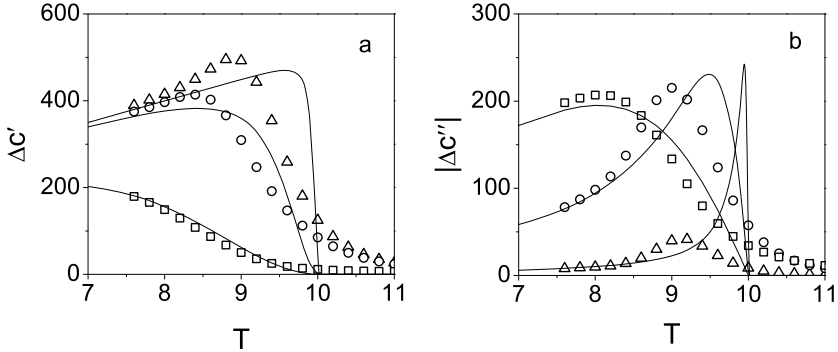


Figure 11: The plots of the real (a) and imaginary part (b) of the dynamic specific heat capacity difference  $\Delta c(\omega)$  vs temperature for  $V = 1$  (points) and  $V \rightarrow \infty$  (solid curves) with frequencies  $\omega = 1$  (triangles),  $\omega = 10$  (circles) and  $\omega = 50$  (squares). For bulk limit the frequency increases from the right curve to the left one.

frequencies. Again, one can conclude that there is a crossover between stochastic and deterministic behavior of the energy response which is supported by the finite minimal value of the energy relaxation rate in spatially restricted samples.

According to the formalism of De Donder-Prigogine-Defay [64], the behavior obtained is the consequence of irreversible thermodynamics near equilibrium in the linear regime. The thermodynamic irreversibility in the evolution of the order parameter is the explanation of the frequency dependent heat capacity, and time-averaged irreversible entropy production is directly proportional to the imaginary part of the complex heat capacity. Thus, as the frequency of the temperature perturbation or volume of the system increases, the thermodynamic irreversibility of the critical region increases. Therefore, the complementarity between stochastic behavior in small systems and deterministic behavior in large systems is accompanied by the crossover between reversible and irreversible thermodynamics of the critical region.

### 3.4 Relaxation channels in two-band superconductors

Multi-component superconductivity models include rather varied physics. In connection with the presence of interacting order parameters, the superconducting ordering, kinetics, and fluctuation properties of the multiband systems are quite different from the corresponding characteristics in one-band superconductors. The examination of these peculiarities has been an object of growing interest. In the present contribution, we focus our attention to the bulk superconducting properties and investigate the relaxation of superconducting order parameters in two-band system. We report the peculiarities of the temperature behavior of the relaxation times characterizing the damping of the deviations of superconducting order parameters from equilibrium in dependence on intra- and interband interactions.

Next, we study the analytical properties of model non-equilibrium free energy

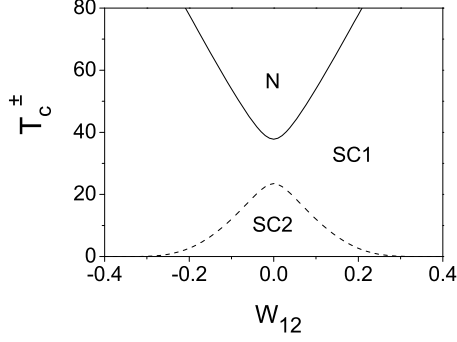


Figure 12: The dependencies of  $T_c^+$  (solid line) and  $T_c^-$  (dashed line) on the interband interaction constant  $W_{12}$ .

(2.68). The equations for the stationary points of  $\tilde{F}(\eta_1, \eta_2)$  are given by

$$\begin{aligned}\eta_1 &= \frac{W_{11}}{2}\eta_1\rho_1\tilde{I}_1(\eta_1) + \frac{W_{12}}{2}\eta_2\rho_2\tilde{I}_2(\eta_2), \\ \eta_2 &= \frac{W_{22}}{2}\eta_2\rho_2\tilde{I}_2(\eta_2) + \frac{W_{12}}{2}\eta_1\rho_1\tilde{I}_1(\eta_1).\end{aligned}\quad (3.31)$$

In the limit, where interband interaction is absent, i.e.  $W_{12} = 0$ , the latter system splits into two independent equations which describe autonomous phase transitions in two bands. The corresponding critical temperatures  $T_{c\alpha}$ ,  $\alpha = 1, 2$ , are determined by the conditions  $W_{\alpha\alpha}\rho_\alpha\tilde{I}_\alpha(0) = 2$  where  $W_{\alpha\alpha} > 0$  (intraband attraction). However, for arbitrary weak interband interaction  $W_{12}^2 < W_{11}W_{22}$ , the temperatures of independent phase transitions  $T_{c1,2}$  transform into critical points  $T_c^\pm$

$$T_c^\pm = 1.13 \frac{\hbar\omega_c}{k_B} e^{-\Theta^\pm}, \quad (3.32)$$

where

$$\Theta^\pm = 2 \left( \rho_1 W_{11} + \rho_2 W_{22} \pm \sqrt{(\rho_1 W_{11} - \rho_2 W_{22})^2 + 4\rho_1\rho_2 W_{12}^2} \right)^{-1}. \quad (3.33)$$

It follows that  $\Theta^+ < \Theta^-$ , consequently,  $T_c^+ > T_c^-$ . The temperature  $T_c^-$  has physical meaning only if  $W_{11}, W_{22} > 0$  and  $W_{12}^2 < W_{11}W_{22}$ . The dependencies of the critical temperatures  $T_c^\pm$  on interband interaction constant  $W_{12}$  are shown in Fig. 12. In this section the following parameters are used:  $W_{11} = 0.7 \text{ eV} \cdot \text{cell}$ ,  $W_{22} = 0.3 \text{ eV} \cdot \text{cell}$ ,  $\rho_1 = 0.5 (\text{eV} \cdot \text{cell})^{-1}$ ,  $\rho_2 = 1 (\text{eV} \cdot \text{cell})^{-1}$ ,  $\hbar\omega_c = 0.05 \text{ eV}$  and  $\text{cell} = 0.1 \text{ nm}^3$ .

There exist two classes of non-trivial solutions of the system (3.31):  $\eta_{1,2}^+ \neq 0$  if  $T < T_c^+$  and  $\eta_{1,2}^- \neq 0$  if  $T < T_c^-$ . One can find [166] that in case of interband repulsion  $W_{12} < 0$  the signs of  $\eta_{1,2}^\pm$  obey the following relations

$$\text{sgn}(\eta_1^+) = -\text{sgn}(\eta_2^+), \quad \text{sgn}(\eta_1^-) = \text{sgn}(\eta_2^-), \quad (3.34)$$

and in case of interband attraction  $W_{12} > 0$

$$\text{sgn}(\eta_1^+) = \text{sgn}(\eta_2^+), \quad \text{sgn}(\eta_1^-) = -\text{sgn}(\eta_2^-). \quad (3.35)$$

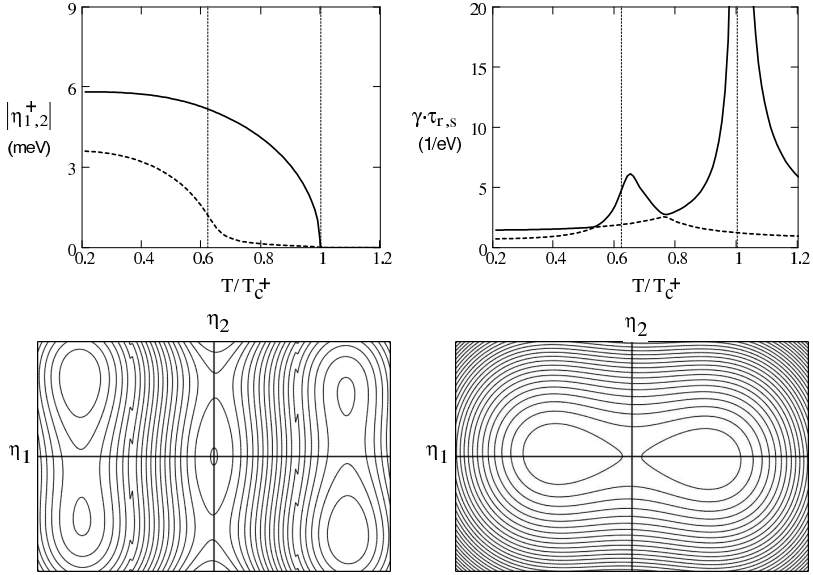


Figure 13: Left upper panel: the dependencies of  $\eta_1^+$  (solid) and  $\eta_2^+$  (dashed) on the reduced temperature  $T/T_c^+$  for  $W_{12} = -0.0018 \text{ eV} \cdot \text{cell}$ . Right upper panel: the corresponding dependencies of  $\gamma\tau_s$  (solid) and  $\gamma\tau_r$  (dashed) on  $T/T_c^+$ . In these figures the critical temperatures  $T_c^- = 23.5 \text{ K}$  and  $T_c^+ = 37.8 \text{ K}$  are depicted by the vertical markers. In the lower panels the contour plots of model free energy density (2.68) are presented for temperatures slightly below  $T_c^-$  (left) and slightly below  $T_c^+$  (right).

Note, that these rules do not determine the signs of the order parameters  $\eta_{1,2}^\pm$  uniquely. The solutions  $\eta_{1,2}^\pm$  define the phase diagram of a bulk two-band superconductor (Fig. 12). Above  $T_c^+$  the superconductor is in the normal (N) state and  $\eta_{1,2}^\pm = 0$ . In the domain  $T_c^- < T < T_c^+$  (SC1) we have a stable superconducting state given by the equilibrium order parameters  $\eta_{1,2}^\pm \neq 0$ . In the region below  $T_c^-$  (SC2), an additional non-zero solutions  $\eta_{1,2}^\pm \neq 0$  of Eqs. (3.31) appear which correspond to a metastable superconducting states (see also [167]) or, at least, to the saddle-points of the free energy density  $\tilde{F}(\eta_1, \eta_2)$ .

In the following we consider the relaxation of small deviations of order parameters  $\Delta\eta_\alpha$  from their equilibrium values  $\eta_\alpha^+$  in the normal and superconducting phases. The corresponding Landau-Khalatnikov equations read as

$$\frac{d\Delta\eta_\alpha}{dt} = - \sum_{\alpha'=1}^2 \gamma_{\alpha\alpha'} \frac{\partial \tilde{F}(\eta_1^+ + \Delta\eta_1, \eta_2^+ + \Delta\eta_2)}{\partial \Delta\eta_{\alpha'}}, \quad (3.36)$$

where  $\gamma_{\alpha\alpha'}$  are the kinetic coefficients. By expanding the model free energy density (2.68) in powers of deviations we linearize the kinetic equations (3.36). As a result, we obtain

$$\frac{d\Delta\eta_\alpha}{dt} = - \sum_{\alpha', \alpha''=1}^2 \gamma_{\alpha\alpha''} \frac{\partial \tilde{F}(\eta_1^+ + \Delta\eta_1, \eta_2^+ + \Delta\eta_2)}{\partial \Delta\eta_{\alpha'} \partial \Delta\eta_{\alpha''}} \Bigg|_{\Delta\eta_{1,2}=0} \Delta\eta_{\alpha'}. \quad (3.37)$$

Using a suitable orthogonal transformation, the latter system decouples into two

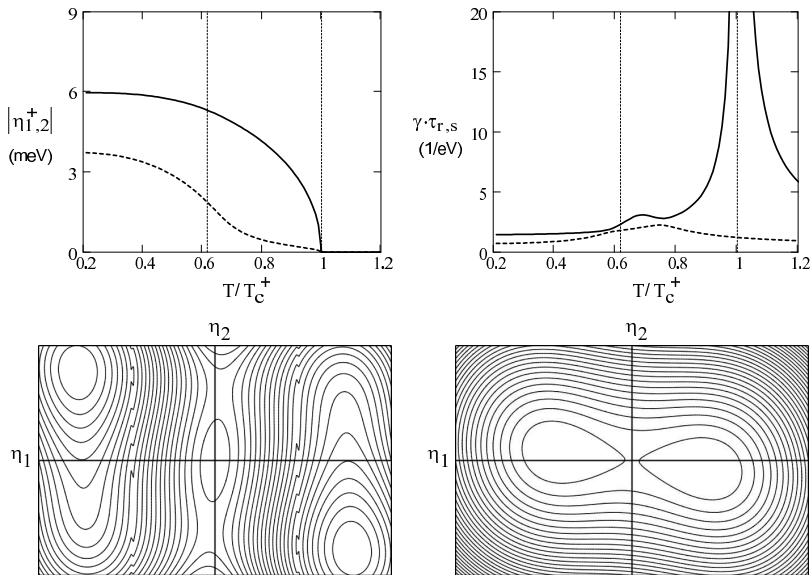


Figure 14: Left upper panel: the dependencies of  $\eta_1^+$  (solid) and  $\eta_2^+$  (dashed) on the reduced temperature  $T/T_c^+$  for  $W_{12} = -0.006$  eV · cell. Right upper panel: the corresponding dependencies of  $\gamma\tau_s$  (solid) and  $\gamma\tau_r$  (dashed) on  $T/T_c^+$ . In these figures the critical temperatures  $T_c^- = 23.4$  K and  $T_c^+ = 37.9$  K are depicted by the vertical markers. In the lower panels the contour plots of model free energy density (2.68) are presented for temperatures slightly below  $T_c^-$  (left) and slightly below  $T_c^+$  (right).

independent equations for the new, noncritical (rigid) and critical (soft) variables

$$\frac{d\Delta\eta_{r,s}}{dt} = -\lambda_{r,s}\Delta\eta_{r,s}. \quad (3.38)$$

Here the relaxation rates  $\lambda_{r,s}$  are the eigenvalues of a matrix based on the proportionality coefficients in Eq. (3.37). These numbers determine the characteristic times  $\tau_{r,s} = 1/\lambda_{r,s}$  for the relaxation of order parameters. Now we present the results of the calculations for the temperature dependencies of  $\tau_{r,s}$  by assuming  $\gamma_{11} = \gamma_{22} = \gamma$  and  $\gamma_{12} = \gamma_{21} = 0$ .

In the absence of interband interaction each of two relaxation times exist in the autonomous one-band system. The critical slowdown appears in the damping of the superconducting ordering near the phase transition temperatures  $T_{ca}$ . However, if an arbitrary weak interband pair-transfer attractive or repulsive interaction is present, the new relaxation channels with characteristic times  $\tau_s$  and  $\tau_r$  are formed (Fig. 13). The soft relaxation time  $\tau_s$  as a function of temperature diverges at the critical point  $T_c^+$  and passes through a maximum in the domain  $T_c^- < T < T_c^+$ . The rigid relaxation channel, characterized by the time  $\tau_r$ , do not exhibit critical slowdown at the phase transition point, but it has a maximum approximately at the same temperature  $T < T_c^+$  where  $\tau_s$  passes through a minimum. In Fig. 13 the temperature dependencies of the equilibrium superconducting gaps and the contour plots of model free energy density  $\tilde{F}(\eta_1, \eta_2)$  near its stationary points are also displayed. In particular, one can see here the formation

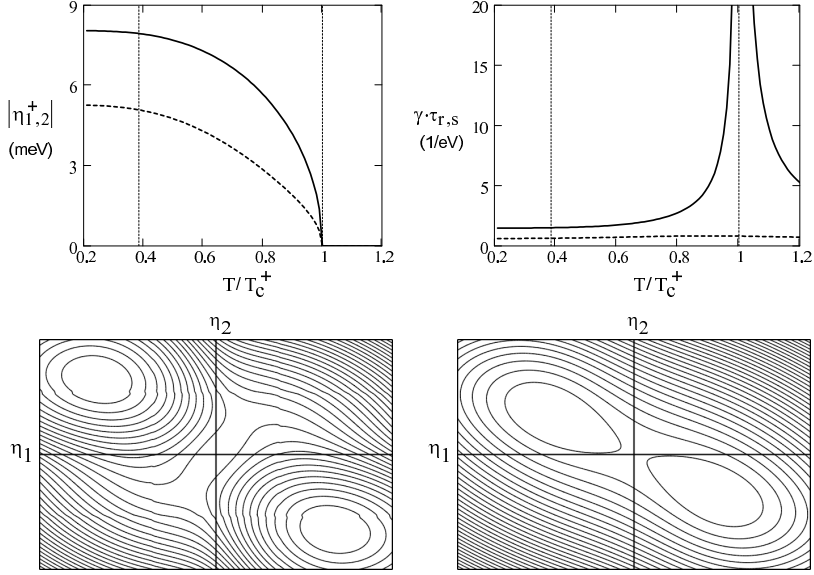


Figure 15: Left upper panel: the dependencies of  $\eta_1^+$  (solid) and  $\eta_2^+$  (dashed) on the reduced temperature  $T/T_c^+$  for  $W_{12} = -0.06$  eV · cell. Right upper panel: the corresponding dependencies of  $\gamma\tau_s$  (solid) and  $\gamma\tau_r$  (dashed) on  $T/T_c^+$ . In these figures the critical temperatures  $T_c^- = 17.5$  K and  $T_c^+ = 45.5$  K are depicted by the vertical markers. In the lower panels the contour plots of model free energy density (2.68) are presented for temperatures slightly below  $T_c^-$  (left) and slightly below  $T_c^+$  (right).

of metastable states below  $T_c^-$ .

The observed temperature behavior of relaxation channels in the superconducting phase ( $T < T_c^+$ ) is sensitive to the strength of interband coupling. As  $|W_{12}|$  increases, the maxima of  $\tau_{s,r}(T)$  are suppressed, cf. Figs. 13 and 14. Finally, one reaches to the characteristic times shown in Fig. 15 (see also [168]). One of these times ( $\tau_s$ ) describes the slowly relaxing component of the order parameters near the phase transition point, decreasing monotonically if temperature moves away from  $T_c^+$ . The other one ( $\tau_r$ ) is practically independent on temperature and characterizes the rapidly relaxing component. In Figs. 13-15 one can also observe the evolution of the temperature behavior of the equilibrium superconducting gaps and the shape of model free energy density  $\tilde{F}(\eta_1, \eta_2)$  as interband interaction increases. We suppose that the peculiarity of relaxation dynamics established here may be of relevance for the interpretation of corresponding experimental data in copper-oxide high- $T_c$  compounds [169–171] and magnesium diboride [172, 173].

Finally, in the vicinity of the transition temperature  $T_c^+$  one can expand the model free energy density (2.68) in powers of  $\eta_\alpha$  and evaluate  $\lambda_{r,s}$  as a function of temperature. As a result, near  $T_c^+$  the leading contributions of the relaxation rates read as

$$\lambda_r = 2\gamma\Theta^+(\rho_1(1 - \rho_1W_{11}\Theta^+) + \rho_2(1 - \rho_2W_{22}\Theta^+)), \quad (3.39)$$

$$\lambda_s = 4\tilde{\gamma} \frac{\rho_1\rho_2 \left(1 - \frac{\Theta^+}{2}(\rho_1W_{11} + \rho_2W_{22})\right)}{\rho_1(1 - \rho_1W_{11}\Theta^+) + \rho_2(1 - \rho_2W_{22}\Theta^+)} \left| \frac{T - T_c^+}{T_c^+} \right|, \quad (3.40)$$

where

$$\tilde{\gamma} = \begin{cases} \gamma, & T > T_c^+ \\ 2\gamma, & T < T_c^+ \end{cases}. \quad (3.41)$$

In this approximation the relaxation rate of rigid component is temperature independent, whereas the damping of the soft component exhibits critical slowdown near  $T_c^+$ . For the latter component the Landau "law of two" is valid, i.e. the relaxation rate below  $T_c^+$  is two times larger than the relaxation rate above  $T_c^+$ . It can be found that  $\lambda_r$  and the coefficient before the factor  $|T - T_c^+|/T_c^+$  in  $\lambda_s$  increase if  $|W_{12}|$  increases. Note that evaluation of  $\lambda_{r,s}$  by means of free energy density (2.92) leads to the quantitatively different results. Near  $T_c^+$ , particularly,  $\lambda_r$  becomes larger than the value (3.39), while  $\lambda_s$  does not differ from value (3.40). This essentially indicates that the schemes based on the Bogolyubov inequality and on the Hubbard-Stratonovich transformation describe the order parameter deviations (fluctuations) from bulk (mean-field) value differently.

### 3.5 Thermal fluctuations in two-band superconductors

The influence of spatially homogeneous thermal fluctuations of superconducting gap order parameter on heat capacity and other thermodynamic characteristics has been earlier investigated in finite-size one-band s- and d-wave superconductors [29, 90]. Here we study the role of homogeneous thermal fluctuations in the thermodynamics of a finite-size two-band superconductor by using the partition function (2.91) derived on the basis of the Hubbard-Stratonovich transformation. We analyze the temperature dependence of the heat capacity for various volumes and investigate the interplay between thermal fluctuations and interband interaction.

The partition function (2.91) of a two-band superconductor is given by

$$Z = \int_0^\infty d|\eta_1| d|\eta_2| \cdot |\eta_1| |\eta_2| \exp\left(-\frac{V\tilde{F}(|\eta_1|, |\eta_2|)}{k_B T}\right), \quad (3.42)$$

where  $\tilde{F}$  can be interpreted as the non-equilibrium free energy density integrated already over the phases of order parameters

$$\begin{aligned} \tilde{F}(|\eta_1|, |\eta_2|) = & \tilde{F}_n - 4k_B T \sum_\alpha \rho_\alpha \int_0^{\hbar\omega_c} \ln \frac{\cosh \frac{\sqrt{\epsilon_\alpha^2 + |\eta_\alpha|^2}}{2k_B T}}{\cosh \frac{\epsilon_\alpha}{2k_B T}} d\tilde{\epsilon}_\alpha \\ & + \frac{W_{22}|\eta_1|^2 + W_{11}|\eta_2|^2}{W_{11}W_{22} - W_{12}^2} - \frac{k_B T}{V} \ln I_0\left(\frac{V}{k_B T} \frac{2|W_{12}||\eta_1||\eta_2|}{W_{11}W_{22} - W_{12}^2}\right). \end{aligned} \quad (3.43)$$

Here  $\tilde{F}_n = \tilde{F}(0, 0)$  is the free energy density in the absence of superconductivity,  $I_0$  is the modified Bessel function of the zeroth order. In Eq. (3.43) the electron spectrum is taken as in the bulk ( $V \rightarrow \infty$ ) system.

In order to analyze the influence of the volume driven thermal fluctuations, we consider the internal energy  $E$  of a finite superconductor. Introducing the fluctuating quantity

$$\varepsilon = V\tilde{F} - T \frac{\partial}{\partial T} V\tilde{F}, \quad (3.44)$$

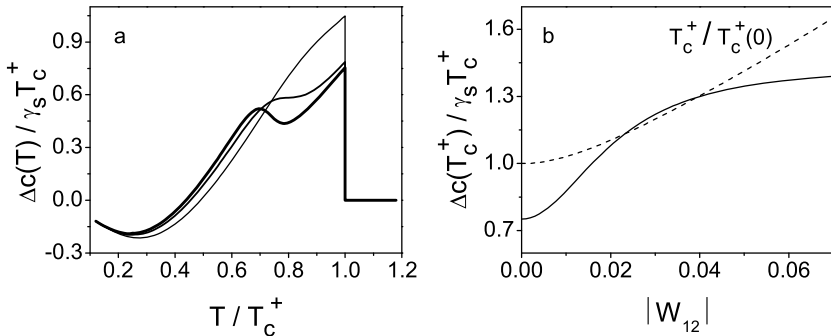


Figure 16: (a) The bulk specific heat capacity difference  $\Delta c(T) = c(T) - c_n(T)$  vs reduced temperature is depicted for various interband interactions  $|W_{12}| = (1.8, 5, 18) \cdot 10^{-3} \text{ eV} \cdot \text{cell}$ . The thickness of the curves decreases with  $|W_{12}|$  increase. The Sommerfeld constant of a two-band superconductor is  $\gamma_S = \frac{2}{3} \pi^2 k_B^2 (\rho_1 + \rho_2)$ . (b) The normalized bulk specific heat capacity difference  $\Delta c(T_c^+)$  vs modulus of interband interaction constant  $|W_{12}|$  is depicted (solid curve). Note that  $T_c^+(W_{12})$  increases with  $|W_{12}|$  increase (dashed curve) and  $T_c^+(0) = 23.5 \text{ K}$ .

one can find that  $E = \langle \varepsilon \rangle$ , where

$$\langle \dots \rangle = \frac{1}{Z} \int_0^\infty d|\eta_1| d|\eta_2| \cdot |\eta_1| |\eta_2| \cdot \dots \cdot \exp\left(-\frac{V\tilde{F}(|\eta_1|, |\eta_2|)}{k_B T}\right). \quad (3.45)$$

Correspondingly, the heat capacity can be expressed as

$$C = \frac{\partial E}{\partial T} = \frac{\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2}{k_B T^2} - T \left\langle \frac{\partial^2}{\partial T^2} V\tilde{F} \right\rangle. \quad (3.46)$$

In a macroscopic sample the heat capacity reduces approximately to the mean-field result

$$C \approx -T \frac{\partial^2}{\partial T^2} V\tilde{F}(|\eta_1^+|, |\eta_2^+|), \quad (3.47)$$

where the modulus of bulk order parameters  $|\eta_{1,2}^+|$  is defined by the minimization of the free energy density (3.43). These quantities depend on temperature and vanish as temperature moves to  $T_c^+$ . The temperature dependence of bulk specific heat capacity difference  $\Delta c = \Delta C/V$  is illustrated in Fig. 16. Note that in this section we use different set of intraband parameters, namely,  $W_{11} = W_{22} = 0.3 \text{ eV} \cdot \text{cell}$ ,  $\rho_1 = 1 \text{ (eV} \cdot \text{cell)}^{-1}$ ,  $\rho_2 = 0.9 \text{ (eV} \cdot \text{cell)}^{-1}$ . We see that in a bulk two-band superconductor the difference between the specific heat capacities in superconducting and normal states,  $\Delta c(T) = c(T) - c_n(T)$ , shows considerably non-monotone behavior in the temperature scale. In the absence of the interband interaction one can expect two autonomous phase transitions with corresponding critical temperatures determined by the dimensionless intraband constants  $\rho_\alpha W_{\alpha\alpha}$ . Thus, in case  $W_{12} = 0$  the quantity  $\Delta c(T)$  consists of two one-band contributions with specific heat jumps at different temperatures. If the interband coupling is turned on the superconducting gaps of different bands are not independent which leads to the formation of joint superconducting order in the both bands below  $T_c^+$ .

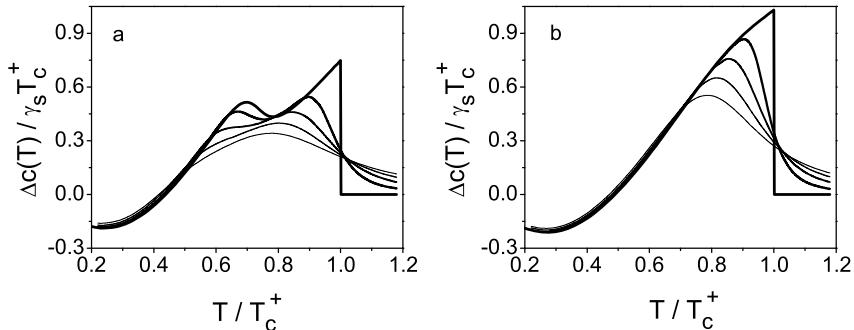


Figure 17: The plot of the specific heat capacity difference  $\Delta c(T) = c(T) - c_n(T)$  vs reduced temperature for various volumes of the system  $V = (\infty, 30, 10, 5, 3) \cdot 10^3$  cell (the thickness of the curves decreases with  $V$  decrease) with (a)  $|W_{12}| = 1.8 \cdot 10^{-3}$  eV · cell ( $T_c^+ = 23.5$  K) and (b)  $|W_{12}| = 18 \cdot 10^{-3}$  eV · cell ( $T_c^+ = 25.5$  K).

However, as one can conclude from the two-maxima structure of  $\Delta c(T)$  in Fig. 16, the memory about the lower one-band phase transition is clearly present if the interband interaction is sufficiently weak. The maximum of  $\Delta c(T)$  below  $T_c^+$  disappears as the interband coupling increases and the temperature behavior of specific heat becomes more similar to the one-band situation (cf. [174–176]). Note that the existence of two minimal one-electron excitation energies in a two-gap superconductor as  $T < T_c^+$  must be still reflected in the dependence  $\Delta c(T)$  (see e.g. [177–179]). Moreover, in a bulk two-band superconductor with interband coupling the quantity  $\Delta c(T_c^+) / \gamma_S T_c^+$  is not longer universal constant as in the one-band Bardeen-Cooper-Schrieffer theory [180], but it substantially changes with  $|W_{12}|$ . The behavior is shown in the right panel of Fig. 16.

The expression (3.46) shows that the fluctuations of superconducting order parameters contribute to the heat capacity via dispersion of internal energy. In particular, in macroscopic sample one can use the Landau expansion for free energy density and find near the phase transition point that

$$-T \left\langle \frac{\partial^2}{\partial T^2} V \tilde{F} \right\rangle \approx C_n. \quad (3.48)$$

As a result, in a macroscopic superconductor the deviation of the heat capacity from its normal state value  $\Delta C = C - C_n$  is predominately determined near  $T_c^+$  by dispersion of internal energy. Obviously, in the bulk limit the order parameters do not fluctuate, and in order to investigate the fluctuations of superconducting order parameters one has to consider the difference  $\Delta c(T)$  for finite (in general non-macroscopic) systems (Fig. 17). It is quite expectable that due to thermal fluctuations the maximum of  $\Delta c(T)$  becomes rounded extremum located in somewhat shifted position. In case of small interband interaction the two-maxima structure of the  $\Delta c(T)$  disappears as thermal fluctuation increases (volume of the system decreases). The only memory about autonomous phase transitions in a sufficiently small superconductor is that the maximum of  $\Delta c(T)$  becomes broader as compared to the case of strong interband interaction. Moreover, in case of small interband interaction the thermal fluctuations affect mostly the vicinities of former autonomous phase transitions, while the region between them remains practically

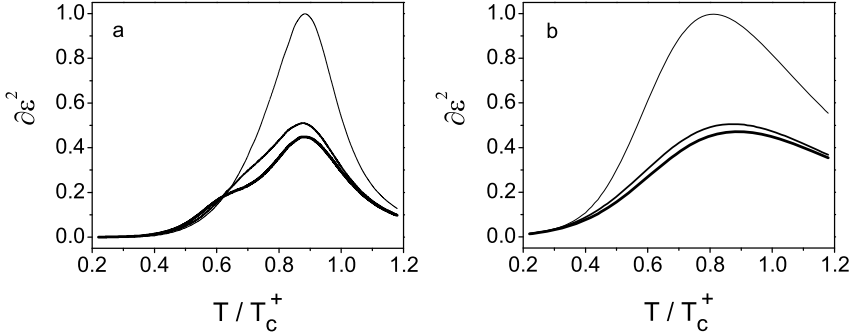


Figure 18: The plot of normalized  $\partial\varepsilon^2 \equiv \langle (\frac{\varepsilon}{V})^2 \rangle - \langle \frac{\varepsilon}{V} \rangle^2$  vs reduced temperature for various interband interactions  $|W_{12}| = (1.8, 5, 18) \cdot 10^{-3} \text{ eV} \cdot \text{cell}$  (the thickness of the curves decreases with  $|W_{12}|$  increase) with (a)  $V = 10^4$  cell and (b)  $V = 10^3$  cell. The maximal value of  $\partial\varepsilon^2$  in the right panel is about 2.5 times larger than in the left one due to different volumes.

unaffected. Therefore, one can conclude that effect of thermal fluctuations in two-band superconductor is somehow controlled by the interband interaction. To check this assumption its natural to consider the quantity  $\partial\varepsilon^2 \equiv \langle (\frac{\varepsilon}{V})^2 \rangle - \langle \frac{\varepsilon}{V} \rangle^2$  as a measure of fluctuations of superconducting order parameters and analyze its dependence on the interband interaction. Generally, this dispersion has a global maximum on the temperature scale, which shifts to the critical temperature  $T_c^+$  and decreases as the volume increases.

In sufficiently small superconductors the fluctuations increase with the increase of the interband coupling, see the right panel in Fig. 18. Therefore, not only the decrease of the volume, but also the increase of the interband interaction favors the fluctuation effects in these systems. The situation is very similar to the one-band case where the variance of internal energy increases with interaction constant.

In larger superconductors (the left panel in Fig. 18) the fluctuations also increase with interband interaction in the vicinity of critical temperature. In particular, using Landau expansion one can find near  $T_c^+$  for macroscopic system  $\Delta c \simeq V\partial\varepsilon^2$ , see Eqs. (3.46) and (3.48). Thus, in a macroscopic system near  $T_c^+$  the quantity  $\partial\varepsilon^2$  increases with interband interaction as follows from Fig. 16. However, at lower temperatures  $\partial\varepsilon^2$  shows opposite tendency: due to the memory about the lower one-band phase transition the fluctuations increase with  $|W_{12}|$  decrease. Thereby, in a macroscopic sample with weak interband interaction the superconducting fluctuations behave non-monotonically below  $T_c^+$ . Correspondingly, there is a redistribution of superconducting fluctuations in the temperature scale driven by the interband interaction. These observations reflect the topological peculiarities of the free energy density as a function of non-equilibrium order parameters.

## Summary

In the present thesis we investigated peculiarities of the ordering in the spatially restricted systems experiencing in macroscopic limit the phase transition. We proceeded from the model where the equation of motion for order parameter includes volume dependent noise and soft potential determined by the phenomenological Landau free energy. We also derived microscopically non-equilibrium free energy for two-band superconductor by means of which kinetics and thermal fluctuations of gap order parameters were analyzed.

We examined the critical slowdown of the order parameter relaxation in the model with bulk second-order phase transition and demonstrated that this phenomenon is determined in spatially restricted systems by the lowest odd eigenvalues of the Fokker-Planck operator. Moreover, the volume independent ratios of the damping rates are predicted at bulk transition temperature and may be verified in the relaxation experiments. We established that the dependence of (pseudo)critical temperature on system size is characterized by the competition of two length scales. The first scale is similar to the correlation length and determines 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.

We demonstrated that the anomaly of susceptibility at the phase transition point transforms into maximal response caused by stochastic resonance if the volume of the system decreases. The phenomenon can also be interpreted as an increase in the diffuseness of a phase transition with lowering of the critical temperature. A clear borderline between deterministic and stochastic behavior is shown.

We derived the frequency dependent complex heat capacity and demonstrated that the dynamics of the energy relaxation, determined in symmetric case by the lowest even eigenvalues of the Fokker-Planck operator, slows down in a critical region. The complementarity between stochastic behavior in small samples and deterministic behavior in large systems is accompanied by the crossover between reversible and irreversible thermodynamics of the critical region. The frequency dependent heat capacity provides an insight into the symmetry of the reduced free energy.

Our results show that the account of the stochastic nature of the order parameter is necessary for interpretation of dielectric and calorimetric measurements, as well as experimental data about the evolution of transition temperature in spatially restricted samples, in ceramic and relaxor ferroelectrics etc.

Additionally, the relaxation of ordering in a two-band model of superconductivity in dependence on intra- and interband interactions was investigated. One can distinguish two different time scales in the damping of the superconducting ordering in a two-band scenario. The formation of these relaxation channels is caused by interband interaction, leading to the redistribution of damping processes of the initially independent bands. The relevant relaxation times characterize the kinetics of the critical and noncritical component which appear as certain linear combinations of the deviations from the equilibrium band superconducting orders. The considerable non-monotonic temperature dependence of the relaxation times

has been established below the phase transition point. The behavior is caused by certain competition between intra- and interband couplings and it allows one to estimate the ratio of these interactions.

The temperature behavior of heat capacity in a two-band superconductor reveals qualitative changes in dependence on interband interaction. The contribution from thermal fluctuations of superconductivity in a spatially restricted samples depends on the strength of interband interaction. This dependence can be substantially different in the vicinities of critical temperatures for corresponding one-band subsystems.

## Summary in Estonian

### Korrastuse stohhastilised ja deterministlikud omadused faasisiirdega süsteemides

Väitekirjas on uuritud korrastuse stohhastilisi iseärasusi ruumiliselt piiratud süsteemides, kus makroskoopilises situatsioonis leiab aset faasisiire. Lähtutud on mudelist, kus korrastusparameetri liikumisvõrrand sisaldab fenomenoloogilise Landau vabaenergiaga määratud pehmet potentsiaali ja ruumalast sõltuvat müra. Samuti on mikroskoopiliselt tuletatud mittetasakaaluline vabaenergia kahetsoonilise ülijuhi jaoks, mille abil on analüüsitud korrastusparameetrite kineetikat ja termilisi fluktuatsioone.

On näidatud, et korrastusparameetri relaksatsiooni kriitilist aeglustumist kirjeldavad ruumiliselt piiratud süsteemides Fokkeri-Plancki operaatori esimesed paari- tud omaväärtused. Leitud on sumbumiskiiruste universaalsed (ruumalast sõltu- matud) suhted, mida saab eksperimentaalselt määrata. On tehtud kindlaks kaks pikkuseskaalat, milliste konkurents kujundab (pseudo)kriitilise temperatuuri sõltu- vust ruumalast.

On demonstreeritud, et dünaamilise vastuvõtlikkuse anomaalia makroskoopilise faasisiirde punkti ümbruses transformeerub ruumala vähenedes stohhastilise resonantsiga seotud vastuvõtlikkuse maksimumiks. Leitud on stohhastilise ja de- terministliku käitumise eralduspiir ruumala-sagedus tasandil.

Tuletatud on kompleksne sagedusest sõltuv soojusmahtuvus ruumiliselt piira- tud faasisiirdega süsteemis ning leitud, et Fokkeri-Plancki operaatori esimeste paaris omaväärtustega määratud siseenergia relaksatsioon aeglustub kriitilises piir- konnas.

Analüüs näitab, et korrastusparameetri stohhastilise iseloomu arvestamine on hädavaajalik dielektriliste ja kalorimeetriliste, aga ka siirdetemperatuuri evolutsiooni mõõtmistulemuste interpreteerimiseks väikese ruumalaga objektides, ke- raamilistes ja relaksor ferroelektrikutes jm.

Uuritud on ülijuhtiva korrastuse relaksatsiooni kahetsoonilises mudelis, võttes arvesse nii tsoonidevahelist kui ka tsoonidesiseseid interaktsioone. Korrastus- parameetrite relaksatsiooniaegade temperatuurisõltuvused on leitud olevat üli- juhtivas faasis mittemonotoonsed, kui tsoonidevaheline interaktsioon on piisavalt nõrk. Selline iseärasus võib olla oluline vastavate katseandmete tõlgendamiseks mitmetes kõrgetemperatuursetes ülijuhtides (vaskoksiidid, magneesiumdiboriid). Tsoonidevahelise interaktsiooni kasvades nimetatud iseärasus kaob.

On analüüsitud ruumiliselt homogeensete ülijuhtpilude termiliste fluktuatsiooni- de mõju kahetsoonilise süsteemi termodünaamikale (soojusmahtuvusele) sõltuvalt selle ruumalast ja tsoonidevahelise interaktsioonist. Varem on analoogne analüüs viidud läbi ühetsooniliste, kas s- või d-laine tüüpi ülijuhtide jaoks.

## Acknowledgments

The author expresses sincere gratitude to Teet Örd and Risto Tammelo for their guidance, continuous support and collaboration. Valuable discussions with colleagues are highly appreciated by the author as well. The gratitude goes also to Toivo Kõhelik for reading the manuscript and for useful remarks.

The study was undertaken with the financial support of the Estonian Science Foundation (Grants Nos. 6789 and 7296), the Estonian Ministry of Education and Research (Themes Nos 0182647s04 and 0180056s09), and partially supported by Graduate School on Functional Materials and Technologies, University of Tartu and Tallinn University of Technology (ESF project 1.2.0401.09-0079).

## References

- [1] J. D. van der Waals, *Over de continuïteit van den gas- en vloeistoestand*, PhD thesis, Leiden, 1873.
- [2] P. Curie, *Lois expérimentales du magnétisme. Propriétés magnétiques des corps à diverses températures*, Ann. Chem. Phys. **5**, 289 (1895).
- [3] P. Weiss, *L'hypothèse du champ moléculaire et la propriété ferromagnétique*, J. Phys. **6**, 661 (1907).
- [4] L. D. Landau, *Theory of phase transformations. I*, Zh. Eksp. Teor. Fiz. **7**, 19 (1937).
- [5] L. D. Landau, *Theory of phase transformations. II*, Zh. Eksp. Teor. Fiz. **7**, 627 (1937).
- [6] V. L. Ginzburg and L. D. Landau, *On the theory of superconductivity*, Zh. Eksp. Teor. Fiz. **20**, 1064 (1950).
- [7] C. N. Yang, *Concept of off-diagonal long-range order and the quantum phases of liquid He and of superconductors*, Rev. Mod. Phys. **34**, 694 (1962).
- [8] V. L. Ginzburg, *To the macroscopic theory of superconductivity*, Zh. Eksp. Teor. Fiz. **29**, 748 (1955).
- [9] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Theory of superconductivity*, Phys. Rev. **108**, 1175 (1957).
- [10] L. P. Gorkov, *On the microscopic deduction of the Ginzburg-Landau equations in the theory of superconductivity*, Zh. Eksp. Teor. Fiz. **36**, 1918 (1959).
- [11] A. A. Abrikosov, *On the magnetic properties of superconductors of the second group*, Sov. Phys. JETP **5**, 1174 (1957).
- [12] V. L. Ginzburg, Zh. Eksp. Theor. Fiz. **15**, 739 (1945).
- [13] A. Devonshire, Philos. Mag. **40**, 1040 (1949).
- [14] V. L. Ginzburg, Zh. Eksp. Theor. Fiz. **19**, 36 (1949).
- [15] V. L. Ginzburg and L. P. Pitaevskii, *On the theory of superfluidity*, Zh. Eksp. Teor. Fiz. **34**, 1240 (1958).
- [16] L. P. Pitaevskii and S. Stringari, *Bose-Einstein condensation*, Clarendon Press, 2003.
- [17] V. L. Ginzburg and A. A. Sobyenin, *Superconductivity, superdiamagnetism, superfluidity*, Mir, 1987.
- [18] W. H. Zurek, *The shards of broken symmetry*, Nature **382**, 296 (1996).
- [19] D. A. Kirzhnits, *Superconductivity and elementary particles*, Sov. Phys. Usp. **21**, 470 (1978).

- [20] L. Gammaitoni, P. Hänggi, P. Jung, and F. Marchesoni, *Stochastic resonance*, Rev. Mod. Phys. **70**, 223 (1998).
- [21] C. R. Doering and J. C. Gadoua, *Resonant activation over a fluctuating barrier*, Phys. Rev. Lett. **69**, 2318 (1992).
- [22] J. Garcia-Ojalvo and J. M. Sancho, *Noise in spatially extended systems*, Springer, 1999.
- [23] P. Reimann, *Brownian motors: noisy transport far from equilibrium*, Phys. Rep. **361**, 57 (2002).
- [24] L. D. Landau and E. M. Lifshits, *Statistical physics. Part 1*, Butterworth-Heinemann, 2000.
- [25] E. M. Lifshits and L. P. Pitaevskii, *Physical kinetics*, Pergamon Press, 1981.
- [26] A. P. Levanyuk, Zh. Eksp. Teor. Fiz. **36**, 810 (1959).
- [27] V. L. Ginzburg, Sov. Phys. Solid State **2**, 1824 (1960).
- [28] B. A. Strukov and A. P. Levanyuk, *Ferroelectric phenomena in crystals*, Springer, 1998.
- [29] B. Mühlshlegel, D. J. Scalapino, and R. Denton, *Thermodynamic properties of small superconducting particles*, Phys. Rev. B **6**, 1767 (1972).
- [30] A. Z. Patashinskii and V. L. Pokrovskii, *Fluctuation theory of phase transitions*, Pergamon Press, 1979.
- [31] D. S. Lemons and A. Gythiel, *Paul Langevin's 1908 paper "On the theory of Brownian motion"*, Am. J. Phys. **65**, 1079 (1997).
- [32] W. T. Coffey, Y. P. Kalmykov, and J. T. Waldron, *The Langevin equation*, World Scientific, 2004.
- [33] A. Einstein, *Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen*, Ann. Phys. **17**, 549 (1905).
- [34] A. Einstein, *Zur Theorie der Brownschen Bewegung*, Ann. Phys. **19**, 371 (1906).
- [35] M. Smoluchowski, *Zur kinetischen Theorie der Brownschen Molekularbewegung und der Suspensionen*, Ann. Phys. **21**, 756 (1906).
- [36] C. W. Gardiner, *Handbook of stochastic methods: for physics, chemistry and the natural sciences*, Springer, 2004.
- [37] H. Risken, *The Fokker-Planck equation*, Springer, 1996.
- [38] H. Nyquist, *Thermal agitation of electric charge in conductors*, Phys. Rev. **32**, 110 (1928).

- [39] L. Onsager, *Reciprocal relations in irreversible processes. I.*, Phys. Rev. **37**, 405 (1931).
- [40] H. B. Callen and T. A. Welton, *Irreversibility and generalized noise*, Phys. Rev. **83**, 34 (1951).
- [41] M. S. Green, *Markoff random processes and the statistical mechanics of time-dependent phenomena. II. Irreversible processes in fluids*, J. Chem. Phys. **22**, 398 (1954).
- [42] R. Kubo, *Statistical-mechanical theory of irreversible processes. I.*, J. Phys. Soc. Japan **12**, 570 (1957).
- [43] M. Doi and S. F. Edwards, *Theory of polymer dynamics*, Oxford University Press, 1986.
- [44] E. A. Turov, *Material'nye uravneniya elektrodinamiki*, Nauka, 1983.
- [45] I. Alig, *Ultrasonic relaxation and complex heat capacity*, Thermochem. Acta **305**, 35 (1997).
- [46] K. F. Herzfeld and F. O. Rice, *Dispersion and absorption of high frequency sound waves*, Phys. Rev. **31**, 691 (1928).
- [47] M. Fixman, *Absorption and dispersion of sound in critical mixtures*, J. Chem. Phys. **36**, 1961 (1962).
- [48] N. O. Birge and S. R. Nagel, *Specific-heat spectroscopy of the glass-transition*, Phys. Rev. Lett. **54**, 2674 (1985).
- [49] N. O. Birge, *Specific-heat spectroscopy of glycerol and propylene-glycol near the glass-transition*, Phys. Rev. B **34**, 1631 (1986).
- [50] R. Zwanzig, *Frequency-dependent specific-heat*, J. Chem. Phys. **88**, 5831 (1988).
- [51] D. H. Jung, T. W. Kwon, D. J. Bae, I. K. Moon, and Y. H. Jeong, *Fully automated dynamic calorimeter*, Meas. Sci. Technol. **3**, 475 (1992).
- [52] S. M. Lee and S. I. Kwun, *Heat-capacity measurement of dielectric solids using a linear surface heater - application to ferroelectrics*, Rev. Sci. Instrum. **65**, 966 (1994).
- [53] I. K. Moon, Y. H. Jeong, and S. I. Kwun, *The  $3\omega$  technique for measuring dynamic specific heat and thermal conductivity of a liquid or solid*, Rev. Sci. Instrum. **67**, 29 (1996).
- [54] K. P. Bohn, A. Prahm, J. Petersson, and J. K. Krüger, *Modulated differential scanning calorimetry: investigation at structural phase transitions*, Thermochem. Acta **305**, 283 (1997).

- [55] J. E. K. Shawe, T. Hütter, C. Heitz, I. Alig, and D. Lellinger, *Stochastic temperature modulation: a new technique in temperature-modulated DSC*, *Thermochim. Acta* **446**, 147 (2006).
- [56] A. Hushur, G. Shabbir, J. H. Ko, and S. Kojima, *The phase transitions of ferroelectric  $Sr_2Ta_2O_7$  crystals by MDSC, Brillouin and dielectric spectroscopy*, *J. Phys. D: Appl. Phys.* **37**, 1127 (2004).
- [57] J. Jäckle, *Heat-conduction and relaxation in liquids of high-viscosity*, *Physica A* **162**, 377 (1990).
- [58] J. K. Nielsen and C. Dyre, *Fluctuation-dissipation theorem for frequency-dependent specific heat*, *Phys. Rev. B* **54**, 15754 (1996).
- [59] P. Scheidler, W. Kob, A. Latz, J. Horbach, and K. Binder, *Frequency-dependent specific heat of viscous silica*, *Phys. Rev. B* **63**, 104204 (2001).
- [60] W. Götze and A. Latz, *Generalized constitutive-equations for glassy systems*, *J. Phys.: Condens. Matter* **1**, 4169 (1989).
- [61] F. Tagawa and T. Odagaki, *Nonlinear energy response of glass forming materials*, *J. Phys.: Condens. Matter* **20**, 035105 (2008).
- [62] J. L. Garden, *Simple derivation of the frequency dependent complex heat capacity*, *Thermochim. Acta* **460**, 85 (2007).
- [63] C. C. Yu and H. M. Carruzzo, *Frequency dependence and equilibration of the specific heat of glass-forming liquids*, *Phys. Rev. E* **69**, 051201 (2004).
- [64] J. L. Garden, *Macroscopic non-equilibrium thermodynamics in dynamic calorimetry*, *Thermochim. Acta* **452**, 85 (2007).
- [65] J. L. Garden and J. Richard, *Entropy production in ac-calorimetry*, *Thermochim. Acta* **461**, 57 (2007).
- [66] P. Hänggi and H. Thomas, *Stochastic processes: time evolution, symmetries and linear response*, *Phys. Rep.* **88**, 207 (1982).
- [67] X. S. Liu, Y. Y. Qi, J. F. He, and P. Z. Ding, *Recent progress in symplectic algorithms for use in quantum systems*, *Commun. Comput. Phys.* **2**, 1 (2007).
- [68] X. S. Liu, X. Y. Liu, Z. Y. Zhou, P. Z. Ding, and S. F. Pan, *Numerical solution of one-dimensional time-independent Schrödinger equation by using symplectic schemes*, *Int. J. Quantum Chem.* **79**, 343 (2000).
- [69] X. S. Liu, Y. H. Chi, and P. Z. Dong, *Symplectic schemes and the shooting method for eigenvalues of the Schrödinger equation*, *Chin. Phys. Lett.* **21**, 1681 (2004).
- [70] X. S. Liu, L. W. Su, and P. Z. Ding, *Symplectic algorithm for use in computing the time-independent Schrödinger equation*, *Int. J. Quantum Chem.* **87**, 1 (2002).

- [71] A. V. Svidzinsky, *Prostranstvenno-neodnorodnye zadachi teorii sverhprovodimosti*, Nauka, 1982.
- [72] A. Larkin and A. Varlamov, *Theory of fluctuations in superconductors*, Clarendon Press, 2005.
- [73] H. Suhl, B. T. Matthias, and L. P. Walker, *Bardeen-Cooper-Schrieffer theory of superconductivity in the case of overlapping bands*, Phys. Rev. Lett **3**, 552 (1959).
- [74] V. A. Moskalenko, Fiz. Met. Metalloved. **8**, 503 (1959).
- [75] J. Kondo, *Superconductivity in transition metals*, Prog. Theor. Phys. **29**, 1 (1963).
- [76] A. Bianconi, *Feshbach shape resonance in multiband superconductivity in heterostructures*, J. Supercond. **18**, 625 (2005).
- [77] S. Tsuda, T. Yokoya, Y. Takano, H. Kito, A. Matsushita, F. Yin, J. Itoh, H. Harima, and S. Shin, *Definitive experimental evidence for two-band superconductivity in MgB<sub>2</sub>*, Phys. Rev. Lett. **91**, 127001 (2003).
- [78] R. Khasanov, A. Shengelaya, A. Maisuradze, F. L. Mattina, A. Bussmann-Holder, H. Keller, and K. A. Müller, *Experimental evidence for two gaps in the high-temperature La<sub>1.83</sub>Sr<sub>0.17</sub>CuO<sub>4</sub> superconductor*, Phys. Rev. Lett. **98**, 057007 (2007).
- [79] H. Ding, P. Richard, K. Nakayama, K. Sugawara, T. Arakane, Y. Sekiba, A. Takayama, S. Souma, T. Sato, T. Takahashi, Z. Wang, X. Dai, Z. Fang, G. F. Chen, J. L. Luo, and N. L. Wang, *Observation of Fermi-surface-dependent nodeless superconducting gaps in Ba<sub>0.6</sub>K<sub>0.4</sub>Fe<sub>2</sub>As<sub>2</sub>*, EPL **83**, 47001 (2008).
- [80] G. Puddu, *Fluctuations in the Bardeen-Cooper-Schrieffer Hamiltonian induced by finite particle number*, Phys. Rev. B **45**, 9882 (1992).
- [81] G. Puddu, P. F. Bortignon, and R. A. Broglia, *The PRA-SPA approximation to level densities*, Ann. Phys. **206**, 409 (1991).
- [82] R. Rossignoli, J. Zagorodny, and N. Canosa, *Parity and finite size effects in the thermodynamics of small superconductors*, Phys. Lett. A **258**, 188 (1999).
- [83] F. Braun and J. von Delft, *Superconductivity in ultrasmall metallic grains*, Phys. Rev. B **59**, 9527 (1999).
- [84] H. Nagao, H. Kawabe, and S. P. Kruchinin, *Electron correlation in new materials and nanosystems*, Springer, 2007.
- [85] J. Hubbard, *Calculation of partition functions*, Phys. Rev. Lett. **3**, 77 (1959).
- [86] R. L. Stratonovich, *On a method of calculating quantum distribution functions*, Sov. Phys. Doklady **2**, 416 (1958).

- [87] B. Mühlshlegel, *Asymptotic expansion of the Bardeen-Cooper-Schrieffer partition function by means of the functional method*, J. Math. Phys. **3**, 522 (1962).
- [88] M. Marinus, H. G. Miller, R. M. Quick, F. Solms, and D. M. van der Walt, *Order parameter for pairing systems*, Phys. Rev. C **48**, 1713 (1993).
- [89] F. Solms, H. G. Miller, and R. M. Quick, *Finite-size effects and polycrystalline high- $T_c$  materials*, Phys. Rev. B **49**, 15945 (1994).
- [90] R. Rossignoli and J. P. Zagorodny, *Thermal gap fluctuations in d-wave superconductors*, Phys. Lett. A **276**, 149 (2000).
- [91] A. Paramekanti, M. Randeria, T. V. Ramakrishnan, and S. S. Mandal, *Effective actions and phase fluctuations in d-wave superconductors*, Phys. Rev. B **62**, 6786 (2000).
- [92] S. G. Sharapov, H. Beck, and V. M. Loktev, *Finite-temperature time-dependent effective theory for the phase field in two-dimensional d-wave neutral superconductors*, Phys. Rev. B **64**, 134519 (2001).
- [93] S. G. Sharapov, V. P. Gusynin, and H. Beck, *Effective action approach to the Leggett's mode in two-band superconductors*, Eur. Phys. J. B **30**, 45 (2002).
- [94] L. Fanfarillo, L. Benfatto, S. Caprara, C. Castellani, and M. Grilli, *Theory of fluctuation conductivity from interband pairing in pnictide superconductors*, Phys. Rev. B **79**, 172508 (2009).
- [95] R. P. Feynman, *An operator calculus having applications in quantum electrodynamics*, Phys. Rev. **84**, 108 (1951).
- [96] J. Jaccard, W. Kanzig, and M. Peter, Helv. Phys. Acta **26**, 521 (1953).
- [97] K. Anliker, H. R. Brugger, and W. Kanzig, Helv. Phys. Acta **27**, 99 (1954).
- [98] N. Setter, D. Damjanovic, L. Eng, G. Fox, S. Gevorgian, S. Hong, A. Kingon, H. Kohlstedt, N. Y. Park, G. B. Stephenson, I. Stolitchnov, A. K. Taganstev, D. V. Taylor, T. Yamada, and S. Streiffer, *Ferroelectric thin films: review of materials, properties, and applications*, J. Appl. Phys. **100**, 051606 (2006).
- [99] O. Auciello, J. F. Scott, and R. Ramesh, *The physics of ferroelectric memories*, Phys. Today **51**, 22 (1998).
- [100] M. E. Fisher, *Critical phenomena*, Academic Press, 1971.
- [101] V. Privman, *Finite size scaling and numerical simulation of statistical systems*, World Scientific, 1990.
- [102] K. Binder, *Computational methods in field theory*, Springer, 1992.
- [103] J. G. Brankov, D. M. Danchev, and N. S. Tonchev, *Theory of critical phenomena in finite-size systems*, World Scientific, 2000.

- [104] V. M. Fridkin, *Critical size in ferroelectric nanostructures*, Phys. Usp. **49**, 193 (2006).
- [105] V. Fridkin, A. Ievlev, K. Verkhovskaya, G. Vizdrik, S. Yudin, and S. Ducharme, *Switching in one monolayer of the ferroelectric polymer*, Ferroelectrics **314**, 37 (2005).
- [106] Q. Jiang, X. F. Cui, and M. Zhao, *Size effects on Curie temperature of ferroelectric particles*, Appl. Phys. A **78**, 703 (2004).
- [107] C. C. Yang and Q. Jiang, *Size and interface effects on critical temperatures of ferromagnetic, ferroelectric and superconductive nanocrystals*, Acta Mater. **53**, 3305 (2005).
- [108] X. Y. Lang and Q. Jiang, *Size and interface effects on Curie temperature of perovskite ferroelectric nanosolids*, J. Nanop. Res. **9**, 595 (2007).
- [109] P. Hänggi, P. Talkner, and M. Borkovec, *Reaction-rate theory: fifty years after Kramers*, Rev. Mod. Phys. **62**, 251 (1990).
- [110] F. Marchesoni, P. Sodano, and M. Zanetti, *Supersymmetry and bistable soft potentials*, Phys. Rev. Lett. **61**, 1143 (1988).
- [111] K. L. Ngai, *Relation between some secondary relaxations and the  $\alpha$  relaxations in glass-forming materials according to the coupling model*, J. Chem. Phys. **109**, 6982 (1998).
- [112] J. G. Brankov and D. M. Danchev, *Finite-size scaling for the correlation function of the spherical model with long-range interactions*, J. Math. Phys. **32**, 2543 (1991).
- [113] W. Koch, V. Dohm, and D. Stauffer, *Order-parameter relaxation times of finite three-dimensional Ising-like systems*, Phys. Rev. Lett. **77**, 1789 (1996).
- [114] V. Dohm, *The superfluid transition in confined  $^4\text{He}$ : renormalization-group theory*, Phys. Scr. **T49**, 46 (1993).
- [115] A. Esser, V. Dohm, and X. S. Chen, *Field theory of finite-size effects for systems with a one-component order parameter*, Physica A **222**, 355 (1995).
- [116] S. Dasgupta, D. Stauffer, and V. Dohm, *Boundary effects in the 3-dimensional Ising-model*, Physica A **213**, 368 (1995).
- [117] L. Wang, K. S. D. Beach, and A. W. Sandvik, *High-precision finite-size scaling analysis of the quantum-critical point of  $S=1/2$  Heisenberg antiferromagnetic bilayers*, Phys. Rev. B **73**, 014431 (2006).
- [118] A. M. Ferrenberg and D. P. Landau, *Critical behavior of the three-dimensional Ising model: a high-resolution Monte Carlo study*, Phys. Rev. B **44**, 5081 (1991).
- [119] M. Stengel and N. A. Spaldin, *Origin of the dielectric dead layer in nanoscale capacitors*, Nature **443**, 679 (2006).

- [120] T. M. Shaw, S. Trolier-McKinstry, and P. C. McIntyre, *The properties of ferroelectric films at small dimensions*, Annu. Rev. Mater. Sci. **30**, 263 (2000).
- [121] A. K. Tagantsev and G. Gerra, *Interface-induced phenomena in polarization response of ferroelectric thin films*, J. Appl. Phys. **100**, 051607 (2006).
- [122] R. Kretschmer and K. Binder, *Surface effects on phase transitions in ferroelectrics and dipolar magnets*, Phys. Rev. B **20**, 1065 (1979).
- [123] K. Binder, *Surface effects on phase transitions in ferroelectrics and antiferroelectrics*, Ferroelectrics **35**, 99 (1981).
- [124] W. L. Zhong, Y. G. Wang, P. L. Zhang, and B. D. Qu, *Phenomenological study of the size effect on phase transitions in ferroelectric particles*, Phys. Rev. B **50**, 698 (1994).
- [125] P. Jung, *Periodically driven stochastic systems*, Phys. Rep. **234**, 175 (1993).
- [126] T. Wellens, V. Shatokin, and A. Buchleitner, *Stochastic resonance*, Rep. Prog. Phys. **67**, 45 (2004).
- [127] V. S. Anishchenko, A. B. Neiman, F. Moss, and L. Schimansky-Geier, *Stochastic resonance: noise enhanced order*, Usp. Fiz. Nauk **169**, 7 (1999).
- [128] M. Abramowitz and I. Stegun, *Handbook of mathematical functions*, Dover, 1970.
- [129] M. Diestelhorst and K. Drozhdin, *Stochastic resonance and domain switching*, Ferroelectrics **291**, 217 (2003).
- [130] M. Diestelhorst, *Chaos and stochastic resonance in ferroelectrics - two effects related to switching*, Ferroelectrics **316**, 65 (2005).
- [131] G. A. Samara, *The relaxational properties of compositionally disordered ABO<sub>3</sub> perovskites*, J. Phys: Condens. Matter **15**, R367 (2003).
- [132] Z. Zhao, V. Buscaglia, M. Viviani, M. T. Buscaglia, L. Mitoseriu, A. Testino, M. Nygren, M. Johnsson, and P. Nanni, *Grain-size effects on the ferroelectric behavior of dense nanocrystalline BaTiO<sub>3</sub> ceramics*, Phys. Rev. B **70**, 024107 (2004).
- [133] B. Li, X. Wang, L. Li, H. Zhou, X. Liu, X. Han, Y. Zhang, X. Qi, and X. Deng, *Dielectric properties of fine-grained BaTiO<sub>3</sub> prepared by spark-plasma-sintering*, Mat. Chem. Phys. **83**, 23 (2004).
- [134] V. S. Tiwari, N. Singh, and D. Pandey, *Diffuse ferroelectric transition and relaxational dipolar freezing in (Ba,Sr)TiO<sub>3</sub>*, J. Phys: Condens. Matter **7**, 1441 (1995).
- [135] X. G. Tang, J. Wang, X. X. Wang, and H. L. W. Chan, *Effects of grain size on the dielectric properties and tunabilities of sol-gel derived Ba(Zr<sub>0.2</sub>Ti<sub>0.8</sub>)O<sub>3</sub> ceramics*, Solid State Commun. **131**, 163 (2004).

- [136] S. Chattopadhyay, P. Ayyub, V. R. Palkar, and M. Multani, *Size-induced diffuse phase-transition in the nanocrystalline ferroelectric PbTiO<sub>3</sub>*, Phys. Rev. B **52**, 13177 (1995).
- [137] X. G. Tang, X. X. Wang, K. H. Chew, and H. L. W. Chan, *Relaxor behavior of (Ba,Sr)(Zr,Ti)O<sub>3</sub> ferroelectric ceramics*, Solid State Commun. **136**, 89 (2005).
- [138] A. A. Bokov and Z. G. Ye, *Phenomenological description of dielectric permittivity peak in relaxor ferroelectrics*, Solid State Commun. **116**, 105 (2000).
- [139] Y. Park, W. J. Lee, and H. G. Kim, *Particle-size-induced diffuse phase transition in the fine-particle barium titanate porcelains*, J. Phys: Condens. Matter **9**, 9445 (1997).
- [140] C. Elissalde and J. Ravez, *Ferroelectric ceramics: defects and dielectric relaxations*, J. Mater. Chem. **11**, 1957 (2001).
- [141] F. Chu, N. Setter, C. Elissalde, and J. Ravez, *High frequency dielectric relaxation in Pb(Sc<sub>1/2</sub>Ta<sub>1/2</sub>)O<sub>3</sub> ceramics*, Mater. Sci. Eng. B **38**, 171 (1996).
- [142] C. Elissalde, J. Ravez, and P. Gaucher, *High frequency dielectric relaxation in Pb(Mg<sub>0.317</sub>Nb<sub>0.633</sub>Ti<sub>0.05</sub>)O<sub>3</sub> ceramics*, in *Proceedings of the Eighth IEEE International Symposium on Greenville*, page 458, 1992.
- [143] C. Elissalde, A. Villesuzanne, P. Dubernet, J. Ravez, and M. Maglione, *Original covalency effect on dielectric and ferroelectric properties of KTN ceramics*, J. Korean Phys. Soc. **32**, S319 (1998).
- [144] C. Elissalde and J. Ravez, *Relaxation mechanisms in Sr<sub>0.3</sub>Ba<sub>0.7</sub>Nb<sub>2</sub>O<sub>6</sub>*, J. Mater. Chem. **10**, 681 (2000).
- [145] C. Elissalde, J. Ravez, and P. Gaucher, *The low and high-frequency dielectric relaxations in lead magnesium niobate ceramics*, Mater. Sci. Eng. B **20**, 318 (1993).
- [146] C. Elissalde, J. Ravez, and Gaucher, *Dielectric relaxations in ceramics with compositions (1-x)Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-xPbTiO<sub>3</sub> (x=0, 0.05, 0.10 and 0.25)*, Mater. Sci. Eng. B **22**, 303 (1994).
- [147] A. Pikovsky, A. Zaikin, and M. A. de la Casa, *System size resonance in coupled noisy systems and in the Ising model*, Phys. Rev. Lett. **88**, 050601 (2002).
- [148] I. Rychetský and O. Hudák, *The ferroelectric phase transition in small spherical particles*, J. Phys: Condens. Matter **9**, 4955 (1997).
- [149] H. Huang, C. Q. Sun, Z. Tianshu, and P. Hing, *Grain-size effect on ferroelectric Pb(Zr<sub>1-x</sub>Ti<sub>x</sub>)O<sub>3</sub> solid solutions induced by surface bond contraction*, Phys. Rev. B **63**, 184112 (2001).
- [150] C. L. Wang and S. R. P. Smith, *Landau theory of the size-driven phase-transition in ferroelectrics*, J. Phys: Condens. Matter **7**, 7163 (1995).

- [151] C. L. Wang, Y. Xin, X. S. Wang, and W. L. Zhong, *Size effects of ferroelectric particles described by the transverse Ising model*, Phys. Rev. B **62**, 11423 (2000).
- [152] W. Y. Shih, W. H. Shih, and I. A. Aksay, *Size dependence of the ferroelectric transition of small BaTiO<sub>3</sub> particles - effect of depolarization*, Phys. Rev. B **50**, 15575 (1994).
- [153] J. M. Casado, J. Gomez-Ordóñez, and M. Morillo, *Stochastic resonance of collective variables in finite sets of interacting identical subsystems*, Phys. Rev. E **73**, 011109 (2006).
- [154] B. von Haefen, G. Izús, and H. Wio, *System size stochastic resonance: general nonequilibrium potential framework*, Phys. Rev. E **72**, 021101 (2005).
- [155] M. A. de la Casa, E. Korutcheva, J. M. R. Parrondo, and F. J. de la Rubia, *System-size resonance in a binary attractor neural network*, Phys. Rev. E **72**, 031113 (2005).
- [156] M. I. Dykman, D. G. Luchinsky, R. Mannella, P. V. E. McClintock, N. D. Stein, and N. G. Stocks, *Stochastic resonance - linear response and giant nonlinearity*, J. Stat. Phys. **70**, 463 (1993).
- [157] I. Gutzow and B. Petroff, *The glass transition in terms of Landau's phenomenological approach*, J. Non-Cryst. Solids **345**, 528 (2004).
- [158] V. I. Dimitrov, *The liquid-glass transition - is it a fourth order phase transition?*, J. Non-Cryst. Solids **351**, 2394 (2005).
- [159] J. Wu, *The glassy state, ideal glass transition, and second-order phase transition*, J. Appl. Polym. Sci. **71**, 143 (1999).
- [160] D. Chakrabarti and B. Bagchi, *Frequency dependent heat capacity within a kinetic model of glassy dynamics*, J. Chem. Phys. **122**, 014501 (2005).
- [161] J. Bisquert, *Master equation approach to the non-equilibrium negative specific heat at the glass transition*, Am. J. Phys. **73**, 735 (2005).
- [162] S. T. Davitadze, S. N. Kravchun, B. A. Strukov, B. M. Goltzman, V. V. Lemanov, and S. G. Shulman, *Specific heat and thermal conductivity of BaTiO<sub>3</sub> polycrystalline thin films*, Appl. Phys. Lett. **80**, 1631 (2002).
- [163] B. A. Strukov, S. T. Davitadze, S. N. Kravchun, S. A. Taraskin, B. M. Goltzman, V. V. Lemanov, and S. G. Shulman, *Specific heat and heat conductivity of BaTiO<sub>3</sub> polycrystalline films in the thickness range 20-1100 nm*, J. Phys.: Condens. Matter **15**, 4331 (2003).
- [164] M. D. Glinchuk and P. I. Bykov, *The peculiarities of the specific heat and dielectric permittivity related to the grain size distribution in ferroelectric nanomaterials*, J. Phys.: Condens. Matter **16**, 6779 (2004).

- [165] Y. K. Kuo, M. J. Skove, D. T. Verebelyi, H. Li, R. Mackay, S. J. Hwu, M. H. Whangbo, and J. W. Brill, *Unusual physical properties of  $KCu_{7-x}S_4$  at diffusive one-dimensional ordering transition*, Phys. Rev. B **57**, 3315 (1998).
- [166] N. Kristoffel, T. Örd, and P. Konsin, *The sign of interband interaction and stability of the superconducting ground state in the multiband model*, Nuovo Cimento D **16**, 311 (1994).
- [167] T. Soda and Y. Wada, *Specific heat of superconductors with overlapping bands*, Progr. Theor. Phys. **36**, 1111 (1966).
- [168] T. Örd and N. Kristoffel, *Two relaxation times and the high- $T_c$  superconductivity two-component scenario*, Physica C **331**, 13 (2000).
- [169] J. Demsar, B. Podobnik, V. V. Kabanov, T. Wolf, and D. Mihailovic, *Superconducting gap  $\Delta_c$ , the pseudogap  $\delta_p$ , and pair fluctuations above  $T_c$  in overdoped  $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$  from femtosecond time-domain spectroscopy*, Phys. Rev. Lett. **82**, 4918 (1999).
- [170] D. Dvorsek, V. V. Kabanov, J. Demsar, S. M. Kazakov, J. Karpinski, and D. Mihailovic, *Femtosecond quasiparticle relaxation dynamics and probe polarization anisotropy in  $YSr_xBa_{2-x}Cu_4O_8$  ( $x=0, 0.4$ )*, Phys. Rev. B **66**, 020510 (2002).
- [171] N. Cao, Y. F. Wei, J. M. Zhao, S. P. Zhao, Q. S. Yang, Z. G. Zhang, and P. M. Fu, *Femtosecond optical detection of quasiparticle dynamics in single-crystal  $Bi_2Sr_2CaCu_2O_{8+\delta}$* , Chin. Phys. Lett. **25**, 2257 (2008).
- [172] J. Demsar, R. D. Averitt, A. J. Taylor, V. V. Kabanov, W. N. Kang, H. J. Kim, E. M. Choi, and S. I. Lee, *Pair-breaking and superconducting state recovery dynamics in  $MgB_2$* , Phys. Rev. Lett. **91**, 267002 (2003).
- [173] Y. Xu, M. Khafizov, L. Satrapinsky, P. Kúš, A. Plecenik, and R. Sobolewski, *Time-resolved photoexcitation of the superconducting two-gap state in  $MgB_2$  thin films*, Phys. Rev. Lett. **91**, 197004 (2003).
- [174] C. Wälti, E. Felder, C. Degen, G. Wigger, R. Monnier, R. Delley, and H. R. Ott, *Strong electron-phonon coupling in superconducting  $MgB_2$ : a specific heat study*, Phys. Rev. B **64**, 172515 (2001).
- [175] A. A. Golubov, J. Kortus, O. V. Dolgov, O. Jepsen, Y. Kong, O. K. Anderson, B. J. Gibson, K. Ahn, and R. K. Kremer, *Specific heat of  $MgB_2$  in one- and two-band model from first-principles calculations*, J. Phys.: Condens. Matter **14**, 1353 (2002).
- [176] J. W. Loram, J. Luo, J. R. Cooper, W. Y. Liang, and J. L. Tallon, *Evidence on the pseudogap and condensate from the electronic specific heat*, J. Phys. Chem. Solids **62**, 59 (2001).

- [177] F. Bouquet, Y. Wang, R. A. Fisher, D. G. Hinks, J. D. Jorgensen, A. Junod, and N. E. Phillips, *Phenomenological two-gap model for the specific heat of  $MgB_2$* , Europhys. Lett. **56**, 856 (2001).
- [178] Y. Nakajima, T. Nakagawa, T. Tamegai, and H. Harima, *Specific-heat evidence for two-gap superconductivity in the ternary-iron silicide  $Lu_2Fe_3Si_5$* , Phys. Rev. Lett. **100**, 157001 (2008).
- [179] N. Oeschler, R. A. Fisher, N. E. Phillips, J. E. Gordon, M. L. Foo, and R. J. Cava, *Specific heat of  $Na_{0.3}CoO_2 \cdot 1.3H_2O$ : two energy gaps, nonmagnetic pair breaking, strong fluctuations in the superconducting state, and effect of sample age*, Phys. Rev. B **78**, 054528 (2008).
- [180] T. Örd and N. Kristoffel, *Modeling  $MgB_2$  two-gap superconductivity*, Physica C **370**, 17 (2002).

Attached original publications

# Curriculum Vitae

**Name** Artjom Vargunin  
**Date of birth** 29.11.1981  
**E-mail** artjom.vargunin@gmail.com

## **Education**

University of Tartu, Faculty of Science and Technology, Institute of Physics:  
BSc (2004), MSc (2006)

## **Present occupation**

University of Tartu, Institute of Physics, researcher

## **Current projects**

Stochastic phenomena in nonlinear physical systems,  
Fluctuations in multi-component superconductors

## **Teaching experience**

Stochastic Methods for Physicists (3EAP, University of Tartu, 08/09 autumn),  
Physics (6EAP, Estonian University of Life Sciences, 08/09 spring)

# Elulugu

**Nimi** Artjom Vargunin  
**Sünniaeg** 29.11.1981  
**E-mail** artjom.vargunin@gmail.com

## Haridus

Tartu Ülikool, Loodus- ja tehnoloogiateaduskond, Füüsika Instituut: BSc (2004),  
MSc (2006)

## Praegune töökoht

Tartu Ülikool, Füüsika Instituut, teadur

## Jooksvad projektid

Stohhastilised nähtused mittelineaarsetes füüsikalistes süsteemides,  
Mitmekomponendiliste ülijuhtsüsteemide korrastuste fluktuatsioonid

## Õppetöö kogemus

Stohhastika füüsikutele (3EAP, Tartu Ülikool, 2008/2009 sügis),  
Füüsika (6EAP, Eesti Maaülikool, 2008/2009 kevad)

# DISSERTATIONES PHYSICAE UNIVERSITATIS TARTUENSIS

1. **Andrus Ausmees.** XUV-induced electron emission and electron-phonon interaction in alkali halides. Tartu, 1991.
2. **Heiki Sõnajalg.** Shaping and recalling of light pulses by optical elements based on spectral hole burning. Tartu, 1991.
3. **Sergei Savihhin.** Ultrafast dynamics of F-centers and bound excitons from picosecond spectroscopy data. Tartu, 1991.
4. **Ergo Nõmmiste.** Leelishalogeniidide röntgenelektronemissioon kiiritamisel footonitega energiaga 70–140 eV. Tartu, 1991.
5. **Margus Rätsep.** Spectral gratings and their relaxation in some low-temperature impurity-doped glasses and crystals. Tartu, 1991.
6. **Tõnu Pullerits.** Primary energy transfer in photosynthesis. Model calculations. Tartu, 1991.
7. **Olev Saks.** Attoampri diapsoonis voolude mõõtmise füüsikalised alused. Tartu, 1991.
8. **Andres Virro.** AlGaAsSb/GaSb heterostructure injection lasers. Tartu, 1991.
9. **Hans Korge.** Investigation of negative point discharge in pure nitrogen at atmospheric pressure. Tartu, 1992.
10. **Jüri Maksimov.** Nonlinear generation of laser VUV radiation for high-resolution spectroscopy. Tartu, 1992.
11. **Mark Aizengendler.** Photostimulated transformation of aggregate defects and spectral hole burning in a neutron-irradiated sapphire. Tartu, 1992.
12. **Hele Siimon.** Atomic layer molecular beam epitaxy of  $A^2B^6$  compounds described on the basis of kinetic equations model. Tartu, 1992.
13. **Tõnu Reinot.** The kinetics of polariton luminescence, energy transfer and relaxation in anthracene. Tartu, 1992.
14. **Toomas Rõõm.** Paramagnetic  $H^{2-}$  and  $F^+$  centers in CaO crystals: spectra, relaxation and recombination luminescence. Tallinn, 1993.
15. **Erko Jalviste.** Laser spectroscopy of some jet-cooled organic molecules. Tartu, 1993.
16. **Alvo Aabloo.** Studies of crystalline celluloses using potential energy calculations. Tartu, 1994.
17. **Peeter Paris.** Initiation of corona pulses. Tartu, 1994.
18. **Павел Рубин.** Локальные дефектные состояния в  $CuO_2$  плоскостях высокотемпературных сверхпроводников. Tartu, 1994.
19. **Olavi Ollikainen.** Applications of persistent spectral hole burning in ultrafast optical neural networks, time-resolved spectroscopy and holographic interferometry. Tartu, 1996.
20. **Ülo Mets.** Methodological aspects of fluorescence correlation spectroscopy. Tartu, 1996.
21. **Mikhail Danilkin.** Interaction of intrinsic and impurity defects in CaS:Eu luminophors. Tartu, 1997.

22. **Ирина Кудрявцева.** Создание и стабилизация дефектов в кристаллах KBr, KCl, RbCl при облучении ВУФ-радиацией. Тарту, 1997.
23. **Andres Osvet.** Photochromic properties of radiation-induced defects in diamond. Tartu, 1998.
24. **Jüri Örd.** Classical and quantum aspects of geodesic multiplication. Tartu, 1998.
25. **Priit Sarv.** High resolution solid-state NMR studies of zeolites. Tartu, 1998.
26. **Сергей Долгов.** Электронные возбуждения и дефектообразование в некоторых оксидах металлов. Тарту, 1998.
27. **Kaupo Kukli.** Atomic layer deposition of artificially structured dielectric materials. Tartu, 1999.
28. **Ivo Heinmaa.** Nuclear resonance studies of local structure in  $\text{RBa}_2\text{Cu}_3\text{O}_{6+x}$  compounds. Tartu, 1999.
29. **Aleksander Shelkan.** Hole states in  $\text{CuO}_2$  planes of high temperature superconducting materials. Tartu, 1999.
30. **Dmitri Navedrov.** Nonlinear effects in quantum lattices. Tartu, 1999.
31. **Rein Ruus.** Collapse of 3d (4f) orbitals in 2p (3d) excited configurations and its effect on the x-ray and electron spectra. Tartu, 1999.
32. **Valter Zazubovich.** Local relaxation in incommensurate and glassy solids studied by Spectral Hole Burning. Tartu, 1999.
33. **Indrek Reimand.** Picosecond dynamics of optical excitations in GaAs and other excitonic systems. Tartu, 2000.
34. **Vladimir Babin.** Spectroscopy of exciton states in some halide macro- and nanocrystals. Tartu, 2001.
35. **Toomas Plank.** Positive corona at combined DC and AC voltage. Tartu, 2001.
36. **Kristjan Leiger.** Pressure-induced effects in inhomogeneous spectra of doped solids. Tartu, 2002.
37. **Helle Kaasik.** Nonperturbative theory of multiphonon vibrational relaxation and nonradiative transitions. Tartu, 2002.
38. **Tõnu Laas.** Propagation of waves in curved spacetimes. Tartu, 2002.
39. **Rünno Lõhmus.** Application of novel hybrid methods in SPM studies of nanostructural materials. Tartu, 2002.
40. **Kaido Reivelt.** Optical implementation of propagation-invariant pulsed free-space wave fields. Tartu, 2003.
41. **Heiki Kasemägi.** The effect of nanoparticle additives on lithium-ion mobility in a polymer electrolyte. Tartu, 2003.
42. **Villu Repän.** Low current mode of negative corona. Tartu, 2004.
43. **Алексей Котлов.** Оксианионные диэлектрические кристаллы: зонная структура и электронные возбуждения. Tartu, 2004.
44. **Jaak Talts.** Continuous non-invasive blood pressure measurement: comparative and methodological studies of the differential servo-oscillometric method. Tartu, 2004.
45. **Margus Saal.** Studies of pre-big bang and braneworld cosmology. Tartu, 2004.

46. **Eduard Gerškevičš.** Dose to bone marrow and leukaemia risk in external beam radiotherapy of prostate cancer. Tartu, 2005.
47. **Sergey Shchemelyov.** Sum-frequency generation and multiphoton ionization in xenon under excitation by conical laser beams. Tartu, 2006.
48. **Valter Kiisk.** Optical investigation of metal-oxide thin films. Tartu, 2006.
49. **Jaan Aarik.** Atomic layer deposition of titanium, zirconium and hafnium dioxides: growth mechanisms and properties of thin films. Tartu, 2007.
50. **Astrid Rekker.** Colored-noise-controlled anomalous transport and phase transitions in complex systems. Tartu, 2007.
51. **Andres Punning.** Electromechanical characterization of ionic polymer-metal composite sensing actuators. Tartu, 2007.
52. **Indrek Jõgi.** Conduction mechanisms in thin atomic layer deposited films containing  $\text{TiO}_2$ . Tartu, 2007.
53. **Aleksei Krasnikov.** Luminescence and defects creation processes in lead tungstate crystals. Tartu, 2007.
54. **Küllike Rågo.** Superconducting properties of  $\text{MgB}_2$  in a scenario with intra- and interband pairing channels. Tartu, 2008.
55. **Els Heinsalu.** Normal and anomalously slow diffusion under external fields. Tartu, 2008.
56. **Kuno Kooser.** Soft x-ray induced radiative and nonradiative core-hole decay processes in thin films and solids. Tartu, 2008.
57. **Vadim Boltrushko.** Theory of vibronic transitions with strong nonlinear vibronic interaction in solids. Tartu, 2008.
58. **Andi Hektor.** Neutrino Physics beyond the Standard Model. Tartu, 2008.
59. **Raavo Josepson.** Photoinduced field-assisted electron emission into gases. Tartu, 2008.
60. **Martti Pärs.** Study of spontaneous and photoinduced processes in molecular solids using high-resolution optical spectroscopy. Tartu, 2008.
61. **Kristjan Kannike.** Implications of neutrino masses. Tartu, 2008.
62. **Vigen Issahhanjan.** Hole and interstitial centres in radiation-resistant MgO single crystals. Tartu, 2008.
63. **Veera Krasnenko.** Computational modeling of fluorescent proteins. Tartu, 2008.
64. **Mait Müntel.** Detection of doubly charged higgs boson in the CMS detector. Tartu, 2008.
65. **Kalle Kepler.** Optimisation of patient doses and image quality in diagnostic radiology. Tartu, 2009.
66. **Jüri Raud.** Study of negative glow and positive column regions of capillary HF discharge. Tartu, 2009.
67. **Sven Lange.** Spectroscopic and phase-stabilisation properties of pure and rare-earth ions activated  $\text{ZrO}_2$  and  $\text{HfO}_2$ . Tartu, 2010.
68. **Aarne Kasikov.** Optical characterization of inhomogeneous thin films. Tartu, 2010.

69. **Heli Valtna-Lukner.** Superluminally propagating localized optical pulses. Tartu, 2010.