Mean Relaxation Time Approximation for Dynamical Correlation Functions in Stochastic Systems near Instabilities

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We present a simple approximation for dynamical correlation functions in stochastic systems which reproduces the high as well as the low frequency behaviour of the exact correlation functions. The approximation is applied in its lowest order to diffusion in a quartic potential and to autocatalytic chemical reaction systems as described by the Schlögl models. The results are compared to those from the conventional Mori-Zwanzig projection operator approach which reproduces only the short-time relaxation of the systems considered. The new approximation describes correctly slow relaxation processes, e.g. barrier crossing in a quartic potential and the slowing down of dynamic processes in finite autocatalytic systems near first and second order transitions.

1. Introduction

Processes occurring in the condensed phase can often be modelled by stochastic dynamics described mathematically by means of master-equations, Fokker-Planck-equations or Langevin equations. Examples are biological processes like the transport of biomolecules in cells [1], the motion of atoms and side groups in proteins [2] as well as the stochastic motion along reaction coordinates in elementary chemical and biochemical reaction steps [3]. Other examples that are more familiar to physicists involve dynamical processes in chemical reaction systems [4], in liquids [5] and, in particular, at equilibrium phase transitions [6]. The quantity of interest for theoretical descriptions, apart from static properties, is the dynamical correlation function of the essential observables, for example in chemical reaction systems the particle number correlation function. Since even the most simple stochastic models of such systems often do not admit exact analytical solutions approximation methods for the evaluation of correlation functions are needed.

A method often applied is furnished by the Mori-Zwanzig projection operator formalism [7, 8]. It involves a continued fraction approximation to the correlation function and employs the correlation function's high frequency moments which can be expressed solely in terms of static properties of the system considered. This method has been applied successfully in many cases and often a termination of the continued fraction after the first few terms gives satisfactory results. However, in case the time scales of the long-time and the short-time behaviour differ considerably one either has to carry out the approximations to a high order to reproduce the correct long-time behaviour or, more likely, the method fails completely.

We recently developed an extension of the moment expansion method described above which employs high frequency as well as low frequency moments of the correlation function [9, 10]. Therefore, this method, termed generalized moment expansion, reproduces short-time as well as long-time effects. It was originally devised for the description of correlation functions connected with diffusion-controlled reactions [11, 12]. The method was subsequently found to work well for stochastic systems in general [13]. In this paper we will apply the method in its lowest order of approximation, the mean relaxation time approximation, to stochastic systems that exhibit instabilities. At instabilities one expects very slow relaxation processes (critical slowing down) and, hence, the Mori-Zwanzig formalism involving only high frequency moments should be inaccurate.

This paper is organized as follows. In Sect. 2 we
present the mean relaxation time approximation and discuss its relation to the Mori-Zwanzig formalism. In Sect. 3 we apply it to diffusion in a quartic potential at the transition from mono- bistability, and in Sect. 4 to chemical reaction systems which exhibit first- and second-order phase transitions, namely the two Schlögl models [14].

2. Mean Relaxation Time Approximation

We will be concerned with stochastic processes that can be described by an evolution equation for the (discrete or continuous) probability distribution \( P(t) \) of the type

\[
\frac{d}{dt} P(t) = L P(t)
\]

(2.1)

where, in case of a master equation, \( L \) is a transition matrix or, in case of a continuous diffusion process, \( L \) is the Fokker-Planck-operator

\[
L = \tilde{V} \cdot [F + (FU)]
\]

(2.2)

with potential \( U \) and appropriate boundary conditions. The operator \( L \) should admit a non-zero stationary distribution \( P_0 \), which, in case of a Fokker-Planck-equation, is given by the Boltzmann-distribution \( P_0 \sim \exp(\omega) \).

We are interested in the steady state time-dependent correlation functions of an observable \( M(t) \)

\[
C(t) = \langle \delta M(0) \delta M(t) \rangle
= \langle \delta M \exp[\lambda^+ t] \delta M \rangle
\]

(2.3)

where \( \delta M = M - \langle M \rangle \) and \( \lambda^+ \) is the operator adjoint to \( L \). \( \langle \cdot \rangle \) denotes the average with respect to \( P_0 \) and has the properties of an inner product on the space of functions \( \delta M \).

An approximation to \( C(t) \) starts with the Laplace-transformed correlation function

\[
\tilde{C}(\omega) = \frac{1}{\omega} \int_0^\infty dt \exp(-\omega t) C(t)
= \langle \delta M \exp[\lambda^+ t] \delta M \rangle.
\]

(2.4)

Usually, the Mori-Zwanzig projection operator formalism [7, 8] is used to derive a continued fraction approximation to (2.4). In case \( \delta M \) is the single slow variable, this method is tantamount (see e.g. [15, 16]) to a Padé-approximation that reproduces the first terms of the high frequency expansion

\[
\tilde{C}(\omega) = (1/\omega) \sum_{n=0}^\infty \mu_n (-1/\omega)^n
\]

(2.5)

where the expansion coefficients (high frequency moments) are given by

\[
\mu_n = (-1)^n \langle \delta M^* [\lambda^+]^n \delta M \rangle
\]

(2.6)

and can be evaluated in a straightforward manner. \( \tilde{C}(\omega) \) can then be written in the form

\[
\tilde{C}(\omega) = C_0 [\omega + \lambda^+ K(\omega)]^{-1}
\]

(2.7)

with

\[
C_0 = \mu_0 = \langle \delta M^* \delta M \rangle
\]

(2.8)

\[
\lambda^+ = \mu_1 / \mu_0 = -\langle \delta M^* \lambda^+ \delta M \rangle / \langle \delta M^* \delta M \rangle.
\]

(2.9)

The memory kernel \( K(\omega) \) is determined by the higher moments (2.6) and gives corrections to the relaxation rate \( \lambda^+ \). Because of

\[
\lambda^+ = - (d/dt)_{t=0} C(t)/C(0)
\]

(2.10)

we call \( \lambda^+ \) the short time relaxation rate.

Neglect of the memory kernel gives a single-exponential approximation to (2.3), the short time approximation

\[
C(t) \approx C_0 \exp(- \lambda^+ t)
\]

(2.11)

which is satisfying in many cases. However in some cases, in particular near instabilities (see e.g. [17]), the corrections due to \( K(\omega) \) are essential and have to be included to derive the correct long-time behaviour of the correlation functions.

In a recent article [10] we reported a generalization of this method which in addition to expansion (2.5) rests on the low frequency expansion

\[
\tilde{C}(\omega) = \sum_{n=0}^\infty \frac{\mu_n}{\omega - n} (-\omega)^n
\]

(2.12)

The expansion coefficients (low frequency moments), formally given again by (2.6), but with negative exponents, can be evaluated in case the inverse of the stochastic operator \( \lambda^+ \) is numerically or analytically available [18]. This is always the case for stochastic processes that have a one-dimensional structure [10], as will be considered in this paper. The generalized moment method involves a two-point Padé-approximation (see e.g. [19]) around \( \omega = \infty \) and \( \omega = 0 \) that reproduces the moments of (2.5) and (2.12) in a balanced way and, thereby, includes short-time as well as long-time effects. For more details we refer the reader to [9, 10]. Here we limit ourselves to the single-exponential approximation (2.11) with \( \lambda^+ \) replaced by the long time relaxation rate \( \lambda_l \), given by

\[
\lambda_l = \mu_0 / \mu_{-1} = -\langle \delta M^* \delta M \rangle / \langle \delta M^* [\lambda^+]^{-1} \delta M \rangle.
\]

(2.13)

This approximation reproduces the leading term of (2.5) and of (2.12). The inverse of \( \lambda_l \) is given by

\[
\tau_l = \lambda_l^{-1} = \int_0^\infty dt \, C(t)/C(0).
\]

(2.14)
and is called mean relaxation time; correspondingly we call (2.11) with \( \lambda_g \) replaced by \( \tilde{\lambda}_g \) the mean relaxation time approximation. It bears a close resemblance to the first passage time in the theory of diffusion controlled reactions [11, 9].

The first low frequency moment \( \mu_{-1} \) has been derived in [10] in terms of the stationary distribution:

1) In case the stochastic process is a one-dimensional single-step birth-death process with the tri-diagonal transition matrix

\[
L = \begin{pmatrix}
-W_{12} & W_{21} & 0 & \cdots \\
W_{12} & -(W_{21} + W_{23}) & W_{32} & \cdots \\
0 & W_{23} & -(W_{32} + W_{34}) & \cdots \\
\vdots & \vdots & \ddots & \ddots
\end{pmatrix}
\]  

(2.15)

where \( W_{ij} \) denotes the transition rate from state \( i \) to state \( j \), one obtains

\[
\mu_{-1} = \sum_{n=1}^{N-1} \left[ W_{n,n+1}P_0 \right]^{-1} \left[ \sum_{n=1}^{N-1} \delta M_n P_0 \right]^2 
\]  

(2.16a)

with \( N \) the number of accessible states.

2) In case the stochastic process entails a one-dimensional Brownian motion in a potential \( U(x) \) restricted to the interval \([a, b]\) as described by the Fokker-Planck-operator (2.2) one derives

\[
\mu_{-1} = \int_{a}^{b} dx \left[ P_0(x) \right]^{-1} \left| \int_{a}^{x} dy \delta M(y) P_0(y) \right|^2 
\]  

(2.16b)

For the high frequency moment \( \mu_1 \) one easily obtains for the respective cases

1) 

\[
\mu_1 = \langle W_{i+1,i} | \Delta M \rangle^2 
\]  

(2.17a)

with \( \Delta M = M_{i+1} - M_i \), and

2) 

\[
\mu_1 = \langle |M'(x)|^2 \rangle. 
\]  

(2.17b)

Of interest is the relationship of \( \lambda_g \) and \( \lambda_i \) to the eigenvalues of the operator \( L \). For simplicity we assume the case that \( L \) has a discrete spectrum. As long as detailed balance (see e.g. [20]) holds, the case considered here, the eigenvalues \( -\lambda_n \) for a stochastic process (2.1) are real with \( \lambda_n \geq 0 \); \( \lambda_0 = 0 \) is the eigenvalue corresponding to the stationary distribution \( P_0 \) and we assume the spectrum to be ordered \( \lambda_0 < \lambda_1 \leq \lambda_2 \leq \ldots \). A formal spectral expansion of (2.3) then leads to

\[
C(t) = \sum_{n=1}^{\infty} |a_n|^2 \exp(-\lambda_n t) 
\]  

(2.18)

where the \( a_n \) are determined by the eigenvectors or eigenfunctions of \( L \). From this it is easily seen that the following relations hold

\[
\lambda_g = \sum_{n=1}^{\infty} \lambda_n |a_n|^2 
\]  

(2.19a)

\[
\tau_g = \sum_{n=1}^{\infty} \frac{1}{\lambda_n} |a_n|^2 
\]  

(2.19b)

\(|a_n|^2 \) can, therefore, be viewed as a discrete weight function for the eigenvalues that contribute to the relaxation of the correlation function. \( \lambda_g \) is essentially determined by the larger eigenvalues, i.e. the fast processes, while \( \lambda_i \) is essentially determined by the large relaxation times, i.e. the slow processes. This is no problem in case the relaxation process takes place on a single time scale. In this case \( \lambda_g \) and \( \lambda_i \) will be of comparable size and the approximation (2.11) with either relaxation rate will give a reasonable description of the correlation function. However, if the relaxation process takes place on different time scales with equal weight, as is the case near instabilities, \( \lambda_g \) will give only the short-time behaviour and will fail at long times, whereas \( \lambda_i \) describes the more important long-time relaxation though it fails at short times. Therefore, an evaluation of \( \lambda_i \) promises to be a better and direct way for a first approximation of the long-time behaviour of observables. An extension of the mean relaxation time approximation involving a series of exponentials can reproduce correctly both the long- and the short-time behaviour [9, 10, 21, 22].

If a simple observable like the position \( x \) of a Brownian particle or the particle number \( N \) in chemical reaction systems is used as a test function for the determination of the lowest non-zero eigenvalue of \( L \) by means of (2.11), then \( \lambda_i \) is a better choice than \( \lambda_g \), since from (2.19) one easily derives

\[
\lambda_1 \leq \lambda_i \leq \lambda_g 
\]  

(2.20)

where the equality holds only if the correlation function has a single exponential decay.

As an important cautionary remark we like to add that the method described above is limited to cases where the long-time relaxation of observables is truly exponential. This is the case for systems of finite size, but must not hold in the thermodynamic limit. For example, a power-law behaviour is encountered for dynamical correlation functions in equilibrium phase transitions and in liquids [5, 6], or, in general, if the eigenvalues have an accumulation point at zero (for examples see [23]). In this case one has to resort to other methods, e.g. self-consistent determination of the memory kernel or renormalization group methods (see e.g. [5, 6]).
3. Diffusion in a Quartic Potential

We consider a diffusive process at the transition from a monostable to a bistable behaviour described by the Fokker-Planck-operator (2.2) with the quartic potential

\[ U(x) = (\kappa/2)x^2 + (1/4)x^4. \]  

(3.1)

This potential has acquired some fame since it is a simple model for the process of symmetry breaking [24]. For positive values of \( \kappa \) this potential has a single minimum at \( x = 0 \), for negative \( \kappa \)-values it develops two minima at \( x = \pm |\kappa|^{1/2} \) and a maximum at \( x = 0 \). We will compare the relaxation rates \( \lambda_1 \) and \( \lambda_2 \) for either of the correlation functions

\[ C_1(t) = \langle \delta x(0) \delta x(t) \rangle \]  

(3.2a)

\[ C_2(t) = \langle \delta x^2(0) \delta x^2(t) \rangle. \]  

(3.2b)

In particular the relaxation rates for \( C_1 \) may be used as an estimate for the smallest relaxation rate \( \lambda_1 \).

Figure 1 presents the dependence on the potential parameter \( \kappa \) of \( \lambda_1 \) and \( \lambda_2 \) resulting from moments obtained by numerical integration of (2.8), (2.16b) and (2.17b). For comparison Fig.1 shows also the eigenvalues \( \lambda_1 \) to \( \lambda_5 \) of the corresponding Fokker-Planck-operator which were calculated numerically by Dekker and van Kampen [25] using the equivalence of (2.2) to a Schrödinger operator [26].

In the monostable region (\( \kappa \geq 0 \)) \( \lambda_1 \) and \( \lambda_2 \) coincide for both correlation functions. The relaxation of \( C_1 \) is completely determined by the eigenvalue \( \lambda_1 \) and that of \( C_2 \) by \( \lambda_2 \), a behaviour which is easily understood considering the symmetry of the respective eigenfunctions.

![Fig. 1. Dependence of the relaxation rates for the correlation functions (a) \( C_1(t) \) and (b) \( C_2(t) \) on the parameter \( \kappa \) of the quartic potential (3.1); the dashed lines denote the \( \kappa \)-dependence of the five smallest negative eigenvalues evaluated in [25]; \( \lambda_1 \) is not distinguishable from \( \lambda_i \) within the accuracy of the drawing; the arrows indicate the values of \( \lambda_1 \) and \( \lambda_i \) resulting from (3.3)]](image)

Near \( \kappa = 0 \) \( \lambda_1 \) and \( \lambda_2 \) begin to differ with \( \lambda_1 < \lambda_2 \). At the instability point (\( \kappa = 0 \)) the relaxation rates for \( C_1 \) can be evaluated analytically (see the Appendix). One obtains

\[ \lambda_1 = 2 \Gamma(5/4)/\Gamma(3/4) \approx 1.479 \]  

(3.3a)

\[ \lambda_1 = \sqrt{2} \{ \pi - \ln[(2 + \sqrt{2})/(2 - \sqrt{2})] \}^{-1} \Gamma(3/4)/\Gamma(5/4) \approx 1.387. \]  

(3.3b)

The value of \( \lambda_1 \) is very close to \( \lambda_1 \approx 1.37 \), determined numerically in [25]. It is one of the best analytical estimates for \( \lambda_1 \), surpassed only by \( \lambda_1 \approx 1.383 \) derived by Bernstein and Brown [27] who exploited the inherent supersymmetry of the Fokker-Planck-equation by a variational approach.

In the bistable region (\( \kappa < 0 \)) \( \lambda_3 \) and \( \lambda_1 \) for \( C_1 \) differ only slightly. In this region the relaxation of \( C_2 \) is mainly determined by the triplet of eigenvalues \( \lambda_3 \) to \( \lambda_5 \). This is due to the symmetry breaking since \( C_2 \) describes mainly relaxation processes inside either potential well. In contrast, the relaxation of \( C_1 \) is still determined by the eigenvalue \( \lambda_1 \). Since \( \lambda_1 \) (and \( \lambda_i \)) nearly vanishes, the relative difference between \( \lambda_1 \) and \( \lambda_i \) is of significance. This is demonstrated in Fig.2 which presents the corresponding relaxation times \( \tau_i \) and \( \tau_1 \). These differ by orders of magnitude and, hence, the short time approximation fails to describe the relaxation of \( C_1 \), underestimating grossly the relaxation time. The large value for \( \tau_1 \) is due to barrier-crossing processes that contribute to \( C_1 \) but not to \( C_2 \). For high barriers the barrier crossing can be described by the Kramers relaxation rate [28, 20]

\[
\lambda_\kappa = \frac{1}{(2\pi)^{1/2}} \left[ \frac{U''(x_{\text{min}})U''(x_{\text{max}})}{2\pi} \right]^{1/2} (2\pi)^{-1} \cdot \exp \left[ \frac{U(x_{\text{min}}) - U(x_{\text{max}})}{4(2\pi)^{-1}} \right] = \sqrt{2\pi^{-1}} |\kappa| \exp(-\kappa^2/4)
\]

(3.4)
which results also from an appropriate approximation to (2.16b) (see e.g. [12]) and holds to a very good degree for $\kappa < -2$.

4. Instabilities in Chemical Reaction Systems

Chemical reaction systems on a mean field level are described by rate equations. To include the effects of fluctuations in the number of molecules that take part in the reaction process, this description is replaced by a master-equation (2.1) for the probability density $P(N, t)$ for the number $N$ of molecules. Local concentration fluctuations are neglected in such a description, i.e. one assumes that the time scale of chemical reactions is much larger than the diffusive time scale [29]. We will assume this throughout the remaining part of this paper (for a recent discussion of the influence of diffusive processes in the Schlögl models see for example [30] and references therein).

Schlögl [14] has introduced two models for autocatalytic reactions that have become standard examples for non-equilibrium systems displaying first and second order phase transitions. The dynamical particle number correlation function

$$C(t) = \langle \delta N(t) \delta N(0) \rangle$$ (4.1)

for the stochastic description of these models has been analyzed by Grossmann and Schranne [17] using the Mori-Zwanzig-formalism and employing high frequency moments. In the following sections we will reconsider their study using the mean relaxation time approximation.

4.1. Schlögl Model 1

The first Schlögl model corresponds to the reactions

$$A + X \xrightarrow{k_1} 2X$$ (4.2a)  
$$A \xrightarrow{k_2} X$$ (4.2b)  
$$X \xrightarrow{k_4} C$$ (4.2c)

where it is assumed that the concentration of the substrate $A$ is kept constant. Following Grossmann and Schranne [17] we scale the time $(k_4 t \rightarrow t)$ and introduce the parameters

$$q = k_1/A/k_4$$ (4.3a)  
$$\kappa = (k_2 k_3)/(k_1 k_4)$$ (4.3b)  
$$\Omega = k_2/k_4.$$ (4.3c)

These substitutions yield for the transition rates connecting the states of $N$ and $N \pm 1$ molecules of species $X$

$$W_{N,N+1} = q N + \Omega \kappa q$$ (4.4a)  
$$W_{N,N-1} = (N(N-1)/\Omega) + N.$$ (4.4b)

Since $\Omega$ is proportional to the volume of the system, it will be used as a dimensionless measure of the system size. $q$ is a control parameter, comparable to the temperature in equilibrium phase transition systems, and $\kappa$ acts as a relevant field.

For the evaluation of expectation values and moments we introduced a cutoff state $N_{\text{max}}$. Low and high frequency moments were evaluated according to (2.8), (2.16a) and (2.17a). For large values of $N_{\text{max}}$ the results were found to be numerically independent of $N_{\text{max}}$.

Figure 3 presents the order parameter of the system, the mean particle number $\langle N \rangle$, as a function of the control parameter $q$ for different values of $\kappa$. In the mean field description there is a second order phase transition at $q = 1$, $\kappa = 0$. Figure 3 shows that for a given system size the transition point is shifted to $q > 1$ for small $\kappa$ in the stochastic version of the model [31].

Figure 4 compares the relaxation rates $\lambda_s$ and $\lambda_t$ for the correlation function (4.1). Outside the transition region $\lambda_s$ and $\lambda_t$ coincide. However, in the transition region $\lambda_s$ exceeds $\lambda_t$. For small $\kappa$ the rates differ by orders of magnitude. According to (2.10) $\lambda_t$ provides an estimate for the true relaxation rate which is more suitable than $\lambda_s$. The inaccuracy of $\lambda_s$ cannot be reduced very much by an inclusion of higher moments in a short-time approximation.

The locations of the minima of the relaxation rates
This relationship has been derived by Jähnig and Richter [32] by means of linearized irreversible thermodynamics.

For systems of finite size in the limit $\kappa \to 0$ the two approximations give very different results as is clearly demonstrated in Fig. 5. From the data for $\lambda_s$ in Fig. 5 we conclude that in this limit the relation

$$\lambda_s \sqrt{\kappa \Omega} \sim (\kappa \Omega)^{-1/2 + \epsilon}$$  \hspace{1cm} (4.6a)

holds, with $\epsilon \gtrless 0$. It is not possible to decide definitely whether $\epsilon$ is really zero or has a small positive value. A value of zero for $\epsilon$ would result in the relation

$$\lambda_s \sim \Omega^{-1/2}$$  \hspace{1cm} (4.6b)

for the minimum value of the short-time relaxation rate in the limit $\kappa \to 0$. That such a relationship holds is supported by the exact result [33] for the mean field transition point ($q = 1, \kappa = 0$)

$$\lambda_s(q = 1) = (\pi/2)^{1/2} \Omega^{-1/2} + O(\Omega^{-1}).$$  \hspace{1cm} (4.6c)

The data presented in Fig. 6a appear to support Eq. 4.6b, too. Altogether this implies that for systems of finite size in the limit $\kappa \to 0$ the short-time approximation predicts a non-vanishing or, at least, a very slowly vanishing relaxation rate of the particle number correlation function. However, this is not the behaviour of the true relaxation rate.

As already noted above, $\lambda_t$ is a better estimate for the true relaxation rate. From the data for $\lambda_t$ in Fig. 5 we conclude that in the limit $\kappa \to 0$ the relationship

$$\lambda_t \sqrt{\kappa \Omega} \sim (\kappa \Omega)^{1/2 - \epsilon}$$  \hspace{1cm} (4.7a)

holds, with $\epsilon \gtrless 0$. Again it is not possible to decide definitely whether the exponent $\epsilon$ is really zero or has a small positive value. For $\epsilon = 0$ relation 4.7a can be written

$$\lambda_t \sim \kappa \Omega^{1/2}$$  \hspace{1cm} (4.7b)

i.e. $\lambda_t$ vanishes linearly with $\kappa$. In fact, the data presented in Fig. 6b for $\lambda_t$ demonstrate that $\lambda_t$ vanishes nearly linearly with $\kappa$.

In closing the discussion of the first Schlögl model we like to note that the data presented in Fig. 5 suggest that the minimum values of the relaxation rates show a scaling behaviour for large but finite systems

$$\lambda_s(\kappa, \Omega) \approx \sqrt{\kappa} f_{s\kappa}(\sqrt{\kappa \Omega})$$  \hspace{1cm} (4.8)

with a scaling function $f_{s\kappa}(\sqrt{\kappa \Omega})$. Such a finite size scaling behaviour is also encountered in second order equilibrium phase transitions [34].
4.2. Schlögl Model 2

In the second Schlögl model the reaction (4.2a) is replaced by

\[ A + 2X \xrightarrow{k_1} 3X. \]  

(4.9)

Scaling again the time \((k_4 \, t \rightarrow t)\) and introducing the parameters

\[ q = (k_1^2 \, k_3 / k_4 \, k_2^2)^{1/4} \, A \]  

\[ a = (k_1 \, k_4^2 / k_3 \, k_2)^{1/2} \]  

\[ \Omega = (k_3 \, k_4 / k_1 \, k_2)^{1/4} \]  

yields the transition rates

\[ W_{N,N+1} = q \, N(N-1) / \Omega + \Omega \, q / a \]  

\[ (4.10a) \]

\[ W_{N,N-1} = N(N-1)(N-2) / a \, \Omega^2 + N. \]  

\[ (4.10b) \]

Again, \( \Omega \) is the dimensionless system size, \( q \) is the control parameter and \( a \) is the relevant field.

Figure 7 presents the order parameter for different values of \( a \) and illustrates qualitatively the mean field results:

i) for \( a < 3 \) there is no transition at all,

ii) for \( a = 3 \) there is a second order transition at \( q = 1 \),

iii) for \( a > 3 \) there is a first order transition at some value \( q \leq 1 \); in the transition region the probability distribution is bimodal (see e.g. [17]).

The relaxation rates for the correlation function (4.1) corresponding to the curves of Fig. 7 are shown in Fig. 8. For \( q < 1 \) \( \lambda_z \) and \( \lambda_i \) coincide. For \( q > 1 \) and \( a < 3 \) \( \lambda_z \) exceeds \( \lambda_i \) insignificantly. Near the critical point \((a = 3)\) the difference between \( \lambda_z \) and \( \lambda_i \) grows larger and the transition point is shifted to \( q > 1 \).
where the locations of the minima of the relaxation rates \( \lambda_s \) and \( \lambda_t \) differ. However, in the thermodynamic limit the minima are shifted back to \( q = 1 \) and, as shown in Fig. 9, the difference between the minimum values of \( \lambda_s \) and \( \lambda_t \) vanishes. Therefore, we conclude from (2.10) that in this limit the smallest relaxation rate has the behaviour derived for \( \lambda_s \) by Grossmann and Schranner [17, 35], i.e.

\[
\lambda_t \approx \lambda_s \approx \lambda_s \approx \lambda_{s0} \quad (4.12a)
\]

with

\[
\lambda_s \approx \frac{1}{\Gamma(5/4) / (5/4)} \Omega^{-1/2} + O(\Omega^{-1}). \quad (4.12b)
\]

The difference of short-time and mean relaxation time description of correlation functions for systems of finite size near a second order phase transition has been demonstrated above also for the first Schlögl model. Again this difference vanishes in the thermodynamic limit.

However, such a convergence is not found in the region of the first order transition \( (a > 3) \), where large differences for the minimum values of the relaxation rates appear. Figure 8 shows that even for a system of small size \( \lambda_s \) and \( \lambda_t \) differ by orders of magnitude. Figure 10 demonstrates that the behaviour

\[
\lambda_t \approx \exp(-\Omega) \quad (4.13)
\]

holds. This relation has been derived by Janssen [29] for the lowest eigenvalue, demonstrating that the mean relaxation time approximation based on the low frequency moment \( \mu_{-1} \) provides a satisfactory description. In contrast, the short-time approxima-

\[
\lambda_s \approx \Omega^{-1} \quad (4.14)
\]

and, hence, fails to describe the correct long-time relaxation even for small system size. This result may be compared with the corresponding result for the correlation function \( C_1 \) (3.2a) for diffusion in the quartic potential of Sect. 3. There an analogous discrepancy between \( \lambda_s \) and \( \lambda_t \) occurred for \( \kappa < 0 \), i.e. in the parameter region where the stationary distribution becomes bimodal. In the bimodal regime of the quartic potential the long relaxation time is due to barrier crossing processes and exhibits the behaviour \( \tau_t \sim \exp(\Delta U) \) where \( \Delta U \) is the barrier height. In the second Schlögl model for \( a > 3 \) the stationary distribution is bimodal as well. The dominant long-time processes contributing to the particle number correlation function (4.1) are transitions between the different distribution peaks corresponding to barrier crossing. For the same reasons as for the quartic potential the short-time description fails even if memory terms are included [17].

5. Summary

Relaxation processes are slow near instabilities corresponding to first and second order phase transitions even in systems of finite size and must be described by approximations which take the low frequency moments \( \mu_{-n}, n > 0 \) into account. Application to the first and second Schlögl model demonstrates that such an approximation, even at its lowest level, sat-
satisfactorily describes the increase of the relaxation time near phase transitions in finite systems and is superior to the conventional Mori-Zwanzig projection operator formalism involving high frequency moments only.

Appendix

At \( \kappa = 0 \) the first high frequency moments for the correlation function \( C_1(t) \) of a diffusion process in the potential \( (3.1) \) are given by

\[
\mu_1 = \langle 1 \rangle = 1
\]

(A1)

\[
\mu_0 = \langle x^2 \rangle = 2 \Gamma(3/4)/\Gamma(1/4).
\]

(A2)

The low frequency moment \( \mu_{-1} \) is determined from (2.16 b) in the following way

\[
\mu_{-1} = (2/N) \int_0^\infty dx \exp(x^4/4) I(x)
\]

(A3)

with (for the last identity see [36])

\[
I(x) = \left\{ \int_0^\infty dyy \exp(-y^4/4) \right\}^2 = \left\{ \int_{x^2/2}^\infty dz \exp(-z^2) \right\}^2 = \int_1^\infty dt \exp[-x^4(1+t^2)/4]/(1+t^2)
\]

(A4)

and

\[
N = 2 \int_0^\infty dx \exp(-x^4/4) = \Gamma(1/4)/\sqrt{2}.
\]

(A5)

After changing the order of integration the evaluation of (A3) is straightforward. One obtains

\[
\mu_{-1} = \int_1^\infty dt t^{-1/2}(1+t^2)^{-1} = \pi \ln [(2+\sqrt{2})(2-\sqrt{2})]/2\sqrt{2}.
\]

(A6)

With these results equations (3.3) follow immediately.

References

18. The evaluation of the inverse operator poses no problems in principle since \( \delta M \) does not belong to the kernel of \( L^* \)
31. Actually there is no transition at \( \kappa = 0 \) in the stochastic model since \( N = 0 \) becomes an absorbing state
33. This relationship can be obtained using the generating function for the moments of the probability distribution given in Jähnig, F., Richter, P.H.: Ber. Bunsengesellsch. Phys. Chem. 80, 1132 (1976)
35. Grossmann and Schranner questioned the validity of the relationship \( \lambda_1 \sim \Omega^{-1/2} \). Their argument is that Janssen [29] derived \( \lambda_1 \sim \exp(-\Omega) \). But Janssen's derivation of this relation holds for the case that the probability distribution is bimodal which is true solely for \( a > 3 \). Since long- and short-time approximation convergence in the limit \( \Omega \rightarrow \infty \) we regard the relationship \( \lambda_1 \sim \Omega^{-1/2} \) to be correct

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