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**Rotational Motion of Molecules in Condensed
Phases**

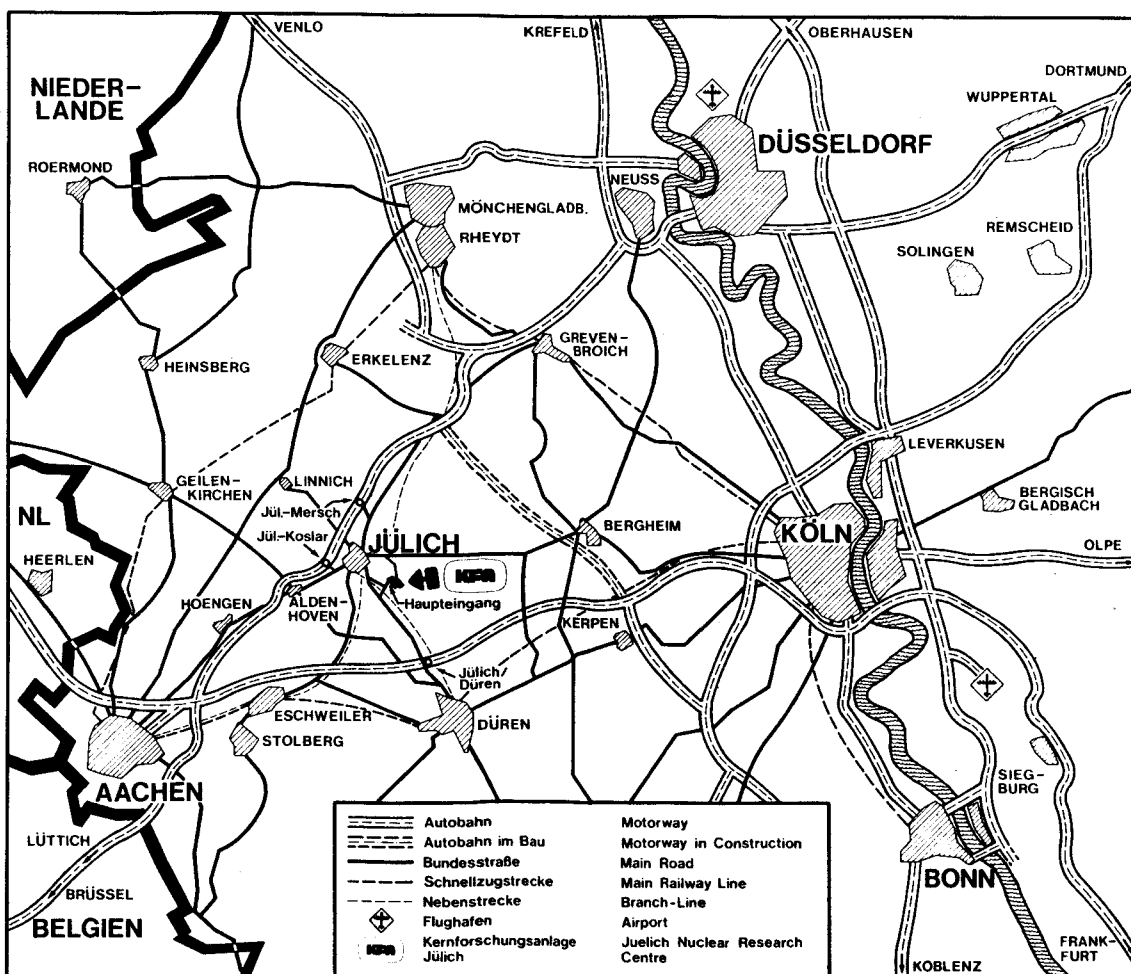
by

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Rotational Motion of Molecules in Condensed Phases

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ZUSAMMENFASSUNG

Die Langevin-Gleichung wird benutzt, um Rotationsbewegungen zu beschreiben. Die Rotations-Langevin-Gleichung wird mit numerischen Methoden für Rotationsbewegungen mit einem, zwei und drei Freiheitsgraden gelöst. Aus diesen Lösungen werden Korrelationsfunktionen berechnet. Es wurden die Korrelationsfunktionen ausgesucht, die in der Neutronenstreuung von Bedeutung sind. Im Fall von ein und zwei Rotationsfreiheitsgraden werden die Ergebnisse der Langevin-Gleichung mit früheren Resultaten anderer Methoden verglichen. Es stellt sich heraus, daß diese anderen Modelle für bestimmte Parameterbereiche die gleichen Ergebnisse liefern, wie die Langevin-Gleichung. Wenn die Potentialbarrieren höher als etwa 8 mal die thermische Energie sind, ist die harmonische Näherung gut. Für große Reibungskonstanten sind Diffusionsmodelle eine gute Näherung.

Für drei Rotationsfreiheitsgrade wird der Ablauf der Bewegung studiert. Man findet, daß Sprungmodelle nur für sehr große Potentialbarrieren gute Ergebnisse liefern. Für kleine Potentialbarrieren ($< 5 k_B T$) ist die Bewegung mehr diffusiv als sprunghaft. Ohne Fitparameter werden die Breite des Neutronenstreugesetzes und die Aktivierungsenergie der Sprünge abgeschätzt. Sie stimmen beide recht gut mit experimentellen Resultaten überein.

SUMMARY

The Langevin-equation is used for rotational motion. The rotational Langevin-equation is solved for rotators with one, two and three degrees of freedom by numerical methods. From the solutions correlation functions are extracted. The calculated correlation functions are chosen with respect to applications in neutron scattering. In the case with one and two rotational degrees of freedom the Langevin-results are compared with earlier results obtained with different methods. It is found that in certain parameter ranges other models are able to describe the problem. If the rotational barrier height is larger than about 8 times the thermal energy the harmonic approximation to the potential give good results. In the case of three rotational degrees of freedom the dynamics of the rotational motion of the molecule is studied in some detail. It is found that the jump models are only reasonable good for very large barrier heights. For smaller barrier heights ($< 5 k_B T$) the motion is much more diffusive than jump like. Without a fitting parameter the width of the neutron scattering law and activation energy are calculated. They both agree very well with experimental results.

1. INTRODUCTION

The problem of rotational motion of a molecule has been studied by various theoretical and experimental methods over the years [1-4].

For molecules and polyatomic ions we distinguish between the internal modes of vibration and the external modes which are connected with the rigid body translations and rotations of a molecule as a whole. All molecules possess three translational degrees of freedom.

Because the rotations of the molecule and its translational motion happen on two different characteristic time scales the two motions can be separated and treated as independent. In the presented work we want to discuss the rotational motion of molecules only.

In molecular gases and liquids the translational and rotational motion is diffusive whereas in molecular crystals the individual molecules are in an equilibrium position around which they perform small amplitude translational oscillations. In most crystals the molecules also are in a deep minimum of their rotational potential. Then they perform small amplitude angular oscillations (generally termed librations) around the minimum orientation of the rotational potential.

There is, however, the case of orientational disorder in crystals (ODIC) where a molecule has the choice between several minima of the orientational potential. The rotational motion between the potential minima (the reorientation) then is diffusive. If the potential is high the reorientation is stepwise, if the potential is shallow one observes a small angle diffusion which is very similar to the rotational diffusion in liquids where the time average of the rotational potential is zero [1,2].

In ODIC materials the rotational diffusion may be partly quenched. This is the case in $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ where due to strong electrostatic forces the dipole moments of the NH_3 groups are aligned along cubic crystals axes. The molecule therefore performs a rotational diffusion around the axis of its dipole moment - around the other two rotation axes it performs small amplitude librations [5]. Other cases of one-dimensional rotation are NO_3^- in NaNO_3 and hydrocarbon rings on surfaces.

Linear molecules as e.g. CO or N_3^- possess two rotational degrees of freedom (the polar coordinates θ and φ).

All other molecules possess three rotational degrees of freedom (the Euler angles ξ , η and ζ or quaternions τ_1, τ_2, τ_3 , and τ_4).

Examples for the different types of molecules are given in Fig. 1. In this figure the molecules are classified according to their chemical bonding in the crystal.

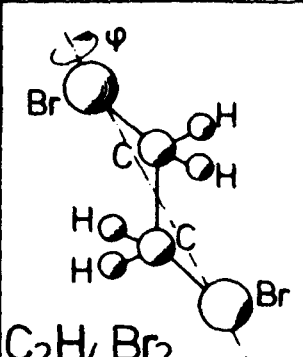
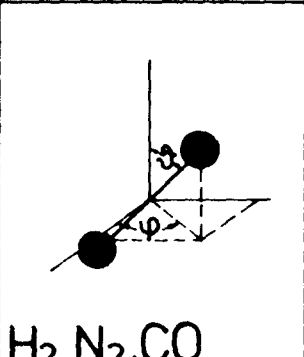
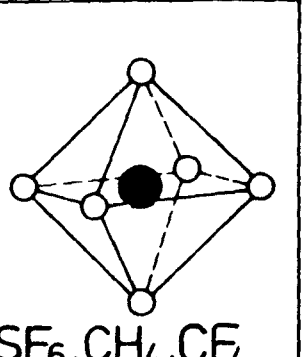
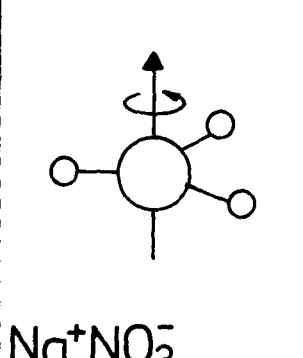
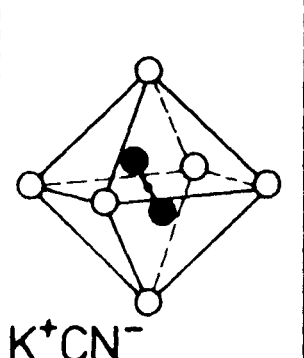
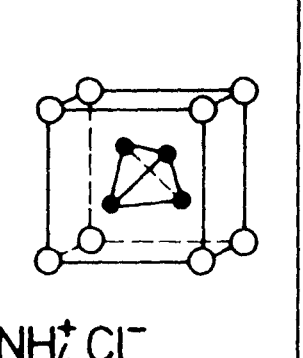
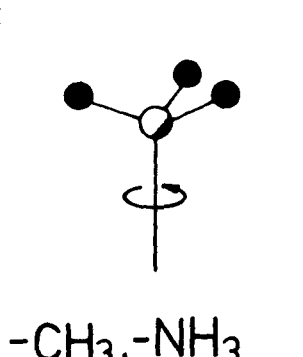
Rotational degrees of freedom	1	2	3
molecules in molecular crystals (van-der-Waals crystals)	 $C_2H_4Br_2$	 H_2, N_2, CO	 SF_6, CH_4, CF_4
polyatomic ions in ionic molecular crystals	 $Na^+NO_3^-$	 K^+CN^-	 $NH_4^+ Cl^-$
radicals in molecular crystals, polymers	 $-CH_3, -NH_3$	—	—

Fig. 1: Examples for one, two and three rotational degrees of freedom [2].

We are interested in the rotational motion of molecules with one, two, and three angular degrees of freedom in gases, liquids, and ODIC materials. In chapter 3 we shall concentrate on cases where the time average of the orientational potential vanishes. So strictly speaking that results are only applicable to gases and liquids and to a few ODIC cases as e.g. CH_4 in phase I [6] or succinonitrile [3] where the orientational potential is rather weak.

In the chapters 4 to 6 we want to discuss the rotational motion with a static potential. For our calculation we look only at one molecule. This particle experiences a static potential from the interactions with its neighbouring particles. This static potential reflects the symmetry of the molecule and the symmetry of the surrounding. In a real crystal the neighbouring particles do not sit at their lattice place. They perform small amplitude oscillations. From these oscillations the static potential receives small fluctuating contributions. In our model we simulate the small fluctuations of the potential by a heat bath, which represents all other degrees of freedom of the crystal.

Furthermore we want to neglect the coupling of rotational and translational motion and all effects which arise from the internal librations of the molecule. In other words, we will regard the molecule as a rigid rotator in a static potential. A fluctuating torque ensures that the molecule is distributed over the whole energy range. The energy of such a system increases without limitation. Therefore one needs a friction term which guarantees the thermal equilibrium.

The quantum mechanical nature of the problem should be taken into account if the temperature is less than the difference of the characteristic energy levels of the system. In the case of a free rotator the difference of the energy levels is given by the rotational constant $B = \hbar^2/2I$. With the exception of a few light molecules (e.g. H_2, D_2) the corresponding temperature is much less than $10^\circ K$.

molecule	$B = \hbar^2/2I$ [$^\circ K$]
H_2	85.4
D_2	43
CH_4	8.5
NH_4	8
N_2	2.9
CO	2.65
O_2	2.1
Cl_2	0.36

Table 1 The rotational constant $\hbar^2/2I$ for different molecules.
From ref. [7-9].

If the particle experiences a static potential the problem is much more complicated [7-9]. If the thermal energy $k_B T$ is less than the energy difference between the lowest librational states ΔE one must perform a quantum mechanical calculation. The energy difference ΔE can be calculated from the individual potential.

For further calculation we will restrict ourselves to classical calculations. That means our temperature must be larger than $\frac{\hbar^2}{2I}$ and/or ΔE which are the characteristic energies of the problem.

Various models have been used to describe the physical situation. In the case of rotational motion without potential the most interesting models are the extended diffusion models of Gordon [10]. Details of these models are discussed in chapter 3. An overview over the other models used is given in the publication.

In the case of a rotator with one degree of freedom in an N-fold potential the diffusion model of Dianoux and Volino [11,12] has been the most successful calculation. This model is discussed in chapter 4.

A dumbbell-molecule in a cubic potential has been treated by de Raedt [7,13]. He used a method which is based on the expansion in symmetry adapted functions and on the use of projection operator techniques. We comment on this calculation in our chapter 5. In the case of a spherical top molecule which experiences an orientational potential no prior calculations exist.

We use a Langevin-equation approach which has been generalized to angle coordinates. This model is described in chapter 2. From the numerical solutions of the different Langevin-equations we can extract correlation functions. The correla-

tion functions can be related to experimental data. One can expand the incoherent neutron scattering law in terms of autocorrelation functions of symmetry adapted functions. In the corresponding chapters we will perform these expansions. Gordon [14] has shown that the Fourier-transforms of infrared and Raman band shapes are related to Legendre polynomial correlation functions $\langle P_1(\cos \beta) \rangle$ and $\langle P_2(\cos \beta) \rangle$. β is the angle between the orientation of the molecule at time zero and at time t .

2. THE MODEL

During the "séance du 9 Mars 1908" of the "academie des sciences" P. Langevin presented a short note "Sur la théorie du mouvement brownien" [15]. In this note he published the equation of motion

$$m \frac{d^2 \mathbf{x}}{dt^2} = -6\pi\mu a \frac{d\mathbf{x}}{dt} + \mathbf{X} \quad (2.1)$$

for a particle of mass m moving in a viscous medium under the influence of a stochastic force $\mathbf{X}$. From Stokes law the resistance resulting from the viscosity is $-6\pi\mu a \frac{d\mathbf{x}}{dt}$. a is the radius of the particle and μ the viscosity of the medium.

Today we call this the Langevin-equation and write usually

$$\ddot{\mathbf{x}} = -\Gamma \dot{\mathbf{x}} + \frac{G^{1/2}}{m} \mathbf{F}(t) \quad (2.2)$$

The acceleration $\ddot{\mathbf{x}}$ of a free particle is determined by a friction term $-\Gamma \dot{\mathbf{x}}$ and a stochastic force. For later convenience the stochastic force $\mathbf{X}$ is written as $G^{1/2} \mathbf{F}(t)$ where $G^{1/2}$ represents the strength of the stochastic force.

In the following we want to derive the Langevin equation from a basic equation and generalize it to rotational motion (angle coordinates).

2.1 THE LANGEVIN-EQUATION

A free particle of mass m is in contact with a bath. The interaction between particle and bath is described by a force A . Generally the force is a function of time t and a functional of the velocity $\dot{x}(t')$ for times t' prior to t . The dependence of $\dot{x}(t')$ describes the "history" of the particle. The differential equation for the $x(t)$ is nonlinear and retarded [16]

$$m \ddot{x} = A(t, [\dot{x}(t')]). \quad (2.3)$$

The force A is decomposed into its mean value $\bar{A}$ which is not explicitly time dependent, and a fluctuating part $R(t)$, which is explicitly time dependent.

$$A = \bar{A} + R(t) \quad (2.4)$$

$R(t)$ is characterized by its selfcorrelation function

$$g(t) = \overline{R(t)R(0)} \quad (2.5)$$

The function $g(t)$ describes the spectrum of the fluctuations of the force A . The time over which $g(t)$ is different from zero defines the correlation time τ_c of the force. τ_c is the characteristic time of the bath. The mean force $\bar{A}$ has normally a different characteristic time τ_A which arises from the $\dot{x}$ dependence of $\bar{A}$. With the assumption that $\dot{x}(t)$ does not change during the time τ_c equation (2.3) leads to the equation of motion:

$$m \ddot{x} = \bar{A}(\dot{x}(t)) + R(t) \quad (2.6)$$

The assumption is justified if the forces $\bar{A}$ and $R(t)$ are both so weak that they do not change $\dot{x}$ appreciably over the time τ_c .

If τ_c is so short that it can be neglected on the time scale where $\dot{x}(t)$ changes the correlation function $g(t)$ can be written

$$g(t) = G(\dot{x})\delta(t) \quad (2.7)$$

The assumption that τ_c is much shorter than the correlation time of the particle velocity is the assumption of a short memory. The other assumption one needs to derive the Langevin-equation is that the velocity of the regarded particle is much smaller than the mean thermal velocity in the bath. Using the later assumption one can expand $\bar{A}(\dot{x})$ and $G(\dot{x})$ with respect to $\dot{x}$

$$\bar{A}(\dot{x}) = K - m\Gamma\dot{x} + \dots \quad (2.8a)$$

$$G(\dot{x}) = G + \dots \quad (2.8b)$$

Now one can write eq. (2.6) in the way of usual Langevin-equation

$$m \ddot{x} = K - m\Gamma\dot{x} + G^{1/2} F(t) \quad (2.9)$$

where we made use of the decomposition

$$R(t) = G^{1/2} F(t) \quad (2.10)$$

The time dependent function $F(t)$ obeys

$$\overline{F(t)} = 0 \quad (2.11a)$$

$$\overline{F(t)F(0)} = \delta(t) . \quad (2.11b)$$

This can be seen from eq. (2.4) and (2.7).

To get the Langevin-equation (2.9) we used two approximations:

- (i) the short memory of the particle
- (ii) linearization with respect to $\dot{x}$

The time scale on which $\dot{x}$ changes is $1/\Gamma$. Therefore the condition of short memory is equivalent to $\Gamma \cdot \tau_c \ll 1$. From the equipartition theorem we know:

$$\frac{m}{2} \dot{x}^2 = \frac{1}{2} k_B T \quad (2.12)$$

This relation implies a relation between Γ , G and T . To get this relation which is normally called fluctuation-dissipation theorem, we assume a free particle. Then we can neglect the constant force K in eq. (2.9). The Langevin equation now reads:

$$\ddot{x} = -\Gamma \dot{x} + \frac{G^{1/2}}{m} F(t) \quad (2.13)$$

Integrating over t once one finds the solution [17,18]

$$\dot{x}(t) = \dot{x}_0 e^{-\Gamma t} + e^{-\Gamma t} \frac{G^{1/2}}{m} \int_0^t e^{\Gamma t_1} F(t_1) dt_1 \quad (2.14)$$

Squaring this solution and taking the mean leads to

$$\overline{\dot{x}^2} = \dot{x}_0^2 e^{-2\Gamma t} + e^{-2\Gamma t} \frac{G}{m^2} \int_0^t \int_0^t e^{\Gamma(t_1+t_2)} \overline{F(t_1)F(t_2)} dt_1 dt_2 \quad (2.15)$$

Introducing new variables $v=t_1+t_2, w=t_1-t_2$ the integral becomes

$$\frac{1}{2} \int_0^{2t} e^{\Gamma v} dv \int_{-\infty}^{\infty} \delta(w) dw = \frac{1}{2\Gamma} (e^{2\Gamma t} - 1) \quad (2.16)$$

Because we have eq. (2.11b) we could do the w integration from $-\infty$ to ∞ . After the integration eq. (2.15) reads

$$\overline{\dot{x}^2} = \dot{x}_0^2 e^{-2\Gamma t} + \frac{G}{2\Gamma m^2} (1 - e^{-2\Gamma t}) \quad (2.17)$$

Using the theorem of the equipartition of energy (2.12) we get

$$\lim_{t \rightarrow \infty} \overline{\dot{x}^2} = \frac{G}{2\Gamma m^2} = \frac{k_B T}{m} \quad (2.18)$$

The fluctuation dissipation-theorem is then

$$G = 2\Gamma m k_B T \quad (2.19)$$

Eq. (2.19) shows that the strength of the fluctuating force $G^{1/2}$, the friction Γ and the temperature T cannot be chosen independently. If two of these variables are set, the third follows from the fluctuation-dissipation theorem.

The relation also shows that it is sufficient for the validity of the Langevin description to demand that $\Gamma\tau_c \ll 1$ i.e. that the systematic forces attenuate the particle only little over the correlation time of the stochastic force. Eq. (2.19) then guarantees that the influence of the fluctuating force is of the same order of magnitude as the systematic forces.

2.2 GENERALIZED ROTATIONAL LANGEVIN-EQUATION

Everything that has been said up to now was concerned with a Brownian particle moving in one dimension. In the present work we want to discuss rotational motion of molecules. Therefore the Langevin-equation must be generalized to the case of rotational motion in one, two, and three dimensions.

The interaction energy of two molecules with orientations denoted collectively by Ω_i and Ω_j and a center of mass distance $\vec{R}_{ij}$ is usually [19] split into two parts:

$$\Phi(\vec{R}_{ij}, \Omega_i, \Omega_j) = \Phi_I(R_{ij}) + \Phi_A(\vec{R}_{ij}, \Omega_i, \Omega_j) \quad (2.20)$$

By definition Φ_I is the spherical average of Φ , i.e. $\Phi_I = \langle \Phi \rangle$ and $\langle \Phi_A \rangle = 0$.

For globular molecules as e.g. methane, neopentane or adamantane the anisotropic part Φ_A of the potential is much weaker than the isotropic part Φ_I . This is clearly demonstrated

by the existence of ODIC phases sometimes also termed solid rotator phases. In these phases the central force have established a crystalline order of the centers of mass of the molecules, but the weak anisotropic forces cannot achieve an orientational order of the molecules. In dense phases of globular molecules the rotational agitation of an individual molecule is permanent but weak at the same time. Therefore the angular momentum of a molecule changes only little on the same scale of the fluctuations of the torques exerted by its neighbors. This is the justification for a description of the rotational motion of globular molecules within the framework of the Langevin equation. This is the assumption leading to eq. (2.6) is fulfilled.

An easy way to get the equation of motion is to use the Lagrange formalism [20]. The Lagrange function $L=T-U$ is given by the kinetic energy T and the potential energy U .

The coordinates of the rotating molecule must satisfy certain conditions. These conditions reduce the freedom of the motion. There exist a formalism to get the equations of motion for systems which are subject to constraints.

If the generalized coordinate is q_i the related generalized velocity is $\dot{q}_i$. Then, in terms of coordinates, the constraints can be written

$$f_j(q_1, q_2, \dots, q_n) = 0 \quad 1 \leq j \leq s \quad (2.21)$$

where n is the number of independent coordinates without constraints and s is the number of restrictions. The equations of motion are determined by

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = \sum_{j=1}^s \lambda_j \frac{\partial f_j}{\partial q_i} \quad 1 \leq i \leq n \quad (2.22)$$

The λ_j are Lagrange's multipliers and they can be calculated from eq. (2.21) and (2.22).

In the case of one angular degree of freedom we use the polar-coordinates r and φ . The restriction is given by $|r| = \text{const}$. The Lagrange function is:

$$L_1 = \frac{I}{2} \dot{\varphi}^2 - U_1(\varphi) \quad (2.23)$$

I is the moment of inertia, which is given by mr^2 .

In the case of a dumbbell-molecule (two degrees of freedom) the best coordinates are the Cartesian coordinates. The Lagrange function then is

$$L_2 = \frac{m_1}{2} \dot{\vec{x}}_1^2 + \frac{m_2}{2} \dot{\vec{x}}_2^2 + U_2(\vec{x}_1, \vec{x}_2) \quad (2.24)$$

The indices 1 and 2 denote the two particles which compound the molecule. We have 5 restrictions. The first two are that $|\vec{x}_1| = |\vec{x}_2| = \text{const}$. The other three arise from the fact that the two particles had to be antipodes. This means $\vec{x}_1 = -\vec{x}_2$.

The most convenient coordinates to describe the rotation

of a spherical top (three degrees of freedom) are the quaternions. The rotations of a spherical top are mapped on the motion of a point on the surface of the four-dimensional unit sphere (see Appendix B of the publication for details). In terms of the quaternions $\vec{\tau} = (\tau_1, \tau_2, \tau_3, \tau_4)$ we get for the Lagrange function

$$L_3 = 2I \dot{\vec{\tau}}^2 - U_3(\vec{\tau}) \quad (2.25)$$

The constraint in this case is $|\tau|=1$.

After some calculations we get from eq. (2.22) using the Lagrange functions L_1 , L_2 and L_3 the equations of motion. Adding a friction term linear in the velocity and a stochastic force term we arrive at the Langevin equation.

One degree of freedom:

$$\ddot{\varphi} = -\frac{1}{I} \frac{\partial U_1}{\partial \varphi} - \Gamma \dot{\varphi} + \frac{G^{1/2}}{I} F(t) \quad (2.26)$$

Two degrees of freedom:

$$\ddot{\vec{x}} = -\frac{1}{I} \text{grad}_{\vec{x}} U_2 - \Gamma \dot{\vec{x}} - |\dot{\vec{x}}|^2 \vec{x} + \frac{G^{1/2}}{I} \vec{F}(t) \quad (2.27)$$

Three degrees of freedom:

$$\ddot{\vec{\tau}} = -\frac{1}{4I} \text{grad}_{\vec{\tau}} U_3 - \Gamma \dot{\vec{\tau}} - |\dot{\vec{\tau}}|^2 \vec{\tau} + \frac{G^{1/2}}{4I} \vec{F}(t) \quad (2.28)$$

In (2.2) we wrote the equation in reduced units with $\vec{x} = \frac{\vec{x}_1}{|\vec{x}_1|}$. The difference between eq. (2.27) and (2.28) is that eq. (2.28) is fourdimensional and (2.27) is three-dimensional. Details of the potential U_1 , U_2 and U_3 are given in chapters 4, 5 and 6.

2.3 LANGEVIN-EQUATION WITH NON-LINEAR FRICTION

In eq. (2.8a) and (2.8b) we expanded the mean-value $\overline{A(\dot{x})}$ and the fluctuating part $G(\dot{x})$ of the force. This is possible if the velocity of the regarded particle is much smaller than the mean thermal velocity in the bath. Now we want to get rid of this restriction. Therefore we decompose $\overline{A(\dot{x})}$.

$$A(\dot{x}) = K + B(\dot{x}) \quad (2.29)$$

The constant part can identified as a static force which arises from a static potential. It is possible that K is a function of x . Using a potential $V(x)$ the static part can be written

$$K = -\frac{\partial}{\partial x} V(x) \quad (2.30)$$

A generalized Langevin equation can be written down now.

$$\ddot{x} = -\frac{1}{m} \frac{\partial}{\partial x} V(x) + B(\dot{x}) + \frac{G^{1/2}(\dot{x})}{m} F(t) \quad (2.31)$$

This new Langevin equation needs only the approximation of

a short memory of the particle. The linearization is not necessary any more. The only requirement is that $B(\dot{x})$ is an odd function.

$$B(-\dot{x}) = -B(\dot{x}) \quad (2.32)$$

As in the case of linear Langevin equation one needs a fluctuation-dissipation-theorem. This theorem should guarantee that the system reaches equipartition. Starting from eq. (2.31) we construct a Fokker-Planck-equation. The way how to do this is described in textbooks [18]. The result is

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial \dot{x}} \left\{ \frac{1}{2m^2} \frac{\partial}{\partial \dot{x}} [Gw] - Bw \right\} - \dot{x} \frac{\partial w}{\partial x} - \frac{K(x)}{m} \frac{\partial w}{\partial \dot{x}} \quad (2.33)$$

The arguments of G , w and B are dropped for clarity.

The equipartition is guaranteed if the stationary solution of eq. (2.33) is the Maxwell distribution

$$w(x, \dot{x}) = C \exp \left\{ - \frac{\frac{m}{2} \dot{x}^2 + V(x)}{k_B T} \right\} \quad (2.34)$$

To set the Maxwell-distribution in eq. (2.33) and putting $\frac{\partial w}{\partial t} = 0$ leads to the generalization of the fluctuation-dissipation-theorem.

$$B(\dot{x}) = \frac{1}{2m^2} \left(\frac{\partial}{\partial \dot{x}} - \frac{m\dot{x}}{k_B T} \right) G(\dot{x}) \quad (2.35)$$

Using this equation one can eliminate $B(\dot{x})$ in equation (2.33). This leads to the generalized Fokker-Planck-equation

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial \dot{x}} \left\{ \frac{1}{2m^2} G \frac{\partial}{\partial \dot{x}} w + \frac{\dot{x}}{2mk_B T} G w \right\} - \dot{x} \frac{\partial w}{\partial x} - \frac{K(x)}{m} \frac{\partial w}{\partial \dot{x}} \quad (2.36)$$

The generalized Langevin equation (2.31), the generalized Fokker-Planck-equation (2.36) and the generalized fluctuation-dissipation-theorem (2.35) reproduce the linearized equations, if one puts $G(\dot{x})$ constant.

For the conventional case where the Langevin theory is applicable, namely for a heavy particle in a bath of light particles, the velocity $\dot{x}$ of the heavy particle is small with respect to the velocities of the bath particles. Then $B(\dot{x})$ can be linearized: $B(\dot{x}) = -\Gamma \dot{x}$ where Γ is the frictional constant. In our case the particle considered is identical with the bath particles: its velocity is not small and therefore the nonlinear terms have to be considered. For translational motions it is expected that the frictional force increases more strongly than linearly with the velocity: $B(\dot{x}) = -\Gamma \dot{x} - \Gamma_3 \dot{x}^3 - \dots$ with $\Gamma_3 > 0$. This is not the case for rotational problems. A molecule rotating around an n-fold symmetry axis with angular velocity $\dot{\phi}$ produces an alternating field of frequency $\omega = n\dot{\phi}$. For large angular velocities $\dot{\phi}$ the surroundings cannot respond to this high frequency field. We conclude that $B(\dot{\phi})$ has to approach zero as $\dot{\phi}$ goes to infinity in the case of rotational motion.

$$\lim_{\dot{\phi} \rightarrow \infty} B(\dot{\phi}) = -0 \quad (2.37)$$

One possible solution of eq. (2.35) which fulfills the conditions (2.32) and (2.37) is

$$B(\dot{\phi}) = - \frac{c}{2I^2} \left(\frac{I}{k_B T} + b \right) \dot{\phi} \exp(-b\dot{\phi}^2/2) \quad (2.38a)$$

$$G(\dot{\phi}) = c \exp(-b\dot{\phi}^2/2) \quad (2.38b)$$

with arbitrary positive b and c . We have replaced $\dot{x}$ by $\dot{\phi}$ and m by I to express the rotational nature of the motion. The constant c denotes the strength of the stochastic force and b is a measure for the nonlinearity. The friction has its maximal strength at the point $\dot{\phi} = \sqrt{1/b}$. If b is zero we reproduce the linear case.

3. ROTATIONAL MOTION WITHOUT POTENTIAL

In the preceding chapter of this work, the Langevin model is discussed in some detail. In this chapter we want to restrict ourselves to the case without a static potential. That means we want to treat the liquid- or gas-case. The rotational motion in solids (with static potential) is discussed in chapters 4 to 6.

3.1 NEUTRON SCATTERING LAW AND CORRELATION FUNCTIONS

Over the years inelastic neutron scattering has become a frequently used method for studying molecular motion. The incoherent neutron scattering law is determined by the dynamic selfcorrelation functions of the scattering centers. The scattering law is given by [1]

$$S(\vec{Q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} I(\vec{Q}, t) dt . \quad (3.1)$$

$S(\vec{Q}, \omega)$ is the scattering law. The intermediate scattering function $I(\vec{Q}, t)$ is defined by

$$I(\vec{Q}, t) = \frac{1}{N} \sum_{j=1}^N \langle \exp\{i\vec{Q}[\vec{r}_j(t) - \vec{r}_j(0)]\} \rangle . \quad (3.2)$$

$\hbar\vec{Q}$ and $\hbar\omega$ are the momentum and energy transfer between the neutron and the scattering centre. The sum over j runs over all scattering centers (i.e. atoms) of the sample. If all scattering centers are equivalent (we will assume that) the sum only cancels the factor $1/N$ so that (3.2) becomes

$$I(\vec{Q}, t) = \langle \exp\{iQ[\vec{r}(t) - \vec{r}(0)]\} \rangle \quad (3.3)$$

where the index j has been omitted.

The vector $\vec{r}(t) = r\vec{n}(t)$ rotates with the molecule. It is determined by its magnitude r and the unit vector $\vec{n}(t)$. The angle β between $\vec{n}$ at time t and at time zero is found from

$$\cos \beta = \vec{n}(t) \cdot \vec{n}(0) \quad (3.4)$$

Sears [21] has shown that one can expand the intermediate scattering function in terms of correlation functions for Legendre polynomials

$$I(\vec{Q}, t) = \sum_{n=0}^{\infty} (2n+1) j_n^2(Q \cdot r) \langle P_n(\cos \beta) \rangle \quad (3.5)$$

The Legendre polynomials are given by [22]

$$P_n(z) = \frac{1}{2^n n!} \left(\frac{d}{dz} \right)^n (z^2 - 1)^n \quad (3.6)$$

$j_n(x)$ is the spherical Bessel function of the first kind and order n [22].

The great advantage of this expansion is, that one needs only the first few terms of the sum to get a good approximation to the scattering law if $Qr \leq 3$. Fig. 2 shows the expression $(2n+1)j_n^2(Q \cdot r)$ for $n = 0, 1, 2, 3$, and 4.

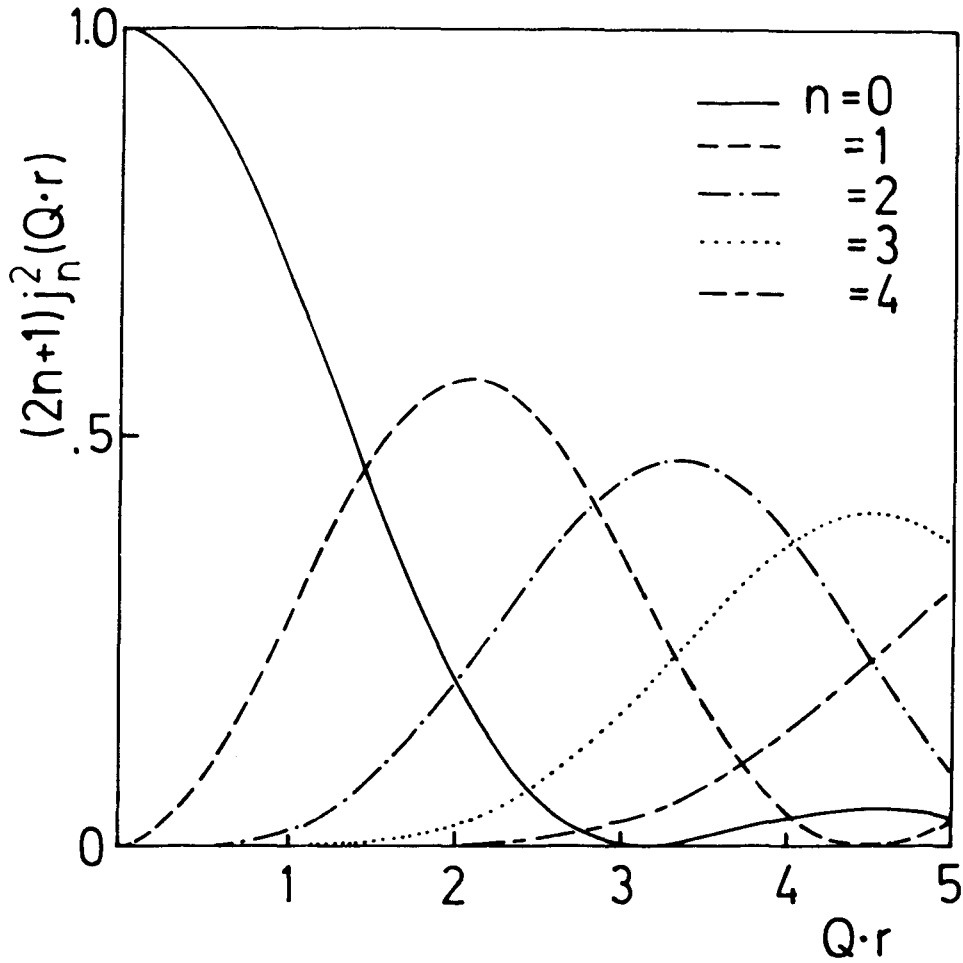


Fig. 2: The functions $(2n+1)j_n^2(Qr)$ for different n as indicated.

Gordon has shown that the infrared and Raman band shapes are related to the Legendre polynomial-correlation functions $\langle P_n(\cos\beta(t)) \rangle$, if the order n is one and two respectively [14]. That is another reason for calculating Legendre polynomial correlation functions.

We have simulated the Langevin equations without potential in the case of one, two, and three rotational degrees of freedom on a computer. From these numerical data we calculated the correlation functions.

In the case of one degree of freedom the Langevin equation can be solved by analytical methods. From this analytic solution we get [23]

$$\langle P_n(\cos\beta(t)) \rangle = \frac{1}{4^n} \sum_{m=0}^n \binom{2m}{n} \binom{2n-2m}{n-m} \exp\left\{ -\frac{(n-2m)^2}{\Gamma^2 \tau^* 2} (\Gamma t - 1 + \exp(-\Gamma t)) \right\}. \quad (3.7)$$

Γ is the friction constant. The numerical results of the simulations and some more details of the calculations are given in the publication, which is reproduced.

3.2 PUBLICATION

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Langevin Model of the Rotational Diffusion of Molecules

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Globular molecules in dense gases, liquids, and orientationally disordered crystals experience an incessant fluctuating torque of rather weak magnitude. In gases and liquids the fluctuating torque perturbs the otherwise free rotational motion which becomes diffusive. We treat the rotational diffusion within the Langevin model where the molecules are driven by a stochastic torque and hindered by a friction term. The Langevin equation for molecules with one, two, and three angular degrees of freedom is solved numerically and the dipole and Raman correlation functions are extracted. In the one-dimensional case we compare with the exact solution of the Langevin equation, in two and three dimensions with earlier work and with experimental results.

I. Introduction

For molecules and polyatomic ions we distinguish between the internal modes of vibration and the external modes which are connected with the rigid body translations and rotations of a molecule as a whole. All molecules possess three translational degrees of freedom. Linear molecules as e.g., CO or N_3^- possess two rotational degrees of freedom (the polar coordinates ϑ and φ) whereas all other molecules possess three rotational degrees of freedom (the Euler angles ξ , η , and ζ).

In molecular gases and liquids the translational and rotational motion is diffusive whereas in molecular crystals the individual molecules are in an equilibrium position around which they perform small amplitude translational oscillations. In most crystals the molecules also are in a deep minimum of their rotational potential. Then they perform small amplitude angular oscillations (generally termed librations) around the minimum orientation of the rotational potential.

There is, however, the case of orientational disorder in crystals (ODIC) where a molecule has the choice between several minima of the orientational potential. The rotational motion between the potential minima (the reorientation) then is diffusive. If the

potential is high the reorientation is stepwise, if the potential is shallow one observes a small angle diffusion which is very similar to the rotational diffusion in liquids where the time average of the rotational potential is zero [1, 2].

In ODIC materials the rotational diffusion may be partly quenched. This is the case in $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ where due to strong electrostatic forces the dipole moments of the NH_3 groups are aligned along cubic crystal axes. The molecule therefore performs a rotational diffusion around the axis of its dipole moment - around the other two rotation axes it performs small amplitude librations [3]. Other cases of one-dimensional rotation are NO_3^- in NaNO_3 and hydrocarbon rings on surfaces.

We are interested in the rotational motion of molecules with one, two, and three angular degrees of freedom in gases, liquids, and ODIC materials. In this paper we shall concentrate on cases where the time average of the orientational potential vanishes. So strictly speaking the results are only applicable to gases and liquids and to a few ODIC cases as e.g. CH_4 in phase I [4] or succinonitrile [5] where the orientational potential is rather weak.

The problem of rotational motion of a molecule has

been studied by theoretical [6–14] and experimental [1–3, 15–18] methods over the years.

If the rotation of a molecule happens through small angular steps, the rotational diffusion equation provides a good description. The rotational diffusion equation has been solved by Debye [6] for spherical molecules and by Perrin [7] for asymmetric molecules.

The rotational diffusion model is plausible for large molecules in liquids, but the model is not a good approximation for small molecules or in gases where the molecule rotates through large angles between collisions.

A generalization of the diffusion model for large angles are the M -, M^* -, and J -diffusion models of Gordon [8]. All of these models start from the same point. A molecule rotates freely between two collisions for a time τ_1 with the angular velocity ω_1 , which is related to an angular momentum $\mathbf{J}_1$. After the collision it rotates for a time τ_2 with ω_2 and the momentum $\mathbf{J}_2$. The number of molecules, which are in the $(n+1)$ -diffusion step at a time t is given by the Poisson distribution $1/n!(t/\tau)^n \exp(-t/\tau)$, where τ is the averaged time between two collisions. The total correlation function is a sum over all possible processes, weighted by the Poisson distribution.

In the M -diffusion case the following assumption is made: each collision randomizes the direction of $\mathbf{J}$, but it leaves the magnitude of $\mathbf{J}$ unchanged. In other words: for a given molecule all $|\omega_i|$ are equal.

In J -diffusion the magnitude and the direction of $\mathbf{J}$ are randomized in each collision. The angular momentum of the n^{th} step is independent of all other steps. In the M^* -diffusion the assumption is made that the time τ between two collisions depends on the rotational frequency ω in the form $\tau = \tau_0 f(\omega)$. Possible functions $f(\omega)$ are $f(\omega) = \exp A \omega^2$ or $f(\omega) = 1 + B \omega^n$.

The J -diffusion case cannot be generalized to a frequency dependent τ , because the system does not reach the thermal equilibrium distribution in that case. The population for large values of J is too high.

Gordon performed such calculations for linear molecules and McClung [9] generalized them to symmetric top molecules.

Another possibility to study rotational motion of molecules is the method used by Steele [10] and others [11]. If $\mathbf{n}(t)$ is a unit vector, which is fixed in the molecule, and $\omega(t)$ the angular velocity vector, then one can get $\mathbf{n}(t)$ from:

$$\frac{d}{dt} \mathbf{n}(t) = \omega(t) \times \mathbf{n}(t). \quad (1.1)$$

The problem is to find a solution for this equation when $\omega(t)$ is the solution of a stationary stochastic process described by the Langevin-equation

$$\frac{d}{dt} \omega(t) = -\Gamma \omega(t) + \frac{1}{I} \mathbf{F}(t). \quad (1.2)$$

Γ is the friction constant, I is the moment of inertia and $\mathbf{F}(t)$ is a stochastic torque, which is governed by a Wiener process. Several approximation are introduced in the procedure of calculating the autocorrelation function $\langle \mathbf{n}(t) \mathbf{n}(0) \rangle$ in [10, 11]. The final result is

$$\langle \mathbf{n}(t) \mathbf{n}(0) \rangle = \exp \left\{ -\frac{2k_B T}{I \Gamma^2} [\Gamma t + \exp(-\Gamma t) - 1] \right\}. \quad (1.3)$$

Rotations with two and three dimensions are not discriminated. The results are claimed to be valid for linear and spherical top molecules. They do, however, not reduce to the results for freely rotating molecules in the limit $\Gamma \rightarrow 0$, which shows that Eq. (1.3) cannot be the general solution of the problem.

Barojas et al. [12] and Kushick and Berne [13] used another method to study properties of liquids: the molecular-dynamics technique. By this method one can get detailed microscopic information about the system. It is possible to study the dynamics of angular velocity relaxation and calculate reorientational autocorrelation functions.

There are two main problems to do the computer simulations. One has to study a large system (10^2 – 10^3 molecules) and it is a problem to choose between the many forms of potentials proposed in literature.

In the present paper we want to discuss the Langevin model for molecular rotational motion. The calculations have been performed for all three kinds of rotations numerically by a molecular dynamics simulation of Eq. (1.2). The case with one degree of freedom is also solved analytically to test the numerical solution. The results are compared with the exact calculations for free rotators and with experimental data from infrared and Raman measurements.

II. The Model

All the models described above used one approximation: They neglect all quantum mechanical effects, so that the molecules can be treated as classical rigid rotators. For a wide range of temperatures this seems to be a good approximation. Therefore we want to restrict ourselves to high temperatures.

The interaction energy of two molecules with orientations denoted collectively by Ω_i and Ω_j and a center

of mass distance $\mathbf{R}_{ij}$ is usually [19] split into two parts:

$$\Phi(\mathbf{R}_{ij}, \Omega_i, \Omega_j) = \Phi_I(R_{ij}) + \Phi_A(\mathbf{R}_{ij}, \Omega_i, \Omega_j). \quad (2.1)$$

By definition Φ_I is the spherical average of Φ , i.e., $\Phi_I = \langle \Phi \rangle$ and $\langle \Phi_A \rangle = 0$.

For globular molecules as e.g. methane, neopentane or adamantane the anisotropic part Φ_A of the potential is much weaker than the isotropic part Φ_I . This is clearly demonstrated by the existence of ODIC phases sometimes also termed solid rotator phases. In these phases the central forces have established a crystalline order of the centers of mass of the molecules, but the weak anisotropic forces cannot achieve an orientational order of the molecules. In dense phases of globular molecules the rotational agitation of an individual molecule is permanent but weak at the same time. Therefore the angular momentum of a molecule changes only little on the time scale of the fluctuations of the torques exerted by its neighbors. This is the justification for a description of the rotational motion of globular molecules within the framework of the Langevin equation:

$$\ddot{\phi} = -\frac{1}{I} \text{grad } V(\phi) + B(\phi) + \frac{1}{I} G^{1/2}(\phi) F(t). \quad (2.2)$$

Equation (2.2) is the Langevin equation for one-dimensional rotation with a rotation angle $\phi(t)$ and an angular velocity $\dot{\phi}(t)$. For the rotation with two and three angular degrees of freedom see Sects. III B and C. I is the moment of inertia of the molecule. $V(\phi)$ is the time average of the rotational angular potential [20] which is finite in crystals. In this paper we will concentrate on dense gases and liquids where $V(\phi) = 0$. The case of ODIC with $V(\phi) \neq 0$ will be left to a later publication. For the conventional case where the Langevin theory is applicable, namely for a heavy particle in a bath of light particles, the velocity $\dot{\phi}$ of the heavy particle is small with respect to the velocities of the bath particles. Then $B(\dot{\phi})$ can be linearized: $B(\dot{\phi}) = -\Gamma \dot{\phi}$ where Γ is the frictional constant. In our case the particle considered is identical with the bath particles: its velocity is not small and therefore the nonlinear terms have to be considered. For translational motions it is expected that the frictional force increases more strongly than linearly with the velocity: $B(\dot{\phi}) = -\Gamma \dot{\phi} - \Gamma_3 \dot{\phi}^3 - \dots$ with $\Gamma_3 > 0$. This is not the case for rotational problems. A molecule rotating around an n -fold symmetry axis produces an alternating field of frequency $\omega = n\dot{\phi}$. For large angular velocities $\dot{\phi}$ the surroundings cannot respond to this high frequency field. We conclude that $B(\dot{\phi})$ has to approach zero as $\dot{\phi}$ goes to infinity.

$$\lim_{\dot{\phi} \rightarrow \infty} B(\dot{\phi}) = -0. \quad (2.3)$$

The stochastic torque $G^{1/2}(\phi)F(t)$ is governed by a Wiener process and has the average mean:

$$\langle F(t) \rangle = 0 \quad (2.4)$$

$$\langle F(t)F(t') \rangle = \delta(t-t') \quad (2.5)$$

$G(\phi)$ and $B(\phi)$ are related by the fluctuation-dissipation theorem. When $B(\phi)$ is linearized, with respect to $\dot{\phi}$ one finds

$$G = 2Ik_B T \Gamma \quad (2.6)$$

i.e., the correlation function of the random torque does not depend on the velocity. To find the corresponding fluctuation-dissipation theorem for a generalized friction function $B(\dot{\phi})$ the Langevin Eq. (2.2) with $V(\phi) = 0$ is used to construct a Fokker-Planck equation. Demanding that the Maxwell distribution for $\dot{\phi}$ fulfills the stationary Fokker-Planck equation one arrives at the generalized dissipation-fluctuation theorem:

$$B(\dot{\phi}) = \frac{1}{2I^2} \left(\frac{d}{d\dot{\phi}} - \frac{I\dot{\phi}}{k_B T} \right) G(\dot{\phi}). \quad (2.7)$$

A solution of (2.7) which fulfills the condition $B(-\dot{\phi}) = -B(\dot{\phi})$ is:

$$B(\dot{\phi}) = -\frac{c}{2I^2} \left(\frac{I}{k_B T} + b \right) \dot{\phi} \exp(-b\dot{\phi}^2/2) \quad (2.8a)$$

$$G(\dot{\phi}) = c \exp(-b\dot{\phi}^2/2), \quad (2.8b)$$

with arbitrary b and c . For $b > 0$ this solution of (2.7) also fulfills the condition (2.3). There is a relation between the shape of $B(\dot{\phi})$ in (2.8a) and Gordon's M^* -diffusion model where the relaxation times depend on the angular velocity; the relaxation times increase with increasing angular velocities. For $b = 0$ we retrieve the special case (2.6).

There is no principal problem to solve the Langevin Eq. (2.2) with $B(\dot{\phi})$ and $G(\dot{\phi})$ given by (2.8) on a computer, both for $V(\phi) = 0$ and $V(\phi) \neq 0$. We do, however, prefer to restrict ourselves to the solution of the linearized friction problem with no potential:

$$\ddot{\phi} = -\Gamma \dot{\phi} + \left(\frac{2k_B T \Gamma}{I} \right)^{1/2} F(t). \quad (2.9)$$

The reason for this restriction is twofold.

1) We do not know the generalized fluctuation-dissipation theorem for two- and threedimensional rotations. Thus we would not be able to treat the three cases on the same footing.

2) For one dimension we can solve (2.9) analytically. Thus we can check our numerical results. The nonlinear friction problem in one dimension as well as the case with nonzero potential in one, two, and three dimensions will be treated in later publications.

Throughout the paper we will assume that due to the relatively weak angular forces between the molecules a separation of the time in which the angular momentum changes and the time scale of the fluctuating torque is possible. That is we will neglect all memory effects.

III. Calculations

We have simulated the Langevin (2.9) and the corresponding equations for two- and three-dimensional rotation on a computer, using a random number generator to create realizations of the stochastic torque. From these calculations one obtains the orientation of the molecule as a function of time. This time function can be used to calculate all possible single molecule correlation functions.

If $\mathbf{n}(t)$ is a unit vector fixed in the rotating molecule, one defines a correlation function $\langle \mathbf{n}(t) \mathbf{n}(0) \rangle = \langle \cos \beta \rangle$, where β is the angle between the vector $\mathbf{n}(t)$ and the vector $\mathbf{n}(0)$. Gordon [15] has shown that the Fourier-transforms of infrared- and Raman-bands are related to

$$\langle P_1(\cos \beta) \rangle = \langle \cos \beta \rangle \quad (3.1a)$$

and

$$\langle P_2(\cos \beta) \rangle = \frac{3}{2} \langle \cos^2 \beta \rangle - 1/2 \quad (3.1b)$$

P_1 and P_2 are Legendre polynomials. In the following we want to calculate $\langle P_1(\cos \beta) \rangle$ and $\langle P_2(\cos \beta) \rangle$ for the one, two, and three-dimensional case.

A) Onedimensional Rotator

For one degree of freedom the convenient coordinate is the rotation angle φ . The equation to be solved is the Langevin (2.9). It is identical with the equation for the onedimensional motion of a Brownian particle. The solution of this problem can be found in textbooks [21, 22].

$$\begin{aligned} \varphi(t) - \varphi(0) &= \frac{\omega_0}{\Gamma} (1 - \exp(-\Gamma t)) \\ &+ \frac{1}{\Gamma} \int_0^t \exp(-\Gamma \tau_1) d\tau_1 \int_0^{\tau_1} \exp(\Gamma \tau_2) G^{1/2} F(\tau_2) d\tau_2 \end{aligned} \quad (3.2)$$

where $\omega_0 = \dot{\varphi}(0)$ is the initial angular velocity. In the thermodynamic equilibrium ω_0 obeys a Maxwell-distribution. Using the properties of ω_0 and $G^{1/2} F(t)$ it can be shown, that the solution (3.2) fulfills:

$$\begin{aligned} \langle (\varphi(t) - \varphi(0))^n \rangle &= \begin{cases} 0 & \text{if } n \text{ is odd} \\ (n-1)!! \langle (\varphi(t) - \varphi(0))^2 \rangle^{n/2} & \text{if } n \text{ is even.} \end{cases} \end{aligned} \quad (3.3)$$

From the geometry of the problem one can see that in (3.1) we can replace β by $\varphi - \varphi_0$. After a short calculation one obtains from relation (3.3)

$$\langle \cos(\varphi - \varphi_0) \rangle = e^{-1/2 \langle (\varphi - \varphi_0)^2 \rangle}. \quad (3.4)$$

The average in the exponential is given in literature [21], too,

$$\langle (\varphi - \varphi_0)^2 \rangle = \frac{2}{\Gamma^2 \tau^{*2}} (\Gamma t - 1 + e^{-\Gamma t}). \quad (3.5)$$

Where τ^* is defined by $(I/k_B T)^{1/2}$.

To calculate $\langle P_2(\cos(\varphi - \varphi_0)) \rangle$ we use the relation

$$\begin{aligned} \langle P_2(\cos(\varphi - \varphi_0)) \rangle &= \frac{3}{2} \langle \cos^2(\varphi - \varphi_0) \rangle - 1/2 \\ &= \frac{3}{4} \langle \cos 2(\varphi - \varphi_0) \rangle + 1/4. \end{aligned} \quad (3.6)$$

A calculation similar to the one which leads to (3.4) yields:

$$\langle \cos 2(\varphi - \varphi_0) \rangle = e^{-2 \langle (\varphi - \varphi_0)^2 \rangle}. \quad (3.7)$$

With the aid of Moivre's formula it is possible to show that $\langle P_n(\cos(\varphi - \varphi_0)) \rangle$ can be expressed as a linear combination of terms of the type $\langle \cos m(\varphi - \varphi_0) \rangle$. For large values of n the actual calculation is rather lengthy. Afterwards one can use the following expression

$$\langle \cos m(\varphi - \varphi_0) \rangle = e^{-\frac{m^2}{2} \langle (\varphi - \varphi_0)^2 \rangle}, \quad (3.8)$$

which is based on (3.3).

In the case of a freely rotating molecule $\beta = \omega t$ and therefore one averages $\cos \omega t$ over ω with a Maxwell-distribution $e^{-\frac{\tau^{*2} \omega^2}{2}}$. The results are

$$\langle P_1(\cos \omega t) \rangle_{\text{free}} = e^{-\frac{t^2}{2\tau^{*2}}}, \quad (3.9a)$$

$$\langle P_2(\cos \omega t) \rangle_{\text{free}} = \left(e^{-\frac{2t^2}{\tau^{*2}}} \right) \cdot \frac{3}{4} + \frac{1}{4} \quad (3.9b)$$

In the limit $\Gamma \rightarrow 0$ the general solution becomes identical with (3.9) as it should.

We have also solved (2.9) numerically and calculated $\langle P_1 \rangle$ and $\langle P_2 \rangle$ from the numerical data (see Appendix A for details of the numerical calculation).

The results are given in Fig. 1 and 2. The curve for $\Gamma \cdot \tau^* = 0.0$ is the free rotator solution. The other curves are the analytical solutions (full lines) and the numerical solutions (dashed lines) for finite $\Gamma \cdot \tau^*$.

B) Linear Molecules

In the case of a linear molecule we consider the motion of a unit vector parallel to the internuclear axis. The most convenient coordinates are cartesian coordinates $\mathbf{x} = (x_1, x_2, x_3)$. A centripetal term has to be added to the Langevin equation to keep the particle on the surface of the three dimensional unit sphere

$$\ddot{\mathbf{x}} = -\Gamma \dot{\mathbf{x}} - |\dot{\mathbf{x}}|^2 \mathbf{x} + G^{1/2} \mathbf{F}(t)/I \quad (3.10)$$

where I is the moment of inertia of the molecule. Now $G^{1/2} \mathbf{F}(t)$ is a stochastic force tangential to the unit sphere. Equation (3.10) is a system of three coupled differential equations with a centripetal potential that depends on the velocity. An analytic solution of Eq. (3.10) cannot be given. We solved the equation numerically and calculated the correlation functions from these data. The results for various friction parameters are given in Fig. 3 and 4. The curve with $\Gamma \cdot \tau^* = 0.0$ is again the freely rotating molecule. The analytic result for the free rotation is well known [23, 14].

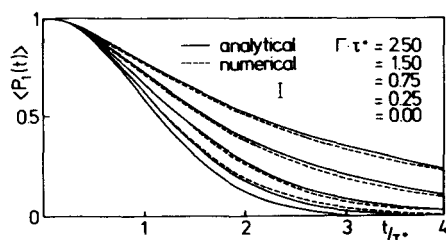


Fig. 1. Dipole correlation function $\langle P_1(t) \rangle$ as a function of time for different values of the friction parameter Γ . (Values as indicated from top to bottom.) The error bar indicates the statistical error of the numerical results. Time scale in units of $\tau^* = (I/k_B T)^{1/2}$ in all figures. One degree of freedom

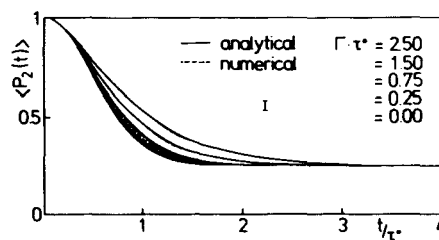


Fig. 2. Raman correlation function $\langle P_2(t) \rangle$. When the difference between the numerical and analytical results is less than the line thickness only the solid line is drawn. One degree of freedom

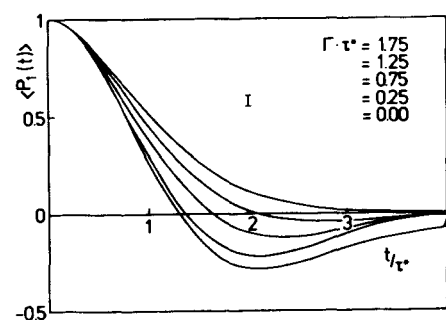


Fig. 3. Dipole correlation function $\langle P_1(t) \rangle$ in the case of two degrees of freedom. Friction constant as indicated from top to bottom

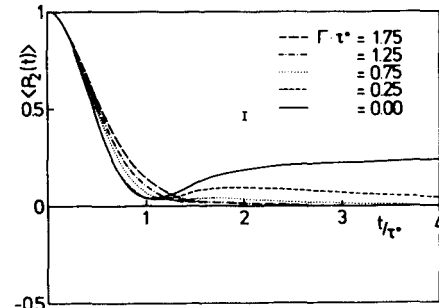


Fig. 4. Raman correlation function $\langle P_2(t) \rangle$ in the case of two degrees of freedom

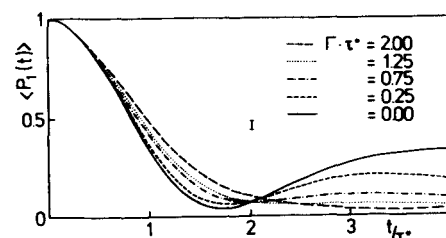


Fig. 5. Dipole correlation function $\langle P_1(t) \rangle$ in the case of three degrees of freedom

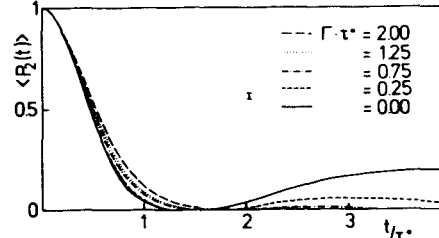


Fig. 6. Raman correlation function $\langle P_2(t) \rangle$ in the case of three degrees of freedom

$$\begin{aligned}\langle P_1(\cos \omega t) \rangle &= \exp -\frac{t^2}{2\tau^{*2}} \Phi \left(-1/2, 1/2; \frac{t^2}{2\tau^{*2}} \right) \\ \langle P_2(\cos \omega t) \rangle &= \frac{3}{4} \langle P_1(\cos 2\omega t) \rangle + 1/4.\end{aligned}\quad (3.11)$$

Where $\Phi(-1/2, 1/2; x)$ is the degenerate hypergeometric function which is given by the series [24]:

$$\Phi(-1/2, 1/2; x) = \sum_{n=0}^{\infty} \frac{1}{1-2n} \frac{x^n}{n!}. \quad (3.12)$$

In the limit $\Gamma \cdot \tau^* \rightarrow 0$ the numerical results converge towards the free rotator limit.

For small values of Γ the correlation function becomes negative. This occurs around the time when the molecules which rotate with the thermal velocity have rotated through and angle π .

C) Spherical Top Molecules

The rotation of a spherical top molecule is most conveniently described in terms of quaternions $(\tau_1, \tau_2, \tau_3, \tau_4)$. The relations (B.1) map a rotation on the motion of a point on the surface of the four-dimensional unit sphere (see Appendix B for details). In terms of quaternions the Langevin equation reads:

$$\ddot{\tau} = -\Gamma \dot{\tau} - |\dot{\tau}|^2 \tau + \frac{1}{I} G^{1/2} F(t). \quad (3.13)$$

It looks like Eq. (3.10) but τ is a vector in four dimensions. Because the solution of the problem must not depend on the starting orientation of the molecule, one can choose the starting point such that β is the second Euler angle η . Then one can see from Eq. (B.1) that in terms of quaternions $\cos \beta$ is

$$\cos \beta = -\tau_1^2 - \tau_2^2 + \tau_3^2 + \tau_4^2. \quad (3.14)$$

Again in the limit of a freely rotating molecule the solution can be found (see Appendix B) and an average over ω and θ yields

$$\begin{aligned}\langle P_1(t) \rangle &= 1/3 + 2/3 A(t) \\ \langle P_2(t) \rangle &= 1/5 + 2/5 A(t) + 2/5 A(2t)\end{aligned}\quad (3.15)$$

with

$$A(t) := \left(1 - \frac{t^2}{\tau^{*2}}\right) e^{-\frac{t^2}{2\tau^{*2}}}. \quad (3.16)$$

In the free rotator case $\langle P_1(t) \rangle$ tends towards 1/3 for $t \rightarrow \infty$. The reason for that is, that it is possible, that a vector of the molecule lies close to the rotation axis. Therefore the vector does not change very much with time. The Fig. 5 and 6 show the results for the numerical calculations. $\Gamma \cdot \tau^* = 0$ is again the analytic result for the freely rotating molecule.

The Langevin approach to the rotational diffusion of molecules depends on the separation of two time scales: the short correlation time τ_c of the fluctuations and the long time $1/\Gamma$ over which the rotational state of the observed molecule changes. If we accept that the fluctuating torque is generated by the z neighbours which rotate with thermal angular velocity around an axis with n fold symmetry, then $\tau_c \approx \tau^*/n \cdot z$ where $n=2$ or 4 would be typical for the globular molecules under consideration and $z \approx 10$ is an average number of neighbours in a liquid. The estimate shows that our calculations should be valid for $\Gamma \tau^* \lesssim 1$.

When different models for the rotational diffusion are compared with each other, it is essential to concentrate on the low friction limit. For high friction constants the molecule loses the memory of its rotational state long before it has performed a complete revolution. Then the characteristic features of the rotational problem are masked and all the different calculations produce very similar results. This includes our own approach which for large values of Γ yields the same behaviour as the diffusion equation despite of the fact that it cannot be justified in this limit.

For two dimensional rotations the most advanced model are the M -, M^* -, and J -diffusion of Gordon [8]. There is a good agreement between our results and the J -diffusion model, but no agreement with M - and M^* -diffusion. In both models $\langle P_1(t) \rangle$ becomes positive after a negative minimum. Moreover in the case of M^* -diffusion such an oscillation is noticeable even for high friction constants where $\langle P_1(t) \rangle$ does not become negative. There might be a better agreement between the M^* -diffusion and a nonlinear Langevin model as described in part II of this paper. The agreement of McClung's [9] generalization of Gordon's models to threedimensional rotation with our calculations is good. The qualitative behaviour is the same.

Fixman and Rider [25] have derived a Fokker-Planck-equation (FP) for a distribution function $G(\omega, \mathbf{n}, t; \omega_0, \mathbf{n}_0, t_0)$ which is the joint probability of finding a molecule at time t_0 in an orientation $\mathbf{n}_0$ with angular velocity ω_0 and at time t in an orientation $\mathbf{n}$ with angular velocity ω . They have obtained $\langle P_1(t) \rangle$ and $\langle P_2(t) \rangle$ from a numerical solution of the FP-equation for the case of linear and spherical top molecules.

The results of Fixman and Rider do not converge to the free rotator limit in the case of a low friction parameter. Their $\langle P_1(t) \rangle$ curve for a very low friction parameter Γ becomes positive again for times $t \gtrsim 4\tau^*$,

whereas in the free case $\langle P_1(t) \rangle$ remains negative after it's first sign change.

O'Dell and Berne [26] have performed a molecular dynamics calculation for a sample of 108 rough spheres. A rough sphere model is a strong collision model in contrast with the Langevin model which is a weak collision model. Nevertheless, O'Dell and Berne also find that the FP calculations not reliable for low densities, i.e., for low friction constants.

For small values of the friction parameter there is no agreement with the work of Steele and others [10, 11]. Their expression does not become negative in the twodimensional case, and there is no maximum in the threedimensional case.

The molecular dynamics calculations [12, 13] look like the high friction region. As mentioned before in this region it is difficult to decide between the different models, because they look more or less similar. It would, however, be interesting to do a molecular dynamic calculation with globular molecules, i.e., for a case where the rotational potential is rather weak.

Gordon [15] shows the experimentally obtained dipole correlation function of CO dissolved in different environments. Our calculation compares favorably with the gas data, because that is the low friction limit. There are, however, marked deviations when CO is dissolved in liquid CHCl_3 or $n\text{-C}_7\text{H}_{16}$. If the solvent molecules are heavier than the CO itself the separation of time scales is no longer valid and furthermore the nonlinear friction terms become more important.

Campbell et al. [16] have obtained results for the spherical top molecule CF_4 at different pressures. They measured the Raman correlation function. Unfortunately they compare their results with the twodimensional free rotation. Obviously the comparison should be performed with the threedimensional case. If you compare it with the threedimensional case there is a much better agreement. The qualitative behaviour of Campbell's measurements and our calculation is the same.

Generally we can say that all models describe the short time behaviour and the high friction region quite well.

The advantage of our model is, that we can generalize it without problems to ODIC materials. In these cases we have to include the grad $V(\varphi)$ term in (2.2). Another point where future work will be done is the question of nonlinear friction terms in the Langevin model.

Appendix A

Numerical Calculations

To integrate the Langevin Eqs. (3.10) and (3.13)

$$\ddot{x}_i = -\Gamma \dot{x}_i - \left(\sum_j \dot{x}_j^2 \right) x_i + \frac{G^{1/2}}{I} F_i(t)$$

$$i, j = 1, \dots, (\text{dim} + 1) \quad (\text{A.1})$$

we use a very simple and straightforward difference scheme

$$\dot{x}_i^{n+1} = \dot{x}_i^n \Delta + x_i^n$$

$$\ddot{x}_i^{n+1} = \ddot{x}_i^n \frac{\Delta^2}{2} + \dot{x}_i^n \Delta + x_i^n. \quad (\text{A.2})$$

n labels the integration step and Δ is the length of the time interval in the simulation. We cannot use techniques described in [27], because our potential depends explicitly on the velocity. The above technique is correct up to order Δ^2 .

After every time step the conditions

$$|\mathbf{x}| = 1$$

$$\mathbf{x} \cdot \dot{\mathbf{x}} = 0 \quad (\text{A.3})$$

must be satisfied. This is necessary because we have the problem of the motion of a point on a sphere. Up to here it is a conventional integration technique of a system of differential equations. Now we have to introduce a stochastic noise source. $\mathbf{F}_0(t)$ is a random vector, with Gaussian distributed components, and $\mathbf{F}(t)$ is the projection of $\mathbf{F}_0(t)$ on a plane tangential to the unit sphere at the point $\mathbf{x}(t)$. In a Gauss-Markov process the time between two collisions is given by [27]

$$p(t) = \frac{1}{T} \exp(-t/T). \quad (\text{A.4})$$

T is the mean time between two collisions. The probability that a collision has happened after a time Δ is the integral over (A.4). For small time intervals Δ it is given by

$$w \approx \frac{\Delta}{T}. \quad (\text{A.5})$$

We have chosen a torque of the following form

$$F_i(t) = \sum_n f(t - n \cdot \Delta) \eta_i(n) \theta \left(\frac{\Delta}{T} - a_i(n) \right). \quad (\text{A.6})$$

The sum runs over all time steps. The $\eta_i(n)$ are Gaussian distributed random numbers; $a_i(n)$ are

equally distributed numbers between zero and one. $\theta(x)$ is Heaviside's step function. The function $f(x)$ is one for arguments between zero and Δ and zero elsewhere. The prefactor $G^{1/2}$ is given by

$$G^{1/2} = \left(\frac{2I k_B T \cdot \Gamma}{w \cdot \Delta} \right)^{1/2}. \quad (\text{A.7})$$

This is the fluctuation-dissipation-theorem as in (2.6). The factor $(w \cdot \Delta)^{-1}$ has its origin in the finite time steps in the computer simulation, leading to a torque which is not strictly δ -correlated. To obtain Gaussian distributed random numbers $\eta_i(n)$ the procedure described in [28] has been used. If N equally distributed random numbers are added an approximation of Gaussian distributed random numbers is obtained. This can be seen from the central limit theorem which states that the distribution becomes Gaussian in the limit $N \rightarrow \infty$.

The variance σ^2 of a so produced distribution is given by

$$\sigma^2 = \frac{N}{12}. \quad (\text{A.8})$$

We choose $N=12$, so that $\sigma^2=1$. To produce random numbers, we used the power-residue-method which is a standard routine of IBM [29].

To do the calculations we use $w=1/5$ and $\Delta=0.004$ in unit of τ^* . One experiment is done over $2.5 \cdot 10^5$ time steps. Every experiment was done 10 times to get the mean value and the variance of ten experiments. In the figures the lines drawn give the mean value, and the error bar indicates the variance.

Appendix B

Quaternions

It is very useful to describe the rotation of a spherical top molecule in terms of the quaternions $\tau_1, \tau_2, \tau_3, \tau_4$ [30, 31]. Euler angles (ξ, η, ζ) [32] and quaternions are related by [33]

$$\begin{aligned} \tau_1 &= \sin \eta/2 \sin \frac{\xi - \zeta}{2} \\ \tau_2 &= \sin \eta/2 \cos \frac{\xi - \zeta}{2} \\ \tau_3 &= \cos \eta/2 \sin \frac{\xi + \zeta}{2} \\ \tau_4 &= \cos \eta/2 \cos \frac{\xi + \zeta}{2}. \end{aligned} \quad (\text{B.1})$$

The τ 's fulfill the relation

$$\sum_{i=1}^4 \tau_i^2 = 1. \quad (\text{B.2})$$

By (B.1) the rotations are mapped on the motion of a point on the fourdimensional unit sphere. One should be aware of the fact that each rotation corresponds to two points in quaternion space. (Antipodes on the sphere describe the same rotation.) In terms of the quaternions the kinetic energy of a spherical top is expressed by

$$T = 2I \sum_{i=1}^4 \tau_i^2 \quad (\text{B.3})$$

I is the moment of inertia. Formally one can say that the mass m of the pseudo-particle is $4I$. In contrast to the Euler angles the quaternions can be interpreted very easily. If $\mathbf{u} = (u_x, u_y, u_z)$ is the unit vector in direction of the rotation axis and φ is the rotation angle, then the quaternions expressed in terms of $\mathbf{u}$ and φ

$$\begin{aligned} \tau_1 &= u_x \sin \varphi/2 \\ \tau_2 &= u_y \sin \varphi/2 \\ \tau_3 &= u_z \sin \varphi/2 \\ \tau_4 &= \cos \varphi/2. \end{aligned} \quad (\text{B.4})$$

To check the relation (B.4) the rotation matrix D is applied on a vector $\mathbf{x}$ to obtain the rotated vector $\mathbf{x}' = D\mathbf{x}$. The result is $\mathbf{x}' = \mathbf{x}$ if $\mathbf{x}$ parallel $\mathbf{n}$ and $\mathbf{x} \cdot \mathbf{x}' = x^2 \cos \varphi$ if $\mathbf{x}$ perpendicular to $\mathbf{n}$. The transformation matrix D is given by [33].

$$D = \begin{pmatrix} \tau_1^2 - \tau_2^2 - \tau_3^2 + \tau_4^2 & 2(\tau_1 \tau_2 - \tau_3 \tau_4) & 2(\tau_1 \tau_3 + \tau_2 \tau_4) \\ 2(\tau_1 \tau_2 + \tau_3 \tau_4) & -\tau_1^2 + \tau_2^2 - \tau_3^2 + \tau_4^2 & 2(\tau_2 \tau_3 - \tau_1 \tau_4) \\ 2(\tau_1 \tau_3 - \tau_2 \tau_4) & 2(\tau_2 \tau_3 + \tau_1 \tau_4) & -\tau_1^2 - \tau_2^2 + \tau_3^2 + \tau_4^2 \end{pmatrix}. \quad (\text{B.5})$$

The equation of motion on the surface of the four-dimensional unit sphere is given in (3.13). In the free rotator limit one gets

$$\ddot{\tau}_j = - \left(\sum_{i=1}^4 \dot{\tau}_i^2 \right) \tau_j \quad j=1, 2, 3, 4. \quad (\text{B.6})$$

With reference to (B.4) and the conservation of angular momentum the solution is

$$\begin{aligned} \tau_1 &= \sin \theta \cos \varphi \sin \frac{\omega}{2} t \\ \tau_2 &= \sin \theta \sin \varphi \sin \frac{\omega}{2} t \\ \tau_3 &= \cos \theta \sin \frac{\omega}{2} t \\ \tau_4 &= \cos \frac{\omega}{2} t \end{aligned} \quad (\text{B.7})$$

θ and φ are the polar angles of the rotation axis in real space and ω is the angular velocity of the spherical top.

From (3.14) we get

$$\cos \beta = \cos^2 \theta + \sin^2 \theta \cos \omega t. \quad (\text{B.8})$$

Averaged with the threedimensional Maxwell-distribution for the angular velocity we get the result (3.15).

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3.3 EXTENDED DIFFUSION MODELS

The extended diffusion models of Gordon [10] have been helpful for the understanding of rotational motion of molecules. Gordon generalized the old Debye model [24] of rotational diffusion in the case of dumbbell molecules. Later McClung generalized Gordon's models for spherical top molecules [25].

The basic idea of these models is, that the molecule rotates freely between two collisions. The mean time between two collisions is τ . In the extended diffusion models the angular velocity of a molecule after a collision is independent of the angular velocity it had before the collision. These models thus are strong collision models. In other words, during the collision the particle loses its memory. In a better model the particle should "remember" its earlier angular velocity which means that the current angular velocity depends on the "history" of the particle. The Langevin-model takes the short time memory of the particle into account. It is a weak collision model and therefore much better to describe realistic systems.

Gordon assumed two different types of collisions. In the M-diffusion model the direction of the angular velocity is randomized whereas its magnitude is left unchanged. This means that the matrix element of the collision operator J_M can be written [26]:

$$\langle \omega_f | J_M | \omega_i \rangle = \delta(\omega_f - \omega_i) \quad . \quad (3.8)$$

ω_i and ω_f are the magnitude of angular velocity before and after the collision respectively.

In the case of J-diffusion the angular velocity is randomized completely. The matrix element is independent of the initial angular velocity ω_i

$$\langle \omega_f | J_J | \omega_i \rangle = \rho_d(\omega_f) . \quad (3.9)$$

The distribution function $\rho_d(\omega)$ is the Maxwell-distribution of dimensionality d .

A more realistic model must be somewhere between M and J diffusion. Therefore several authors have tried an interpolation model which takes this into account. In the case of dumbbell molecules Dattagupta and Sood [26] assumed a matrix element

$$\langle \omega_f | J | \omega_i \rangle = \gamma \rho_2(\omega_f) + (1-\gamma) \delta(\omega_f - \omega_i) \quad (3.10)$$

With the parameter γ they can interpolate smoothly between M-diffusion ($\gamma=0$) and J-diffusion ($\gamma=1$). Fixman and Rider [27] did similar work in the case of spherical molecules.

We now want to write down a compact formalism which allows the calculation of the autocorrelation functions for M and J diffusion in the case of one, two, and three rotational degrees of freedom.

For clarity we want to restrict our calculation of $\langle P_\ell(\cos \beta) \rangle$ to the cases $\ell=1$ and $\ell=2$. But, of course, this

restriction is not a principal one; the formalism can be easily generalized to $\ell > 2$. The average denoted by the brackets $\langle \rangle$ stands for an ensemble average over the ensemble of one particle systems which is equivalent to a realization of all possible diffusion processes (time average = ensemble average).

At a certain starting time the ensemble is characterized by a Maxwell distribution over angular velocities. At a later time the ensemble is subdivided into different classes. The first class is characterized by the fact that all systems in it are in the first diffusion step. That means they are before the first collision. In the second class all ensembles are in the second diffusion step, between the first and the second collision, and so on. Therefore we can decompose the correlation function

$$\langle P_{\ell}^X(\cos \beta) \rangle = \sum_{n=1}^{\infty} F_{\ell}^X(n, \cos \beta) . \quad (3.11)$$

The sum over n runs over all the different classes. The parameter x stands for M respective J -diffusion. The time dependence of the problem is contained in $\cos \beta$, the argument t in $\beta(t)$ has been dropped for clarity.

The number of particles which are in the n -th diffusion step at time t is determined by the Poisson distribution

$$p_n(t) = \frac{1}{(n-1)!} \left(\frac{t}{\tau} \right)^{n-1} \exp(-t/\tau) \quad (3.12)$$

where τ is the mean time between two collisions.

To separate the functions $F_{\ell}^X(n, \cos \beta)$ into one part which depends on the angular momentum correlation time τ and another part which is independent of τ we make the Ansatz [25]

$$F_{\ell}^X(n, t) = \frac{\exp(-t/\tau)}{\tau^{n-1}} G_{\ell}^X(n, t) \quad (3.13)$$

This Ansatz has the advantage, that the decomposite correlation function $G_{\ell}^X(n, t)$ must be calculated only once. One need not to repeat the calculation of $G_{\ell}^X(n, t)$ for the different τ . There is no free parameter left in the $G_{\ell}^X(n, t)$.

The functions $G_{\ell}^X(n, t)$ are given by

$$G_{\ell}^M(n, t) = \int_0^t dt_{n-1} \int_0^{t_{n-1}} dt_{n-2} \dots \int_0^{t_2} dt_1 \cdot \quad (3.14a)$$

$$\cdot \langle g_{\ell}(t-t_{n-1}) g_{\ell}(t_{n-1}-t_{n-2}) \dots g_{\ell}(t_2-t_1) g_{\ell}(t_1) \rangle_d$$

$$G_{\ell}^J(n, t) = \int_0^t dt_{n-1} f_{\ell}(t-t_{n-1}) \int_0^{t_{n-1}} dt_{n-2} f_{\ell}(t_{n-1}-t_{n-2}) \cdot \quad (3.14b)$$

$$\dots \cdot \int_0^{t_2} dt_1 f_{\ell}(t_2-t_1) f_{\ell}(t_1)$$

where the brackets $\langle \rangle_d$ denote an average with the d-dimensional Maxwell-distribution. The relation between the functions $g_{\ell}(t)$ and $f_{\ell}(t)$ is given by

$$f_{\ell}(t) = \langle g_{\ell}(t) \rangle_d \quad (3.15)$$

The equations can be derived by geometrical arguments from the collisions of the molecules [10].

The integrations in eq. (3.14a) and (3.14b) must be performed numerically. Details of such numerical calculations and recursion formulas are given in ref. [10] for two degrees of freedom and in ref. [25] for three degrees of freedom.

In Table 2 the functions f_ℓ and g_ℓ are given explicitly for $\ell=1$ and $\ell=2$. The function Φ is the degenerate hypergeometric function, which is given in eq. (3.12) of the publication. τ^* is $(I/k_B T)^{1/2}$. The information of Table 2 can easily be generalized to $\ell > 2$.

If the angular momentum correlation time goes to infinity we get the free rotator limit. From eq. (3.10) and (3.12) we get in this limit

$$\langle P_\ell^x(\cos \beta) \rangle_{\text{free}} = G_\ell^x(1, t) \quad (3.16)$$

From eq. (3.13) and (3.14) we obtain

$$G_\ell^M(1, t) = G_\ell^J(1, t) = f_\ell(t) \quad (3.17)$$

This is the same result which we got in the publication.

The results for $\langle P_1(\cos \beta) \rangle$ and $\langle P_2(\cos \beta) \rangle$ of M and J-diffusion are presented in figs. 3-5. The data for the extended diffusion models are taken from ref. [10] in the case of two degrees of freedom and from ref. [25] in the case of three degrees of freedom.

Table 2 The correlation functions which are necessary for the extended diffusion models.

dimension	ℓ	g_ℓ	$\cos \beta$	$f_\ell(t)$	$\rho_d(\omega) d^d \omega$
1	1	$P_1(\cos \beta)$ $= \cos \beta$	$\cos \omega t$	$\exp\left(-\frac{t^2}{2\tau^{*2}}\right)$	$\exp\left(-\frac{1}{2} \omega^2 \tau^{*2}\right) d\omega$
	2	$P_2(\cos \beta)$ $= \frac{3}{4} \cos 2\beta + \frac{1}{4}$		$\frac{3}{4} \exp\left(-\frac{2t^2}{\tau^{*2}}\right) + \frac{1}{4}$	
2	1	$P_1(\cos \beta)$	$\cos \omega t$	$\exp\left(-\frac{t^2}{2\tau^{*2}}\right) \cdot \Phi\left(-\frac{1}{2}, \frac{1}{2}, \frac{t^2}{2\tau^{*2}}\right)$	$\omega \exp\left(-\frac{1}{2} \omega^2 \tau^{*2}\right) d\omega$
	2	$P_2(\cos \beta)$		$\frac{3}{4} \exp\left(-\frac{2t^2}{\tau^{*2}}\right) \Phi\left(-\frac{1}{2}, \frac{1}{2}, \frac{2t^2}{\tau^{*2}}\right) + \frac{1}{4}$	
3	1	$P_1(\cos \beta)$	$\cos^2 \theta + \sin^2 \theta \cos \omega t$	$\frac{1}{2\ell+1} \sum_{j=-\ell}^{\ell} A(\ell t)$	$\omega^2 \exp\left(-\frac{1}{2} \omega^2 \tau^{*2}\right) d\omega \sin \theta d\theta$
	2	$P_2(\cos \beta)$ $= \frac{3}{4} \cos^2 \beta - \frac{1}{2}$		with $A(t) = \left(1 - \frac{t^2}{\tau^{*2}}\right) \cdot \exp\left(-\frac{t^2}{2\tau^{*2}}\right)$	

3.4 COMPARISON OF RESULTS

The fig. 3 and 4 show the results of Gordon's [10] M- and J-diffusion in the case of two degrees of freedom. Fig. 3 shows the results for $\Gamma_1(t) = \langle P_1(\cos \beta) \rangle$ and fig. 4 shows the corresponding results for $\Gamma_2(t) = \langle P_2(\cos \beta) \rangle$.

From our results of the Langevin-model we took only the curves for the lowest ($\Gamma^* = .25$) and the largest ($\Gamma^* = 1.75$) friction parameter. From Gordon's results we took curves which fall into the same range. We did not try to fit one model by the other model. An analytic relation between our friction parameter Γ and Gordon's correlation time τ does not exist.

From the figures one can see that there is a good qualitative agreement between Langevin-model and the J-diffusion model, but no agreement with M-diffusion.

Fig. 5 shows the results for $\Gamma_1(t) = \langle P_1(\cos \beta) \rangle$ in the case of a spherical top molecule. The results for M- and J-diffusion are taken from McClung [25]. Again we can see that the agreement between J-diffusion and Langevin model is better than between M-diffusion and Langevin model

Fig. 6 shows the experimentally obtained dipole correlation function of CO dissolved in different environments [14]. Our calculation compares favorably with the gas data, because that is the low friction limit. There are, however, marked deviations when CO is dissolved in liquid CHCl_3 or $n\text{-C}_7\text{H}_{16}$.

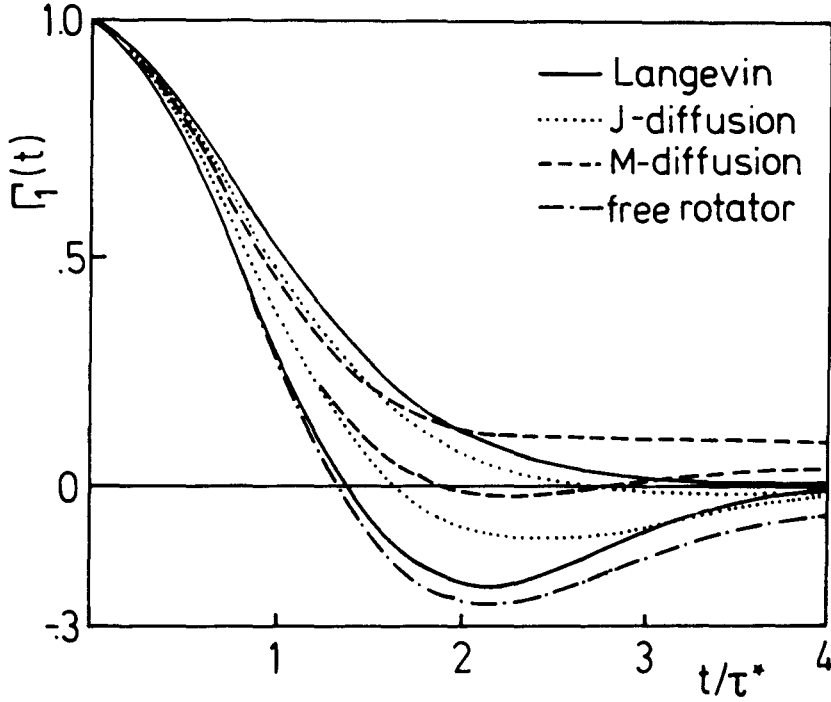


Fig. 3: The dipole correlation function $\Gamma_1(t)$ for different models as indicated. Two degrees of freedom. The parameters are (from top to bottom): Langevin $\Gamma^* = 1.75$ and 0.25 ; J-diffusion $\tau = 0.8$ and 1.75 ; M-diffusion $\tau = 1.0$ and 1.8 .

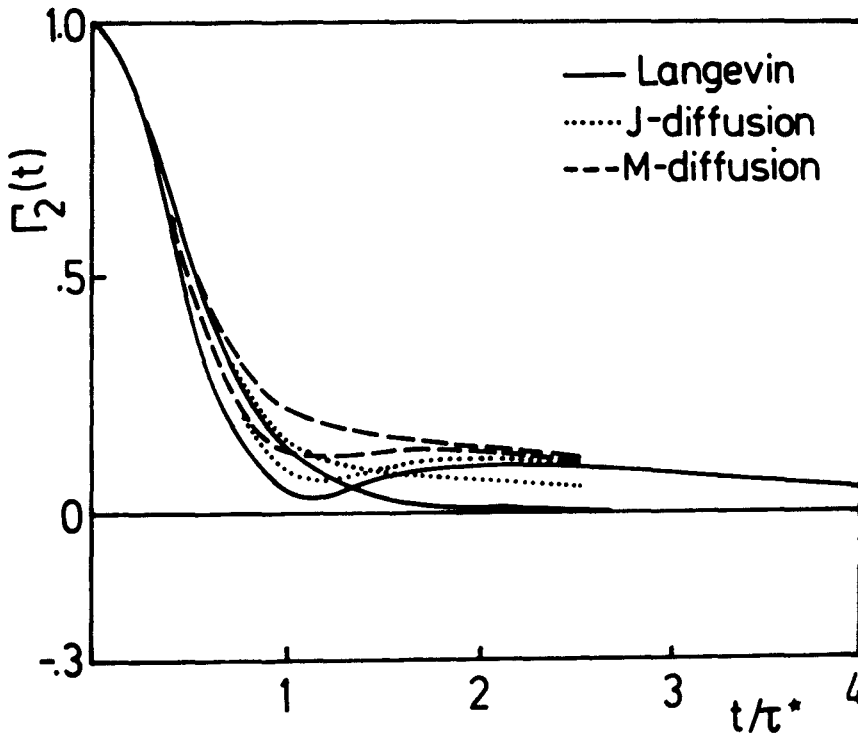


Fig. 4: The Raman correlation function $\Gamma_2(t)$ for different models as indicated. Two degrees of freedom. The parameters are (from top to bottom): Langevin $\Gamma^* = 1.75$ and 0.25 ; J-diffusion $\tau = 0.8$ and 1.75 ; M-diffusion $\tau = 0.8$ and 1.75 .

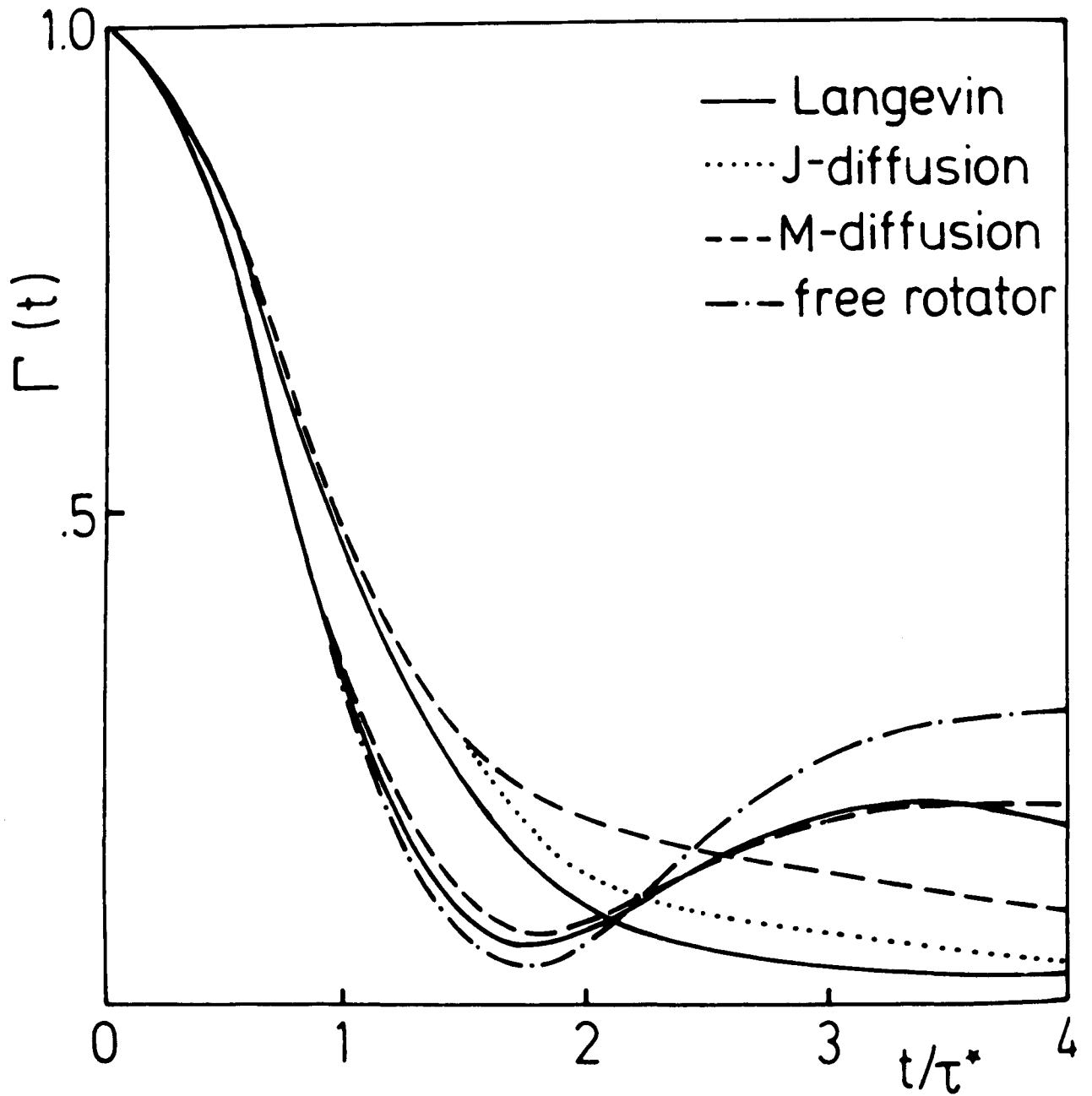


Fig. 5: The dipole correlation function $\Gamma_1(t)$ for different models as indicated. Three degrees of freedom. The parameters are (from top to bottom): Langevin $\Gamma^* = 1.0$ and 0.125 ; J-diffusion $\tau = 1.0$ and 5.0 ; M-diffusion $\tau = 1.0$. For $\tau = 5.0$ the solution of M and J diffusion are identical.

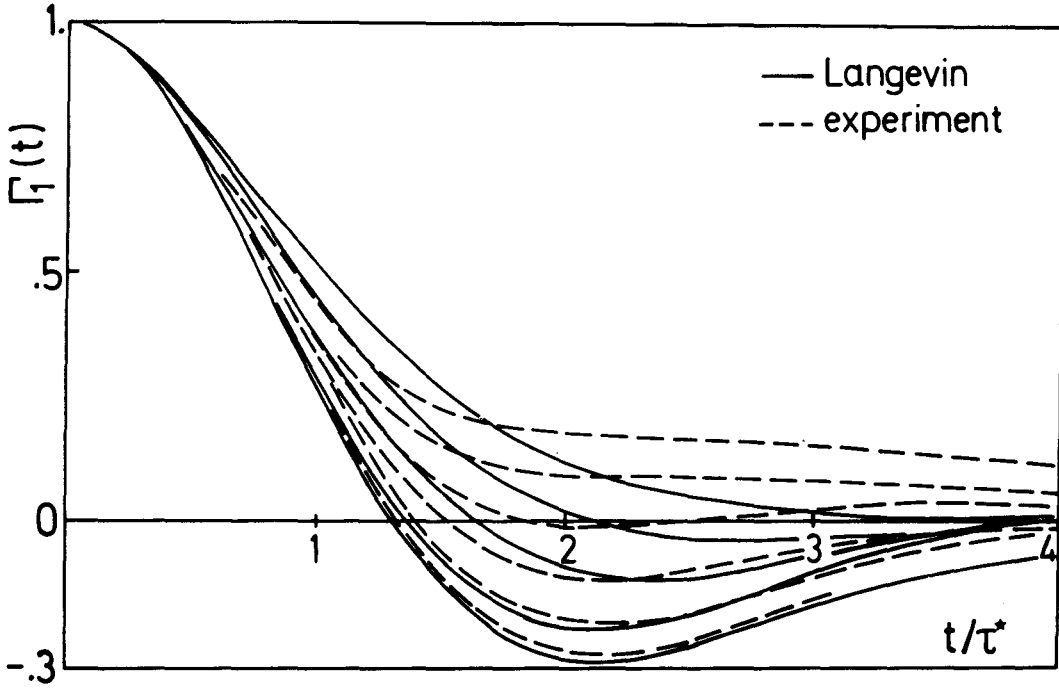


Fig. 6: The dipole correlation function $\Gamma_1(t)$ for Langevin model and from experimental data. Two degrees of freedom. The friction parameter Γ^* is (from top to bottom): 1.75, 1.25, 0.75, 0.25, and 0.0. The experimental data are (from top to bottom): CO in CHCl_3 (liquid), CO in CCl_4 (liquid), CO in $n\text{-C}_7\text{H}_{16}$ (liquid), CO in argon (gas, 510 amagat), CO in argon (gas, 270 amagat), CO in argon (gas, 66 amagat) From ref. [14].

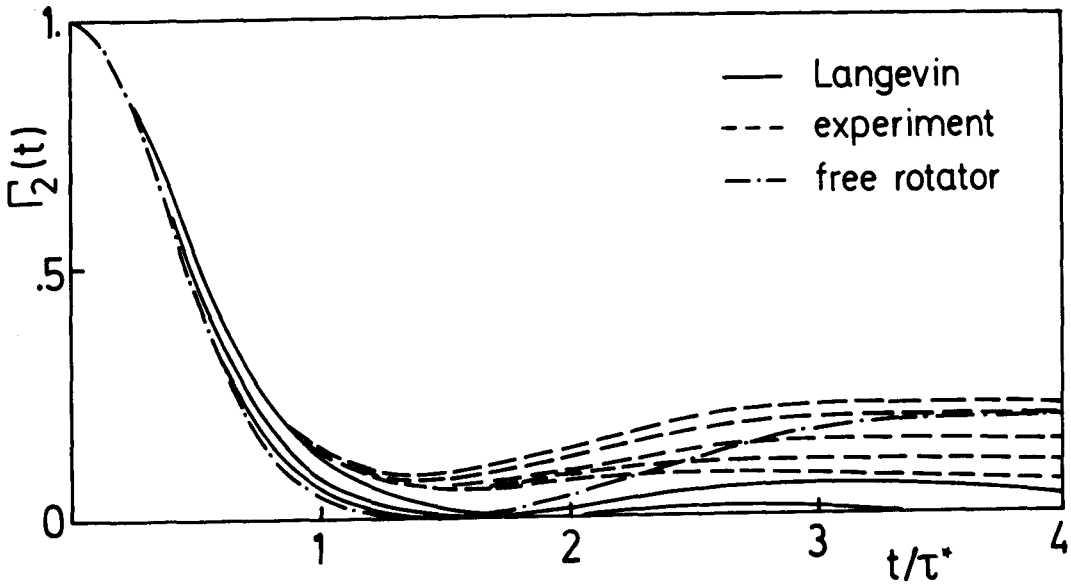


Fig. 7: The Raman correlation function $\Gamma_2(t)$ for Langevin model and from experimental data. Three degrees of freedom. The friction parameter Γ^* is (from top to bottom): 1.0, 0.375 and 0.125. The experimental data are (from top to bottom): CF_4 at 23 °C and at pressure: 9, 23, 51, 85, and 120 amagat. From ref. [28].

If the solvent molecules are heavier than the CO itself the separation of time scales is no longer valid and furthermore the nonlinear friction terms become more important.

Campbell et al. [28] have obtained results for the spherical top molecule CF_4 at different pressures. They measured the Raman correlation function. Fig. 7 shows a comparison between our theoretical results and Campbell's measurements. The qualitative agreement is very good. The experimental curves do not reach zero between $t^* = 1$ and $t^* = 2$. This seems to be an error resulting from the Fourier transformation of the experimental data.

Summing up we can say, if one tries a fit with an extended diffusion model one should use the J-diffusion model. The Langevin-model is the best model to fit experimental data. The other advantage of the Langevin-model is that it can be generalized without problems to problems with a static potential. That will be done in the following chapters.

4. ONEDIMENSIONAL ROTATIONAL MOTION IN AN N-FOLD POTENTIAL

In this chapter we want to look at the rotational motion with one degree of freedom, i.e. to onedimensional rotators.

4.1 THE POTENTIAL

The only variable necessary to describe the rotational motion is the rotation angle φ . The molecular potential depends only on this variable, too. The potential should have the symmetry of both the surrounding and of the rotating molecule. And, of course, the potential has to be periodic with 2π .

$$V(\varphi) = V(\varphi + 2\pi) \quad (4.1)$$

The simplest functions, which fulfill these conditions are the trigonometric functions. To get a good comparison with earlier work we choose a cosine-potential.

The potential is characterized by the barrier height V and the periodicity N . Neglecting constant terms, because they are not relevant to the resulting forces, we get

$$V(\varphi) = - \frac{V}{2} \cos N\varphi \quad (4.2)$$

This potential has a minimum at $\varphi = 0$.

4.2 NEUTRON SCATTERING LAW

In the preceding chapter the intermediate scattering functions $I(\vec{Q}, t)$ have been expanded in terms of Legendre-polynomials. Now it is much more convenient to expand the $I(\vec{Q}, t)$ in terms of trigonometric functions. During the calculations of $I(\vec{Q}, t)$ we closely follow the lines of Dianoux and Volino [11].

In the case of a uniaxial rotator the molecule moves in a plane and therefore $\vec{r}(t)$ has the form $(r \cos \varphi(t), r \sin \varphi(t), 0)$, where $\varphi(t)$ is the rotational angle. Writing $\vec{Q}$ in a coordinate system, with the z-axis perpendicular to the plane of the rotator and with polar coordinates Q , θ and α , it can be shown that

$$\vec{Q} \cdot \vec{r}(t) = Qr \sin \theta \cos (\varphi(t) - \alpha). \quad (4.3)$$

Using the expansion [22,23]

$$\exp(\pm iz \cos \psi) = \sum_{\nu=-\infty}^{\infty} \pm i^{\nu} J_{\nu}(z) e^{i\nu\psi} \quad (4.4)$$

where $J_{\nu}(t)$ is the Bessel function of first kind and order ν , a general form of $I(\vec{Q}, t)$ can be written down.

$$I(\vec{Q}, t) = \sum_{\mu, \nu=-\infty}^{\infty} -i^{\nu+\mu} J_{\nu}(Qr \sin \theta) J_{\mu}(Qr \sin \theta) \cdot e^{i\nu(\varphi-\alpha)} e^{i\mu(\varphi_0-\alpha)} >_{\varphi, \varphi_0} \quad (4.5)$$

For clarity we used the abbreviations $\varphi := \varphi(t)$ $\varphi_0 := \varphi(0)$.

In practice, most samples are powder samples and therefore we want to restrict our calculations to powder samples, too. There is, of course, no problem to generalize the calculation to single crystals. In a powder sample the orientations of all scattering centers are distributed randomly. This means that we must average over all values of the angles α and θ . The result of averaging over α first is:

$$I(\vec{Q}, t) |_{\alpha} = \sum_{\mu=-\infty}^{\infty} J_{\mu}^2(Qr \sin \theta) \langle e^{i\mu(\varphi - \varphi_0)} \rangle_{\varphi, \varphi_0} \quad (4.6)$$

which is the same result as equation (47) in ref. [11]. To get the full powder average we write [23]

$$\begin{aligned} A_n(Qr) &= J_n^2(Qr \sin \theta) \\ &= \frac{1}{\pi} \int_0^{\pi} J_0(2Qr \sin \theta \sin x) \cos 2nx dx \quad (4.7) \end{aligned}$$

Averaging over θ with $\sin \theta d\theta$ we get [23]

$$A_n(Qr) = \frac{1}{\pi} \int_0^{\pi} dx j_0(2Qr \sin x) \cos 2nx \quad (4.8)$$

The integral of eq. (4.8) can be given in a series

$$\frac{1}{\pi} \int_0^{\pi} dx j_0(2a \sin x) \cos 2nx = \sum_{\ell=0}^{\infty} \frac{(-1)^{\ell} a^{2(\ell+n)}}{[2(\ell+n)+1] \ell! (2n+\ell)!} \quad (4.9)$$

The functions $A_n(Qr)$ can easily be calculated on a computer. Fig. 8 shows the plot for $n = 0, 1, 2, 3$, and 4. It can be seen that for Q -values which are experimentally accessible one

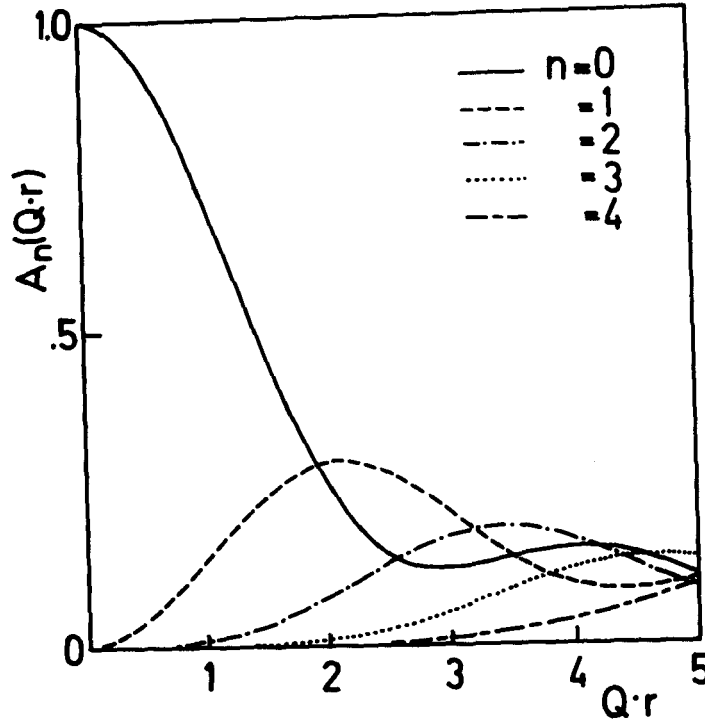


Fig. 8: The functions $A_n(Qr)$ for different n . The functions are defined in eq. (4.7) and (4.11).

needs only the first few terms in eq. (4.6) to get a good approximation to the scattering law. For $Qr > 3$ the Debye-Waller-factor is too small to obtain significant intensity.

For further calculations we shall introduce the abbreviation:

$$\Gamma_n(t) := \langle \cos(n[\varphi - \varphi_0]) \rangle_{\varphi, \varphi_0} \quad (4.10)$$

Eq. (4.6) can now be written:

$$I(Qt) |_{\alpha, \theta} = A_0(Qr) + 2 \sum_{k=1}^{\infty} A_k(Qr) \Gamma_k(t) \quad (4.11)$$

To obtain $S(Q, \omega)$, eq. (4.11) must be Fourier transformed. Therefore it is helpful to separate the time independent part of eq. (4.11). We divide $\Gamma_k(t)$ into two parts

$$\Gamma_k(t) = \Gamma'_k(t) + \Gamma_k(\infty) \quad (4.12)$$

with the property

$$\lim_{t \rightarrow \infty} \Gamma'_k(t) = 0 \quad (4.13)$$

In the case of the powder sample $S(\vec{Q}, \omega)$ is given by

$$\begin{aligned} S(\vec{Q}, \omega) = & \left\{ A_0(Qr) + 2 \sum_{k=1}^{\infty} A_k(Qr) \Gamma_k(\infty) \right\} \delta(\omega) \\ & + 2 \sum_{k=1}^{\infty} A_k(Qr) F[\Gamma'_k(t)] \end{aligned} \quad (4.14)$$

where $F[\Gamma'_k(t)]$ stands for the Fourier transform of $\Gamma'_k(t)$.

Up to here no specific model assumptions have been made. To calculate the correlation functions $\Gamma_k(t)$ we need a model. In the next part of this chapter we want to calculate $\Gamma_k(t)$ for different models and approximations, to see the differences and to discuss the physical validity.

4.3 LANGEVIN EQUATION

With finite potentials $V(\varphi)$ the eq. (2.26) cannot be solved analytically. Therefore we want to regard two limits first.

4.3.1 $T \gg V$

In the limit $T \gg V$ one can neglect the potential. The mean kinetic energy of the molecule is so high that it does not feel the potential. In this case we get the simplified Langevin equation:

$$\ddot{\varphi} = -\Gamma \dot{\varphi} + \frac{1}{I} G^{1/2} F(t) \quad (4.15)$$

This equation has been solved in the publication. The final result for the cosine-correlation function is:

$$\langle \cos m(\varphi - \varphi_0) \rangle = \exp \left\{ -\frac{m^2}{\Gamma^2 \tau^{*2}} [\Gamma t - 1 + \exp(-\Gamma t)] \right\} \quad (4.16)$$

where $\tau^* = (I/k_B T)^{1/2}$.

4.3.2 $T \ll V$

In this case the motion is that of a damped harmonic oscillator driven by a stochastic force around the minima of the potential. All minima are physically equivalent and therefore we need treat only one minimum. Because of the

small amplitude one can expand the potential up to second order

$$V(\varphi) = -\frac{V}{2} \cos N\varphi = -\frac{V}{2} \left(1 - \frac{N^2 \varphi^2}{2} + \dots\right) \quad (4.17)$$

From this we get the Langevin equation:

$$\ddot{\varphi} = -\omega^2 \varphi - \Gamma \dot{\varphi} + \frac{1}{I} G^{1/2} F(t) \quad (4.18)$$

with $\omega^2 = \frac{N^2 V}{2I}$. The eq. (4.18) can be solved analytically and the solution can be found in textbooks [17]

$$\begin{aligned} \varphi(t) = & \frac{\varphi_0 + 2\dot{\varphi}_0}{2\omega_1} e^{-\frac{\Gamma t}{2}} \sin \omega_1 t + \varphi_0 e^{-\frac{\Gamma t}{2}} \cos \omega_1 t \\ & + \frac{G^{1/2}}{\omega_1} \int_0^t F(\xi) e^{-\frac{\Gamma(t-\xi)}{2}} \sin \omega_1 (t-\xi) d\xi \end{aligned} \quad (4.19)$$

where φ_0 and $\dot{\varphi}_0$ are the initial values of the rotation angle and the angular velocity. ω_1 is given by $\left(\omega^2 - \frac{\Gamma^2}{4}\right)^{1/2}$. The Langevin equation is linear in φ . We get for the cosine correlation function

$$\langle \cos m(\varphi - \varphi_0) \rangle = \exp \left\{ -\frac{n^2}{N^2} \frac{1}{\gamma} \left[1 - e^{-\frac{\Gamma t}{2}} \left(\frac{\Gamma}{2\omega_1} \sin \omega_1 t + \cos \omega_1 t \right) \right] \right\} \quad (4.20)$$

with $\gamma = \frac{V}{2k_B T}$.

4.3.3 NUMERICAL SOLUTION

We solved the Langevin equation

$$\ddot{\varphi} = -\Gamma\dot{\varphi} - \frac{1}{I} \frac{\partial}{\partial \varphi} V(\varphi) + \frac{1}{I} G^{1/2} F(t) \quad (4.21)$$

with the cosine potential from eq. (4.2) by a numerical simulation technique. Because we want to compare our results with earlier results we choose the periodicity $N=2$. This is, of course, no principal limitation of theory.

The simulation is performed by the method which is described in the publication. The new parameter $\gamma = \frac{V}{2k_B T}$ denotes the strength of potential in units of the temperature. The values chosen 0.25, 0.5 and 0.75 correspond to $V = \frac{1}{2} k_B T$, $V = k_B T$ and $V = \frac{3}{2} k_B T$, respectively.

Together with the analytic results of the approximations and the diffusion data the results are presented in fig. 9-13. A discussion of these results is given in part 4.7.

4.4 SMOLUCHOWSKI-DIFFUSION-EQUATION

Starting from the Langevin eq. (4.21) one can derive a Fokker-Planck-equation (FP). The prescription, how to do this, can be found in textbooks [18]. The FP-equation is an equation to determine the probability density G . The probability of finding a particle in the interval $[\varphi, \varphi+d\varphi]$ and $[\dot{\varphi}, \dot{\varphi}+d\dot{\varphi}]$ is then given by $G(\varphi, \dot{\varphi}, t) d\varphi d\dot{\varphi}$.

The resulting FP equation is

$$\frac{\partial G}{\partial t} = \Gamma \frac{\partial}{\partial \dot{\varphi}} \left(G \dot{\varphi} + \frac{k_B T}{I} \frac{\partial G}{\partial \dot{\varphi}} \right) - \dot{\varphi} \frac{\partial G}{\partial \varphi} + \frac{1}{I} \frac{\partial V}{\partial \varphi} \frac{\partial G}{\partial \dot{\varphi}} \quad (4.22)$$

The stationary solution of eq. (4.22) is

$$G(\varphi, \dot{\varphi}, t) = C \exp \left\{ - \frac{\frac{I}{2} \dot{\varphi}^2 + V(\varphi)}{k_B T} \right\} \quad (4.23)$$

As discussed in ref. [18,29] one can make an approximation under the conditions

$$\frac{\partial^2 V}{\partial \varphi^2} (\tau^* \cdot \Gamma)^{-1} \ll \frac{\partial V}{\partial \varphi} \quad (4.24a)$$

and

$$\frac{\partial G}{\partial \varphi} (\tau^* \cdot \Gamma)^{-1} \ll G \quad (4.24b)$$

where τ^* is of the order of the mean thermal angular velocity of the molecule. The product $(\tau^* \cdot \Gamma)^{-1}$ has the physical meaning of a mean friction length. The eq. (4.24a) and (4.24b) express, that the torque $\frac{\partial V}{\partial \varphi}$ and the probability G may not change very much with the length $(\tau^* \cdot \Gamma)^{-1}$. Under these conditions we get the differential equation

$$\frac{1}{D} \frac{\partial \rho}{\partial t} = \frac{\partial}{\partial \varphi} \left[\frac{\partial \rho}{\partial \varphi} + \frac{1}{k_B T} \frac{\partial V}{\partial \varphi} \rho \right] \quad (4.25)$$

with a diffusion constant $D = \frac{k_B T}{I \Gamma}$. The new probability density ρ is related to G by the relation [18]

$$\rho(\varphi, t) = \int_{-\infty}^{\infty} G(\varphi, \dot{\varphi}, t) d\dot{\varphi} \quad (4.26)$$

The so-called Diffusion equation (4.25) is the same as eq. (1) in ref. [11].

Eq. (4.25) should be valid in the region of a large friction parameter Γ and in the case of a small parameter γ which means a small potential. Dianoux and Volino calculated $\langle \cos\{m(\phi - \phi_0)\} \rangle$ starting from eq. (4.25). The calculation is an analytic one apart from a matrix diagonalization and a matrix inversion which were performed numerically. Using the equations given by Dianoux and Volino we wrote a computer program to calculate the correlation functions in the framework of the Diffusion equation. Instead of infinite matrices we used 50 x 50 matrices. To test the error of this approximation we used in a few cases 30 x 30 and 100 x 100 matrices, too. We could not see any difference in the results. The cpu-time used for calculation of one correlation function is less than 5 seconds on an IBM-3033. The results are found in fig. 9-12.

4.5 SACK-DIFFUSION-EQUATION

Sack [30] made a modification of Smoluchowski's diffusion equation. He derived the so-called Sack-equation, which differs from the diffusion equation only by a term with second time derivative

$$\frac{\partial}{\partial t} \rho + \frac{1}{\Gamma} \frac{\partial^2}{\partial t^2} \rho = \frac{1}{\Gamma I} \frac{\partial}{\partial \varphi} [k_B T \frac{\partial \rho}{\partial \varphi} + \frac{\partial V}{\partial \varphi} \rho] \quad (4.27)$$

This ad hoc equation should be better than the normal diffusion equation. The diffusion equation is valid only for times $t > \Gamma^{-1}$, but the Sack-equation is aimed to be valid for short times like the original Fokker-Planck equation. The second order term corrects the initial behaviour of the correlation functions. The mean square displacement is found to be

$$\langle (\varphi(t) - \varphi(0))^2 \rangle = \frac{k_B T}{I \Gamma^2} [\Gamma t - 1 + \exp(-\Gamma t)] . \quad (4.28)$$

We used the Dianoux-Volino-formalism to solve equation (4.27). The generalization of this formalism is given in the Appendix. And with the choice

$$H_t = \frac{\partial}{\partial t} + \frac{1}{\Gamma} \frac{\partial^2}{\partial t^2} \quad (4.29)$$

the solution can be found. This choice of the operator H_t leads to a differential equation

$$\frac{\partial^2}{\partial t^2} f_p + \Gamma \frac{\partial}{\partial t} f_p = -\lambda_p \frac{k_B T}{I} f_p \quad (4.30)$$

Which can be solved by analytic methods. The result is

$$f_p(t) = \exp\left(-\frac{\Gamma^*}{2} t^*\right) \left(\frac{\Gamma^*}{2\omega^*} \sin\omega^* t^* + \cos\omega^* t^*\right) \quad (4.31)$$

where Γ^* and t^* are given by $\Gamma^* = \Gamma \cdot \tau^*$ and $t^* = t/\tau^*$. τ^* is a factor which makes the representation independent of temperature. It is given by $\tau^* = (I/k_B T)^{1/2}$. Take into account the complex nature of ω^* , which is given by $\omega^* = (\lambda_p - \Gamma^{*2}/4)^{1/2}$.

But the function $f_p(t)$ is always real. If you replace λ_p by μ_p you get the functions $g_p(t)$.

4.6 ORDER PARAMETER

Dianoux and Volino [11] introduced an order parameter γ_n which is defined by

$$\gamma_n = \langle \cos n\varphi \rangle_\varphi \quad (4.32)$$

To calculate this order parameter we start from the equilibrium distribution function which is

$$p(\varphi) = A^{-1} \exp\left[-\frac{1}{k_B T} V(\varphi)\right] \quad (4.33)$$

with normalization

$$A = \int_0^{2\pi} \exp\left[-\frac{1}{k_B T} V(\varphi)\right] d\varphi \quad (4.34)$$

With the cosine potential (5.2) one can use the expansion of the exponential function [22,23]

$$\exp\{\gamma \cos(N\varphi)\} = I_0(\gamma) + 2 \sum_{k=1}^{\infty} I_k(\gamma) \cos(kN\varphi) \quad (4.35)$$

where I_k is the modified Bessel function of first kind and order k . With this expansion one finds for the normalization factor

$$A = 2\pi I_0(\gamma) \quad (4.36)$$

and using the orthogonality of trigonometric functions we find for the order parameter

$$\langle \cos n\varphi \rangle_{\varphi} = \frac{I_k(\gamma)}{I_0(\gamma)} \delta_{n,kN} \quad (4.37)$$

We used our numerical simulation data to calculate the order parameters $\gamma_n = \langle \cos(n\varphi) \rangle_{\varphi}$ and $\delta_n = \langle \sin(n\varphi) \rangle_{\varphi}$ from $n=1$ to $n=5$ with $N=2$. The only order parameters which are not equal to zero are γ_2 and γ_4 . The theoretical value and the numerical values are given in table 3 for different friction and potential parameters. In all other cases the zeros are reproduced within the numerical error, which is about $\lesssim 0.03$ in those cases.

$\frac{V}{2k_B T}$	$\Gamma^* = .25$	.75	1.5	2.5	theory
.25	.13 $\pm$.02	.13 $\pm$.03	.11 $\pm$.02	.13 $\pm$.02	.12
.50	.21 $\pm$.03	.23 $\pm$.02	.24 $\pm$.03	.24 $\pm$.02	.24
.75	.32 $\pm$.03	.34 $\pm$.02	.34 $\pm$.03	.34 $\pm$.03	.35

$\langle \cos 2\varphi \rangle$

$\frac{V}{2k_B T}$	$\Gamma^* = .25$	.75	1.5	2.5	theory
.25	-	-	-	-	.01
.50	.02 $\pm$.02	.02 $\pm$.01	.05 $\pm$.02	.03 $\pm$.01	.03
.75	.05 $\pm$.02	.06 $\pm$.02	.07 $\pm$.01	.05 $\pm$.02	.06

$\langle \cos 4\varphi \rangle$

Table 3 The order parameter $\langle \cos 2\varphi \rangle$ and $\langle \cos 4\varphi \rangle$ for various friction and potential parameters. The theoretical values are from eq. (4.37).

4.7 DISCUSSION

Only a few papers have been written about the rotational motion of onedimensional rotators in an N-fold periodic potential. To our knowledge there exists only three papers, which treat the problem. The first one is by B. Lassier et al. [31]. They used a generalized version of Gordon's J-diffusion model [10]. Because they used a 3-fold potential, we cannot compare their results with ours in a quantitative way. The other difference is the fact that Lassier et al. expand the neutron scattering law in terms of Legendre-polynomials instead of trigonometric functions. The latter are the symmetry adapted functions for the present problem. For $t \rightarrow \infty$ the Legendre-polynomial-correlation functions tend to

$$\langle P_1(\infty) \rangle = 0$$

$$\langle P_2(\infty) \rangle = 1/4$$

$$\langle P_3(\infty) \rangle = \frac{5}{8} \frac{I_1^2\left(\frac{V}{2k_B T}\right)}{I_0^2\left(\frac{V}{2k_B T}\right)} \quad (4.38)$$

$$\langle P_4(\infty) \rangle = \frac{9}{64}$$

$$\langle P_5(\infty) \rangle = \frac{35}{128} \frac{I_1^2\left(\frac{V}{2k_B T}\right)}{I_0^2\left(\frac{V}{2k_B T}\right)}$$

Lassier et al. [31] calculated $\langle P_1(\infty) \rangle$ to $\langle P_5(\infty) \rangle$ by a numerical integration technique and within their numerical errors they find the same values for the long time decay of the Legendre-polynomials as in (4.38). Unfortunately,

in their fig. 3, they do not plot the correlation functions $\langle P_n(\cos(\varphi - \varphi_0)) \rangle$. Instead, they plot the functions

$$F_n(t) = \langle P_n(\cos(\varphi - \varphi_0)) \rangle - \langle P_n(\infty) \rangle . \quad (4.39)$$

They have simulated Gordon's J-diffusion model [10] in a threefold potential. In fact they cannot extract the long time values from their simulation data in the case of a high potential ($V = 7.5 k_B T$). The values they extract from their simulation data for large barriers are represented in our table 3 in the column $F_n(\infty)$. If one adds the theoretical long time values of the Legendre-polynomials to the long time results of the simulation of Lassier et al., the results are in very good agreement (error less than 3%) with the corresponding results from the harmonic approximation. The values from the harmonic approximation are given in the last column of table 4.

n	$\langle P_n(\infty) \rangle$	$F_n(\infty)$	$F_n(\infty) + \langle P_n(\infty) \rangle$	harmonic approximation
1	0	.968	.968	.971
2	.250	.655	.905	.916
3	.455	.360	.815	.843
4	.141	.590	.731	.759
5	.199	.434	.633	.652

Table 4 The values to which the functions $\langle P_n(\cos(\varphi(t) - \varphi(0))) \rangle$ would tend for very long times. The argument ∞ is used for $t = \infty$. The values for $\langle P_n(\infty) \rangle$ are from eq. (4.38). The $F_n(\infty)$ are from ref. [31]. The values for the harmonic approximation are from (4.20).

In the harmonic approximation jumps between the different minima are impossible. In the short times available for the simulation in a high potential only a few jumps occur, so that the harmonic approximation is a rather good description. From fig. 3 of ref. [31] one can see that the frequency of the oscillation of the correlation functions is independent of n . That this is correct in the case of the harmonic approximation can be seen in our eq. (4.20).

If the potential is higher than $5k_B T$ the harmonic approximation is a good one and analytic results for the correlation functions can be given.

As stated in the publication the best region to compare different models is the low friction-region. Significant differences between the models only occur in this region. In the model of Lassier et al., this means the region of long times τ_i . As discussed in part 3 the so-called J-diffusion model is a strong collision model. This means the particle loses its memory during the collision. In contrast the Langevin model is a weak collision model, because the angular momentum experiences only small changes at each collision.

Dianoux and Volino [11] solved the diffusion-equation, and calculated the correlation-functions $\langle \cos n(\varphi - \varphi_0) \rangle$. They, of course, obtained the right long time behaviour, but the short time behaviour is not correct. This is a well known fact, that the diffusion-equation does not have

the right initial behaviour. The great advance of Dianoux and Volino is the analytic solution of the problem.

Zatsepin [32] solved the Sack-equation. He gave only an explicit expression for the solution in the limiting cases of large and small potential barriers.

We used the generalized formalism of Dianoux and Volino to solve the Sack-equation. Our solution is equivalent to Zatsepin's in the two limiting cases. The figures 9 to 12 give the results for all these models for the correlation functions $\Gamma_1(t)$ and $\Gamma_2(t)$.

In fig. 9 the correlation function $\Gamma_1(t)$ is plotted for a small friction parameter. For short times all models except the diffusion model gave the correct initial behaviour. The solution of the Sack equation deviates strongly from the correct solution for times t^* larger than 1. It shows unphysical oscillations, which do not arise from the potential. (For clarity the oscillations are not plotted). Fig. 10 shows the correlation function $\Gamma_1(t)$ for a ten times larger friction. For clarity the results for $V = k_B T$ are omitted, and the result of the Sack-equation is plotted only for $V = \frac{1}{2} k_B T$, because the behaviour is nearly the same for the other cases.

Fig. 11 and 12 show the correlation function $\Gamma_2(t)$ for the same friction parameters. Again the solution from Sack-equation shows these unphysical oscillations. In fig. 12 one can see the last remains of these oscillations. Fig. 13 shows results for $V = \frac{3}{2} k_B T$ and different friction parameters.

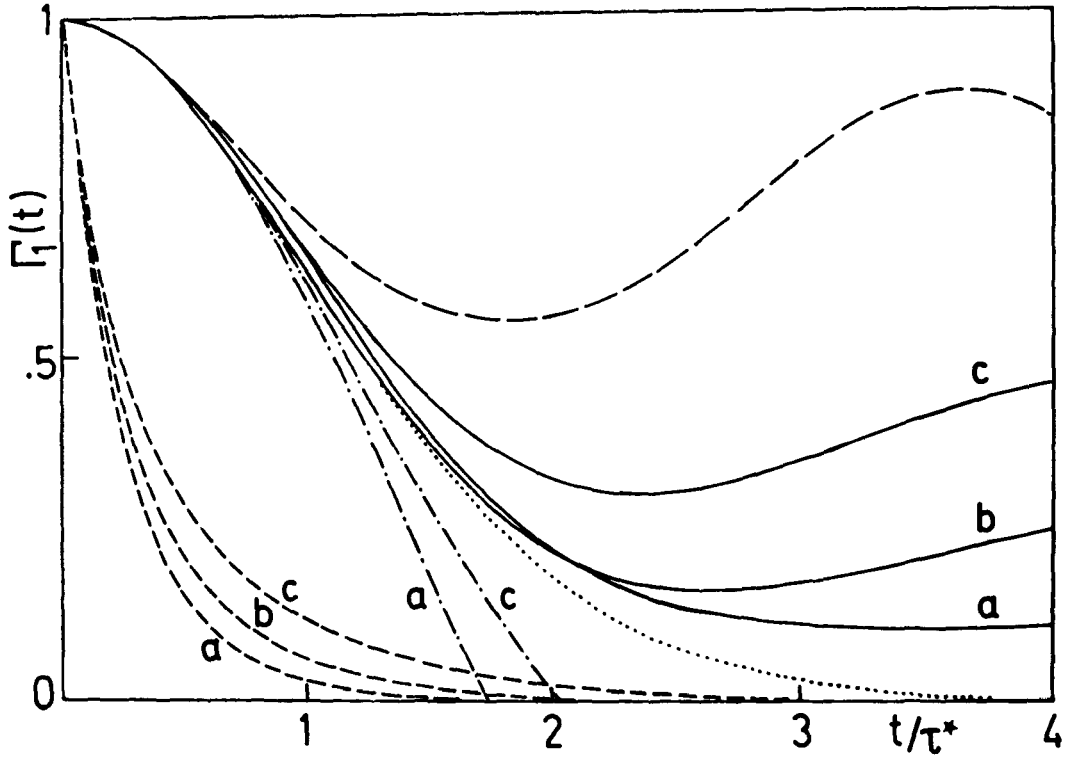


Fig. 9: The correlation function $\Gamma_1(t)$ for the different models. In figures 9-12 we use: --- solution of diffusion equation, ... analytic solution with $V=0$, ——— analytic solution of harmonic potential with stochastic force ($V = 1.5 k_B T$), — · — the computer simulation, — · — solution of Sack equation. The letter at the lines indicates the potential parameters: $a \hat{=} V = 0.5 k_B T$, $b \hat{=} V = k_B T$, $c \hat{=} V = 1.5 k_B T$. The friction constant $\Gamma^* = 0.25$. Both friction and time are in units of $\tau^* = (k_B T / I)^{1/2}$.

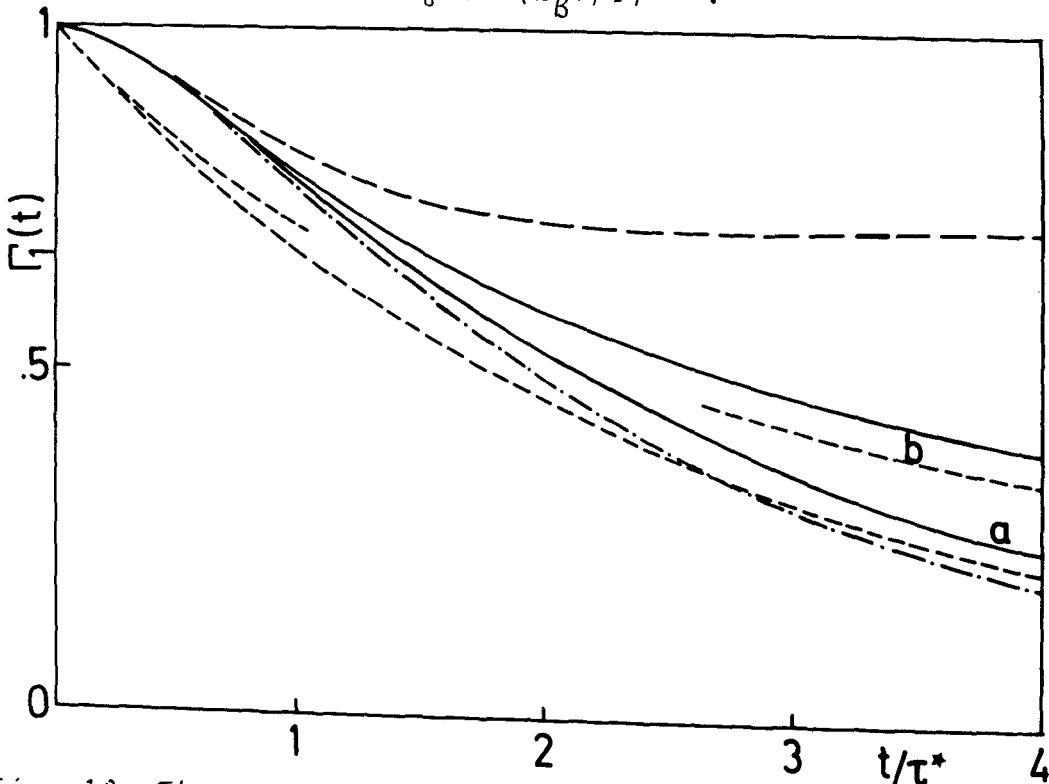


Fig. 10: The correlation function $\Gamma_1(t)$ with a friction constant $\Gamma^* = 2.50$. Same convention as in figure 9.

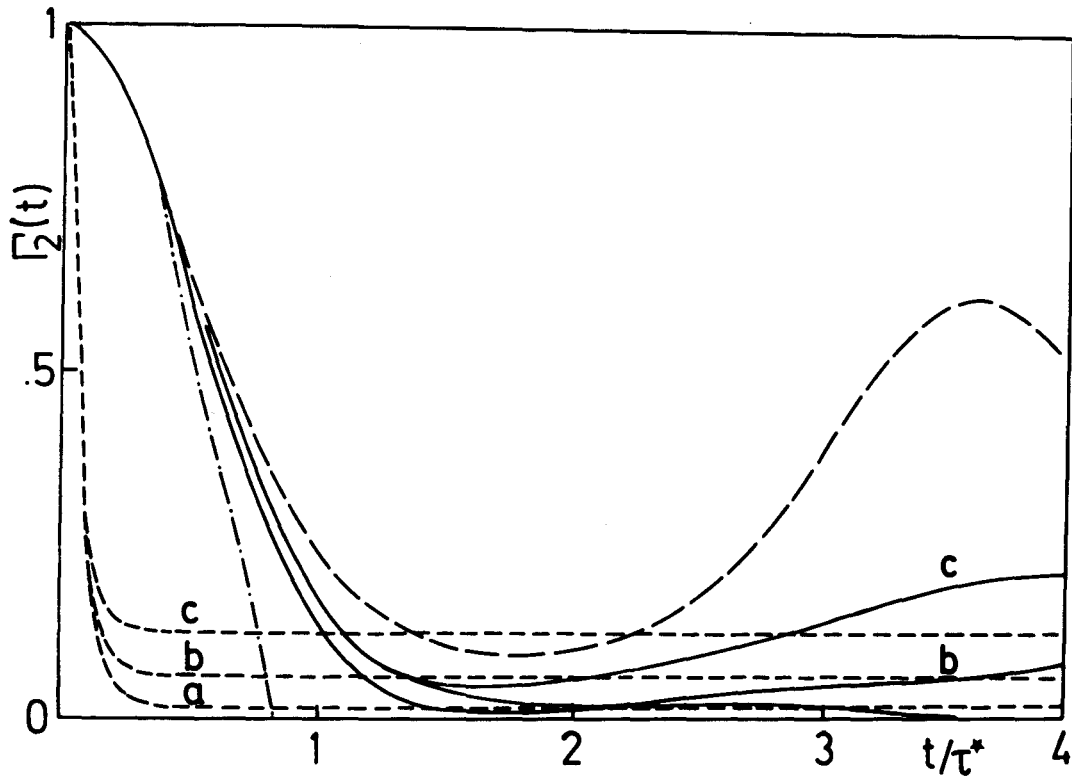


Fig. 11: The correlation function $\Gamma_2(t)$ with a friction constant $\tau^* = .25$. Same convention as in figure 9.

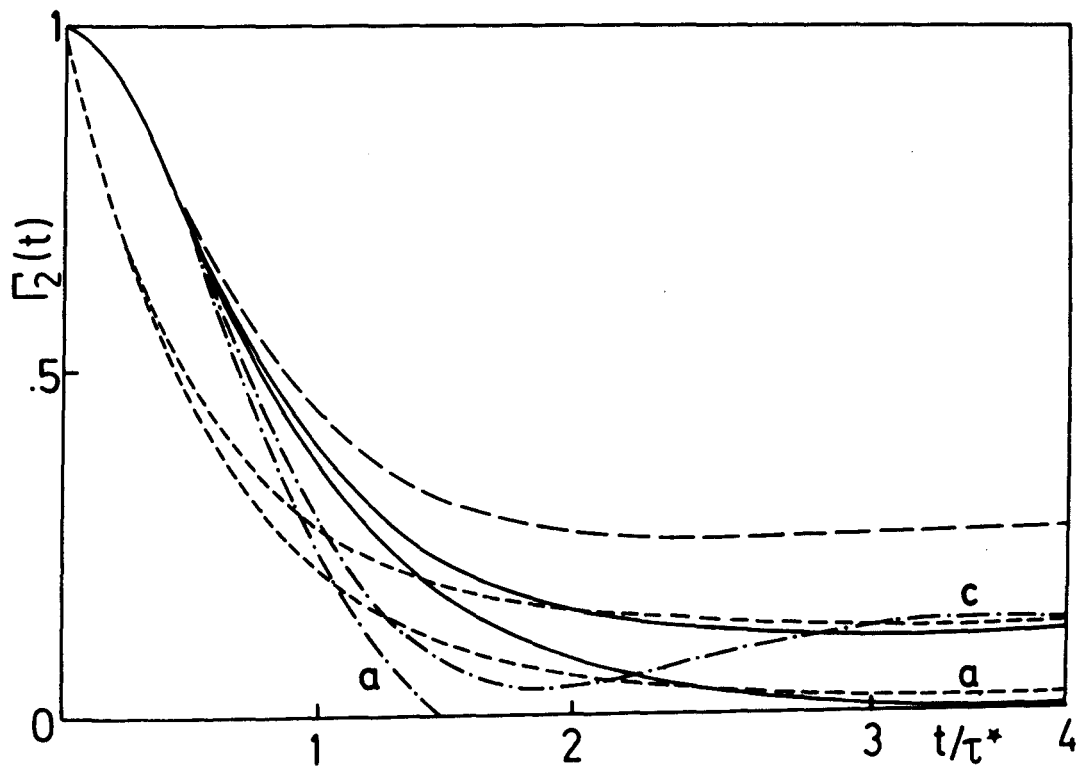


Fig. 12: The correlation function $\Gamma_2(t)$ with a friction constant $\tau^* = 2.50$. Same convention as in figure 9.

For large friction parameters all oscillation effects are damped out.

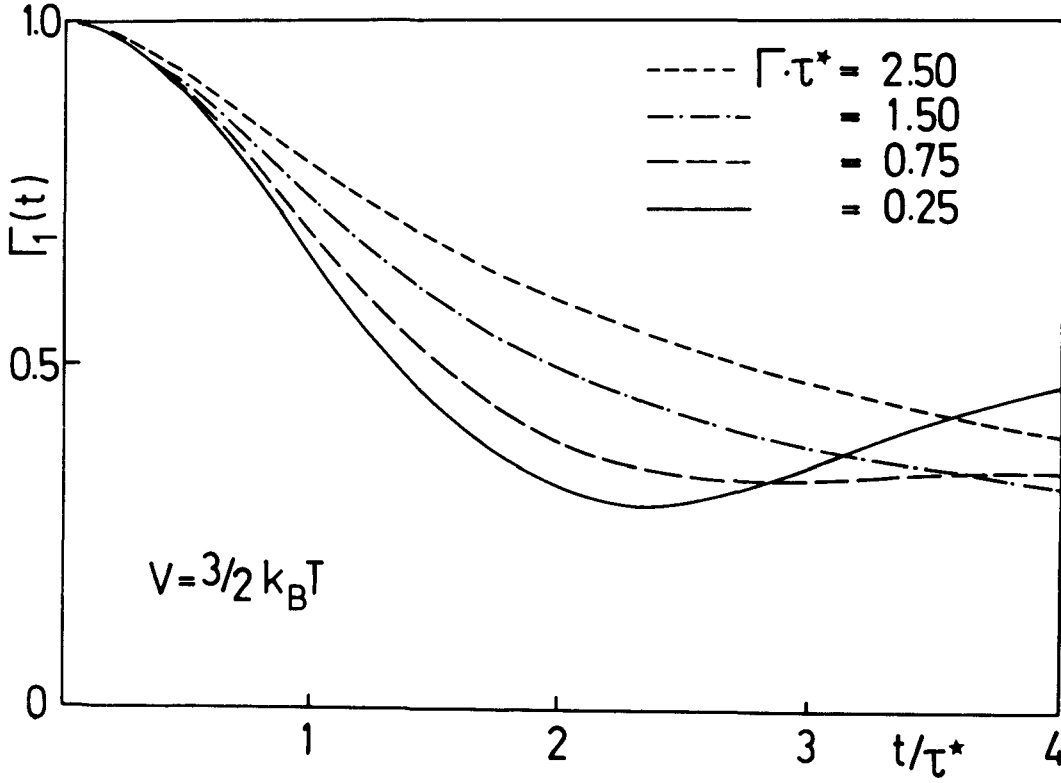


Fig. 13: The correlation function $\Gamma_1(t)$ for various friction parameters as indicated.

To answer the question which is the best model to use, we start by looking at the solution with potential $V = 0$. Then all three models can be solved by analytical methods and the results for the correlation functions Γ_n are.

Langevin:

$$\Gamma_n^L(t) = \exp - \frac{n^2}{\Gamma^* 2} (\Gamma^* t^* - 1 + \exp(-\Gamma^* t^*)) \quad (4.40)$$

Diffusion:

$$\Gamma_n^D(t) = \exp\left(- \frac{n^2}{\Gamma^*} t^*\right) \quad (4.41)$$

Sack:

$$\Gamma_n^S(t) = \exp\left(-\frac{\Gamma^*}{2} t^*\right) \cdot \left[\frac{\Gamma^*}{2\omega_n^*} \sin\omega_n^* t + \cos\omega_n^* t \right] \quad (4.42)$$

$$\text{with } \omega_n^* = \left(n^2 - \frac{\Gamma^{*2}}{4}\right)^{1/2}.$$

For these three equations we get for large friction constant Γ^* the same results

$$\Gamma_n(t) = \exp\left(-\frac{n^2}{\Gamma^*} t^*\right) \quad (4.43)$$

which shows us that in high friction limit all models are quite good. In the low friction limit problems arise. We know the free rotator result (see publication), which implies $\Gamma^* = 0$. The Langevin equation shows the right behaviour

$$\Gamma_n^L(t) = \exp(-n^2 t^{*2}) \quad (4.44)$$

The diffusion equation is not valid in this limit, and the Sack equation is

$$\Gamma_n^S(t) = \cos(nt^*) \quad (4.45)$$

which is the wrong oscillatory behaviour. It is possible to say that an approximation is good, if the error is less than 5%. To get a feeling, in which region the different models are valid, we compared eq. (4.40) with (4.41) and (4.42). The result is plotted in fig. 14a. The Langevin model is valid in the whole plane. Another model is considered to be valid, if the difference to the Langevin model is less

than 0.05. The fact that there exists a region where the diffusion equation is better than the Sack equation arises from the spurious oscillations of the solution of the Sack equation.

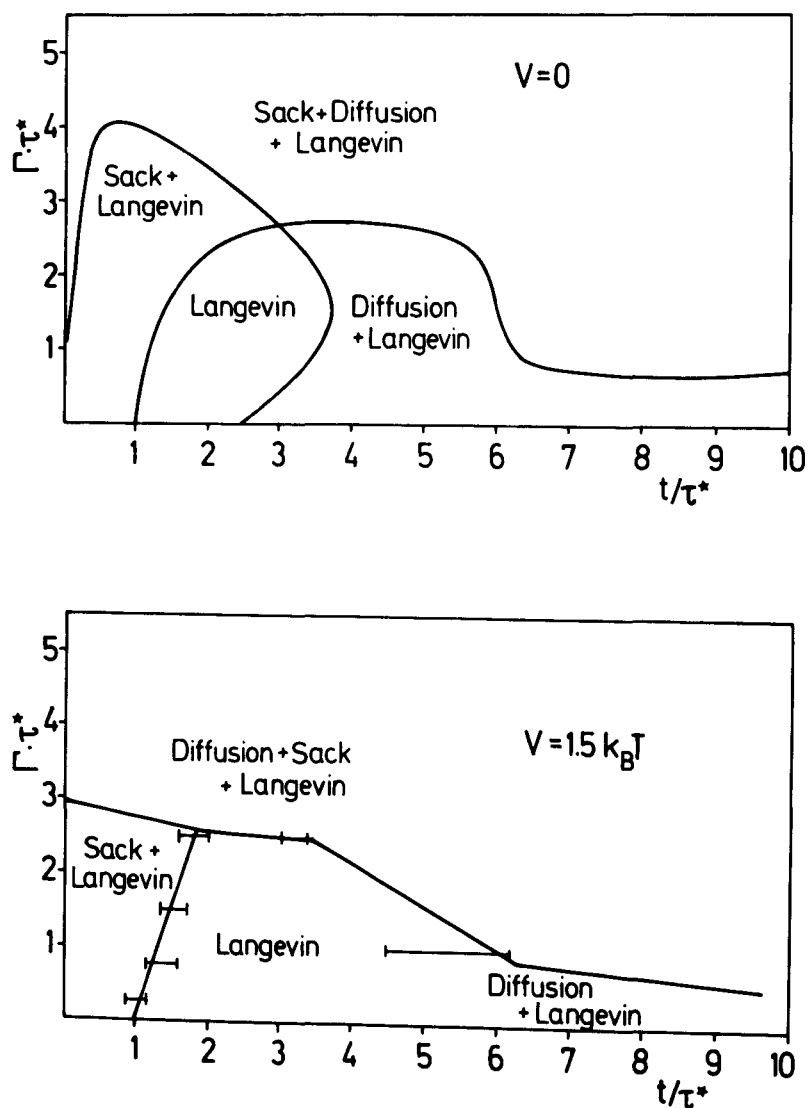


Fig. 14: The regions in which the different models are valid. A model is valid if it differs less than .05 from the computer simulation.

a) $V=0$. In this case an analytic solution of the Langevin model is known. Therefore Langevin means the analytic solution.

b) $V = 1.5 k_B T$. Here means Langevin the computer simulation. This figure shows only the qualitative behaviour.

For high barriers the results for the validity are quite similar to the findings for low barriers. We could only extract a few points from the computer simulation. Therefore the lines have an uncertainty. The results for $V = \frac{3}{2} k_B T$ are shown in fig. 14b. It looks quite similar to fig. 14a. The line which separates the region where only the Langevin model is valid from the "Diffusion-Langevin"-region could not be extracted from the numerical data. The Sack-equation is an advance in calculating the correlation functions of rotational motion. For short times we get the correct behaviour. For long times and/or for large friction parameters the Sack-equation yields results which are quite similar to the Diffusion equation. They do not differ very much from the solution of the Langevin equation. In the range of intermediate friction parameter there are spurious oscillations which do not have their origin in the librational motion in the potential minimum. The correlation function becomes negative which is not the correct behaviour. In a frequency-representation (Fourier transformed correlation functions) the wrong behaviour would not be so important. To answer the question, how important it will be, we should Fourier transform the simulation-data. That is not possible with our present data, because one needs very long simulation-times to get data which can be Fourier transformed. To sum up we can say the Sack equation is an advance compared to the Diffusion equation. The numerical solution of the Langevin equation yields a good criterion to test other models.

5. TWODIMENSIONAL ROTATIONAL MOTION IN A CUBIC POTENTIAL

In this chapter we want to look at the rotational motion with two degrees of freedom, i.e. to motion of linear molecules.

5.1 THE POTENTIAL

For linear molecules with two rotational degrees of freedom the only variables necessary to describe the motion are the polar angles θ and φ . The potential $V(\theta, \varphi)$ should be expanded in terms symmetry adapted functions. We want to restrict ourselves to cubic symmetry of the surrounding of the molecule under consideration. The expansion into cubic harmonics, which are the symmetry adapted functions for cubic symmetry is [33]:

$$V(\theta, \varphi) = \sum_{\ell=0}^{\infty} \sum_{m=1}^{2\ell+1} B_{\ell m} K_{\ell m}(\theta, \varphi) \quad (5.1)$$

Only those functions $K_{\ell m}$ contribute which are invariant under all 48 symmetry operations of the cubic group. The only non-vanishing coefficients are B_{01} , B_{41} , B_{61} , ... The corresponding cubic harmonics are simple if one uses cartesian coordinates x, y, z . (See table 6 for details). To get results which can be compared with earlier work, we restrict to the fourth order term B_{41} . The K_{01} is constant and therefore irrelevant. The resulting potential is usually called Devonshire potential [33] and we write it

$$V(x, y, z) = s\gamma(x^4 + y^4 + z^4 - \frac{3}{5}) \quad x^2 + y^2 + z^2 = 1 \quad (5.2)$$

The constant term in K_{41} is neglected, too. s is the sign of the potential, which can be $+1$ and -1 . γ denotes the strength of the potential in units of temperature and is given by

$$\gamma = \frac{B_{41}}{k_B T} \cdot \frac{5}{4} \sqrt{\frac{21}{4\pi}}. \quad (5.3)$$

$\gamma = 1$ means that the thermal energy is 1.5 times the maximum of the potential.

An important factor is the sign s of the potential. The properties of the potential are given in table 5.

direction	$s = +1$	V_+	$s = -1$	V_-
111	8 minima	$-\frac{8}{30} \gamma$	8 maxima	$\frac{8}{30} \gamma$
110	12 saddle points	$-\frac{3}{30} \gamma$	12 saddle points	$\frac{3}{30} \gamma$
100	6 maxima	$\frac{12}{30} \gamma$	6 minima	$-\frac{12}{30} \gamma$
barrier hight	$1/6 \gamma$		$1/2 \gamma$	

Table 5 Properties of the Devonshire potential for the different signs.

In cases where the minimum of the potential is in 110 direction it is necessary to include the next term ($B_{61} \neq 0$) into the expansion (5.1).

5.2 THE NEUTRON SCATTERING LAW

We start again from the intermediate scattering function $I(\vec{Q}, t)$, which is given in eq. (3.3). Sears [21] made use of the expansion of the exponential function into spherical harmonics [34].

$$e^{+i\vec{Q}\vec{r}(t)} = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} j_{\ell}(Qr) (\pm i)^{\ell} Y_{\ell m}^*(\Omega_Q) Y_{\ell m}(\Omega(t)) \quad (5.4)$$

j_{ℓ} is the spherical Bessel function of the first kind and order ℓ [22]. Ω_Q stands for the polar angles of $\vec{Q}$ and $\Omega(t)$ stands for the polar angles of $\vec{r}(t)$.

Substituting equation (5.4) into equation (3.3) we get

$$I(\vec{Q}, t) = 16\pi^2 \sum_{\ell\ell'} \sum_{mm'} j_{\ell}(Qr) j_{\ell'}(Qr) i^{\ell} (-i)^{\ell'} Y_{\ell m}^*(\Omega_Q) Y_{\ell' m'}^*(\Omega_Q) \cdot \\ \cdot \langle Y_{\ell m}(\Omega(t)) Y_{\ell' m'}(\Omega(0)) \rangle \quad (5.5)$$

Making use of the symmetry considerations this expression can be simplified [13]. Therefore we decompose the spherical harmonics into symmetry adapted functions.

$$Y_{\ell m} = \sum_{\rho=1}^{2\ell+1} a_{\ell, \rho}^m U_{\ell, \rho} \quad (5.6)$$

Here we made use of the fact that these symmetry adapted functions are only linear combinations of spherical harmonics with the same ℓ .

The unitarity of the transformation (5.6) implies

$$\sum_{m=-\ell}^{\ell} \left(a_{\ell, \rho}^m \right)^* a_{\ell, \rho'}^m = \delta_{\rho \rho'} \quad . \quad (5.7)$$

Using the transformation (5.6) in eq. (5.5) we arrive at expectation values of the kind $\langle U_{\ell \rho}(\Omega(t)) U_{\ell' \rho'}(\Omega(0)) \rangle$. Making use of group theory we find that only expectation values with $\rho = \rho'$ are different from zero [35]. Therefore we finally get from eq. (5.5)

$$I(\vec{Q}, t) = 16\pi^2 \sum_{\ell \ell'} \sum_{\rho} j_{\ell}(Qr) j_{\ell'}(Qr) i^{\ell} (-i)^{\ell'} U_{\ell \rho}(\Omega_Q) U_{\ell' \rho}(\Omega_Q) \cdot \\ \cdot \langle U_{\ell \rho}(\Omega(t)) U_{\ell' \rho}(\Omega(0)) \rangle \quad (5.8)$$

This expression is valid for any symmetry.

We want to regard a dumbbell molecule in a cubic surrounding. The symmetry adapted functions are the cubic harmonics $K_{\ell m}$. They are simple if one uses cartesian coordinates. Up to order 3 the cubic harmonics are given in table 6.

Now we want to write down the intermediate scattering function up to order $\ell + \ell' = 4$. We use the abbreviation $\hat{Q}$ for the unit vector in direction of $\vec{Q}$. Similarly we write $\hat{x}(t)$ for the unit vector in direction of $\vec{x}(t)$. Then we get

$\ell \backslash m$	symmetry	prefactor	1	2	3	4	5	6	7
0	A_{1g}	$\frac{1}{\sqrt{4\pi}}$	1						
1	T_{1u}	$\sqrt{\frac{3}{4\pi}}$	x	y	z				
2	E_g	$\sqrt{\frac{15}{16\pi}}$	$\frac{1}{\sqrt{3}} (3z^2-1)$	(x^2-y^2)					
	T_{2g}	$\sqrt{\frac{15}{4\pi}}$			yz	zx	xy		
3	A_{1u}	$\sqrt{\frac{105}{4\pi}}$	xyz						
	T_{1u}	$\sqrt{\frac{175}{16\pi}}$		$x^3 - \frac{3}{5} x$	$y^3 - \frac{3}{5} y$	$z^3 - \frac{3}{5} z$			
	T_{2u}	$\sqrt{\frac{105}{16\pi}}$					$x(y^2-z^2)$	$y(z^2-x^2)$	$z(x^2-y^2)$
4	A_{1g}	$\frac{5}{4} \sqrt{\frac{21}{4\pi}}$	$x^4+y^4+z^4 - \frac{3}{5}$						

Table 6 The cubic harmonics $K_{\ell,m}(x,y,z)$ up to order $\ell=3$. The association of the index m to special function is arbitrary [43].

$$\begin{aligned}
 I(Q, t) = & j_0^2(Qr) + 3j_1^2(Qr) \langle \hat{x}(t) \hat{x}(0) \rangle \\
 & + 6\pi j_2^2(Qr) \{E_g^{(2)}(t) + 2 T_{2g}^{(2)}(t)\} \\
 & + K_{41}(\hat{Q}) \{8\pi j_0(Qr) j_4(Qr) \langle K_{41}(\hat{x}) \rangle \\
 & \quad + 24\pi \sqrt{\frac{4\pi}{21}} j_2^2(Qr) [E_g^{(2)}(t) - T_{2g}^{(2)}(t)] \\
 & \quad + 16\pi \sqrt{4\pi} j_1(Qr) j_3(Qr) T_{1u}^{(3,1)}(t)\} \quad (5.9) \\
 & + \dots
 \end{aligned}$$

where the three timedependent correlation functions are given by

$$\begin{aligned}
 E_g^{(2)}(t) &= \frac{5}{16\pi} \langle (3z^2(t) - 1)(3z^2(0) - 1) \rangle \\
 &= \frac{15}{16\pi} \langle (x^2(t) - y^2(t))(x^2(0) - y^2(0)) \rangle \quad (5.10a)
 \end{aligned}$$

$$\begin{aligned}
 T_{2g}^{(2)}(t) &= \frac{15}{4\pi} \langle y(t)z(t)y(0)z(0) \rangle \\
 &= \frac{15}{4\pi} \langle z(t)x(t)z(0)x(0) \rangle \\
 &= \frac{15}{4\pi} \langle x(t)y(t)x(0)y(0) \rangle \quad (5.10b)
 \end{aligned}$$

$$\begin{aligned}
 T_{1u}^{(3,1)}(t) &= \frac{\sqrt{21 \cdot 5}}{8\pi} \langle x^3(t)x(0) - \frac{3}{5} x(t)x(0) \rangle \\
 &= \frac{\sqrt{21 \cdot 5}}{8\pi} \langle y^3(t)y(0) - \frac{3}{5} y(t)y(0) \rangle \\
 &= \frac{\sqrt{21 \cdot 5}}{8\pi} \langle z^3(t)z(0) - \frac{3}{5} z(t)z(0) \rangle \quad (5.10c)
 \end{aligned}$$

The intermediate scattering function is decomposed into one part which is proportional to $K_{41}(\hat{Q})$ and in one part which is not infact this part is isotropic in $\vec{Q}$ space. If the potential decreases the term proportional to K_{41} decreases, too. The remaining part is identical to the first three term of eq. (3.5).

It is a question of the different models to calculate the correlation functions.

5.3 LANGEVIN-EQUATION

In the presence of the Devonshire potential the Langevin-equation (2.27) cannot be solved by analytic methods. Therefore we will first regard the low temperature limit which can be solved analytically.

5.3.1. $T \ll V$

In the case that the temperature is much less than the saddle-point energy one can use the harmonic approximation of the potential in the vicinity of a minimum. In this approximation no jumps from one minimum to another can occur, but the oscillatory motion of the molecule in the potential minimum (the pocket) is well described. To do the harmonic approximation one must treat the two cases with $s = +1$ and $s = -1$ independently. From table 5 we know the minima of the potential

$$\vec{x}_{\min} = \left(\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}} \right) \quad s = +1 \quad (5.11a)$$

$$\vec{x}_{\min} = (1, 0, 0) \quad s = -1 \quad (5.11b)$$

Starting from $\vec{x}_{\min}$ we must expand the potential on the sphere. For a two-dimensional harmonic oscillator the two motions

decouple and it is sufficient to solve only one of them.

The resulting harmonic potential is:

$$V(\varepsilon) = \frac{4}{3} \gamma \varepsilon^2 \quad s = +1 \quad (5.12a)$$

$$V(\xi) = 2 \gamma \xi^2 \quad s = -1 \quad (5.12b)$$

where ε respective ξ is the displacement from the minimum position. The Langevin-equations resulting from the potentials (5.12) are

$$\ddot{\varepsilon} = - \frac{8}{3} \frac{\gamma}{I} \varepsilon - \Gamma \dot{\varepsilon} + \frac{G^{1/2}}{I} F(t) \quad s = +1 \quad (5.13a)$$

$$\ddot{\xi} = - 4 \frac{\gamma}{I} \xi - \Gamma \dot{\xi} + \frac{G^{1/2}}{I} F(t) \quad s = -1 \quad (5.13b)$$

The centripetal term disappeared, because the condition that the motion has to happen on a sphere is used to do the harmonic expansion. The Langevin-equations are identical with the Langevin-equation (4.18) in the onedimensional case. The solution is given in eq. (4.19).

Now we have to calculate the correlation functions $\langle \hat{x}(t) \hat{x}(0) \rangle$ and the correlation functions which are defined in eq. (5.10a) and (5.10b). Expanding the correlation functions up to second order in ε respective ξ we get the results

$$\langle \hat{x}(t) \hat{x}(0) \rangle = 1 - \langle \varepsilon^2 \rangle + \langle \varepsilon \varepsilon_0 \rangle \quad s = +1 \quad (5.14)$$

$$\langle \hat{x}(t) \hat{x}(0) \rangle = 1 - \langle \xi^2 \rangle + \langle \xi \xi_0 \rangle \quad s = -1$$

$$E_g(t) = \frac{5}{4\pi} \langle \varepsilon \varepsilon_0 \rangle \quad s = +1 \quad (5.15)$$

$$E_g(t) = \frac{5}{4\pi} \left\{ \frac{1}{2} - \frac{3}{2} \langle \xi^2 \rangle \right\} \quad s = -1$$

$$T_{2g}(t) = \frac{5}{4\pi} \left\{ \frac{1}{3} - \langle \varepsilon^2 \rangle + \frac{1}{3} \langle \varepsilon \varepsilon_0 \rangle \right\} \quad s = +1 \quad (5.16)$$

$$T_{2g}(t) = \frac{5}{4\pi} \langle \xi \xi_0 \rangle \quad s = -1$$

For clarity the arguments have been dropped and the argument $t=0$ is replaced by the index 0. Also we made use of the relation $\langle \varepsilon \rangle = \langle \varepsilon_0 \rangle = 0$. The time independent average $\langle \varepsilon^2 \rangle$ is given by

$$\langle \varepsilon^2 \rangle = \frac{2\pi}{Z} \int_{-\infty}^{\infty} \varepsilon^2 e^{-V(\varepsilon)} \varepsilon d\varepsilon \quad (5.17)$$

with the normalization factor

$$Z = 2\pi \int_{-\infty}^{\infty} e^{-V(\varepsilon)} \varepsilon d\varepsilon \quad (5.18)$$

The result of integration with the use of the potentials (5.12) is:

$$\langle \varepsilon^2 \rangle = \frac{3}{4\gamma} \quad (5.19a)$$

$$\langle \xi^2 \rangle = \frac{1}{2\gamma} \quad (5.19b)$$

The results for the harmonic approximation is shown in fig. 16-21 and discussed in some detail in part 5.6.

5.3.2 NUMERICAL SIMULATION

We solved the three-dimensional Langevin-equation

$$\ddot{\vec{x}} = - \frac{1}{I} \text{grad}_{\vec{x}} U_2 - \Gamma \dot{\vec{x}} - |\dot{\vec{x}}|^2 \frac{\dot{\vec{x}}}{|\dot{\vec{x}}|} + \frac{G^{1/2}}{I} \vec{F}(t) \quad (5.20)$$

with the cubic potential from eq. (5.2) by the numerical simulation technique which is described in the publication. The only difference is a new way of producing normally distributed random numbers. The new method is described in the Appendix.

The simulation was done for 40 parameter sets. The sign of the potential which may be positive or negative is one of the parameters. In both cases the strength $\gamma = 0.5, 1.0, 2.0, 4.0$, and 10.0 . And the friction parameter is chosen $\Gamma^* = .25, .75, 1.50$, and 2.50 .

Together with the other analytic results from the harmonic approximation the results are presented in fig. 16-21 and discussed in part 5.6.

5.4. MONTE-CARLO-SIMULATION

De Raedt [36] solved the free (without stochastic torque and without friction) twodimensional rotator in a cubic potential by a Monte-Carlo-Method. He started with the equation of motion

$$\ddot{\vec{x}} = - \frac{1}{I} \text{grad}_{\vec{x}} U_2 - |\dot{\vec{x}}|^2 \vec{x} \quad (5.21)$$

This equation cannot be solved by analytic methods. Therefore he solved it by a standard numerical integration technique. Starting from a given initial space coordinate $\vec{x}_0$ and a velocity $\vec{v}_0$ the motion is of course completely deterministic. The solution of eq. (5.21) depends on the initial velocity $\vec{v}_0$ and the initial place $\vec{x}_0$. To get the correlation functions we must average over the initial conditions with a Boltzmann-distribution.

$$\rho(\vec{x}_0, \vec{v}_0) = \frac{1}{Z} \exp \left\{ - \frac{1}{\beta} \left(\frac{I}{2} \vec{v}_0^2 + V(\vec{x}_0) \right) \right\} \quad (5.22)$$

where Z is the normalization factor.

The average is done with the Monte-Carlo-technique. The initial conditions are chosen randomly. The only condition is that they must obey the Boltzmann distribution. This condition guarantees the thermal equilibrium.

In practice De Raedt has chosen 15 000 initial values then he took the mean over this 15 000 values at every time t .

There is one basic difference to the Langevin-model. The model of a free rotator in a potential is not ergodic. Fig. 15 helps to explain the physical situation. The initial conditions $\vec{x}_0$ and $\vec{v}_0$ determine the total energy of the particle. This energy will not change for this certain particle. For each of these 15 000 particles we have a defined and constant energy. In Fig. 15 the four lines indicates the

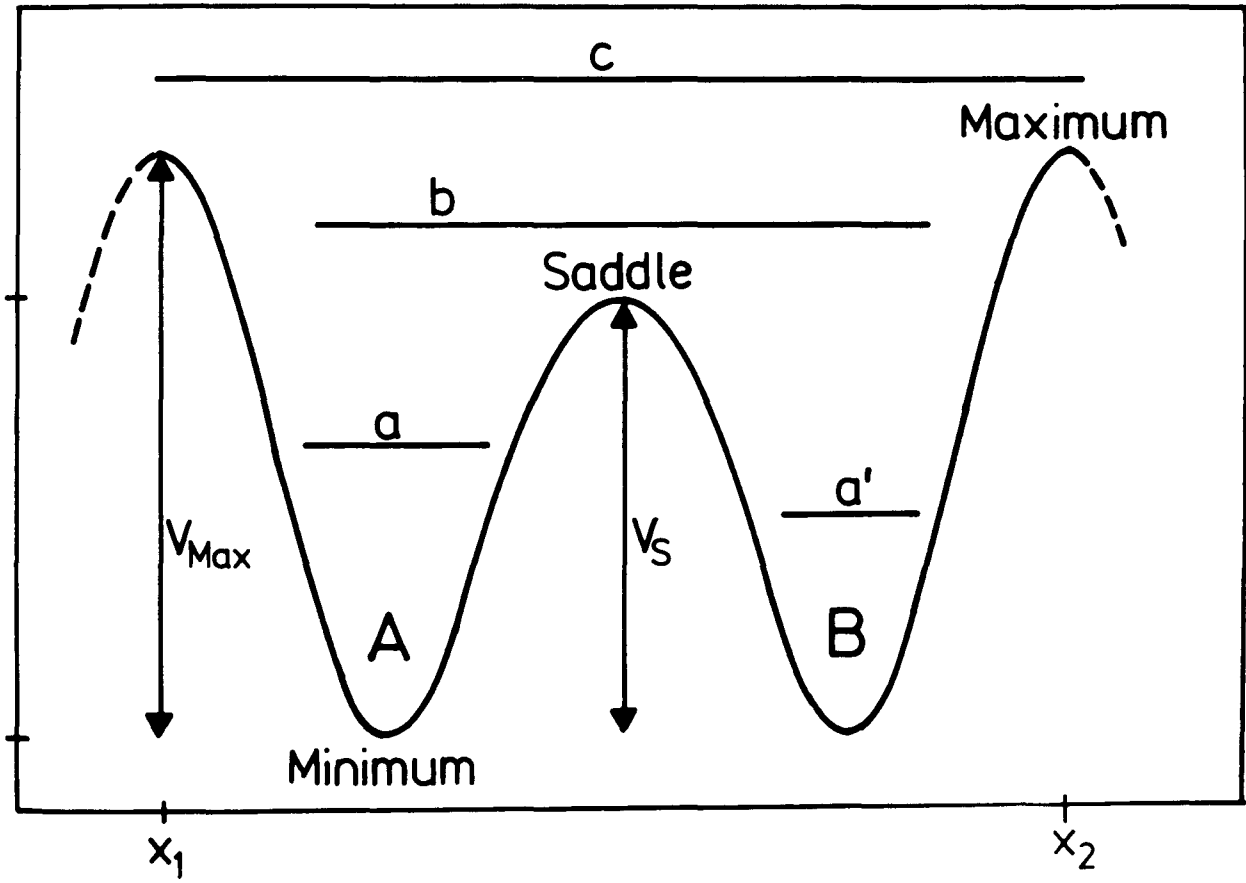


Fig. 15: Two minima (pockets) A and B of a potential are plotted. The four lines a, a', b, and c denote the total energy of four particles. The interval x_1 x_2 shows the periodicity of the potential.

total energy for four different particles. The particle a has to stay in the pocket A. Its energy ($<V_s$) does not allow to cross the barrier. The same is valid for the particle a' which has to stay in the pocket B. They both perform an oscillatory motion in its pocket. The particle b would change between the pockets A and B, because its energy ($>V_s$) allows to cross the small barrier. All particles with total energies less than V_{max} can not move over the whole possible range of x . Only particles with energy larger than V_{max} can move over the whole range of x . This effect can be seen in the resulting correlation functions. They approach a constant value as time goes to infinity. Let us look e.g. at the correlation function

$\langle r(t)r(0) \rangle$. If the particle stays in a certain pocket the vector $r(t)$ does not change very much with time. This means that the product $r(t)r(0)$ is nearly r^2 for all times. Therefore all particles, which stay in a pocket, contribute a constant to the correlation function.

For the Langevin-model these difficulties do not exist because the interplay between the friction-force and the stochastic force dissipates the particle over the whole energy range.

The correlation functions extracted from these Monte-Carlo data are also presented in part 5.6 of this work.

5.5 THE METHOD OF UNIFIED ROTATIONAL DYNAMICS

Michel et al. [37] have developed a unified theory to treat the orientational dynamics of molecular crystals. De Raedt [7,13] used this theory to treat the dynamics of a dumbbell molecule in a cubic potential.

Because the cubic harmonics K_{11} , K_{12} , and K_{13} are equivalent and also K_{21} , K_{22} respective K_{23} , K_{24} , and K_{25} we will abbreviate each of the three groups of equivalent functions by a single symbol U_1 , U_2 , and U_3 , respectively. Then the correlation functions $\langle r(t)r(0) \rangle$, $E_g^{(2)}$ and $T_{2g}^{(2)}$ are defined by

$$\frac{3}{4\pi} \langle r(t)r(0) \rangle = \langle U_1(t)U_1(0) \rangle \quad (5.23a)$$

$$E_g(t) = \langle U_2(t)U_2(0) \rangle \quad (5.23b)$$

$$T_{2g}(t) = \langle U_3(t)U_3(0) \rangle \quad (5.23c)$$

These correlation functions are the experimentally relevant quantities and therefore one can choose the functions $U_i(t)$ as the secular variables [37]. The full set of secular variables is then given by $\{U_i, \dot{U}_i\}$, $i=1,2$ and 3 , where $\dot{U}_i = \frac{d}{dt} U_i$. The variables are uncoupled.

The correlation functions in ω -space are given by the Fourier transform of the correlation functions in t -space.

$$C_i(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle U_i(t)U_i(0) \rangle \quad (5.24)$$

To calculate the correlation function $C_i(\omega)$ de Raedt used the projection-operator technique of Mori and Zwanzig [38]. The correlation function can be expressed in terms of the Laplace transformed of Kubo's relaxation function ϕ [34]

$$C_\alpha(\omega) = \frac{k_B T}{\pi} \lim_{\epsilon \rightarrow 0} \frac{1}{2i} [\phi_\alpha(\omega+i\epsilon) - \phi_\alpha(\omega-i\epsilon)] \quad (5.25)$$

Calculating the relaxation function ϕ one must evaluate the memory kernels. De Raedt evaluates the memory kernels up to fourth moment. The $2n$ th moment is defined by

$$\langle \omega_i^{2n} \rangle = \frac{\left\langle \left(\frac{d^n}{dt^n} U_i \right) \left(\frac{d^n}{dt^n} U_i \right) \right\rangle}{\langle U_i U_i \rangle} \quad (5.26)$$

The final result for the correlation function $C_i(\omega)$ is

$$C_i(\omega) = \frac{\frac{\langle U^\alpha U^\alpha \rangle}{\pi} \left[\frac{\langle \omega_i^4 \rangle - \langle \omega_i^2 \rangle^2}{\langle \omega_i^2 \rangle} \right]^{1/2}}{\omega^2 \left(\omega^2 - \frac{\langle \omega_i^4 \rangle}{\langle \omega_i^2 \rangle} \right)^2 + \frac{\langle \omega_i^4 \rangle}{\langle \omega_i^2 \rangle} (\omega^2 - \langle \omega_i^2 \rangle)^2} \quad (5.27)$$

A more detailed discussion of the calculation and explicit expression of $\langle \omega_i^2 \rangle$ and $\langle \omega_i^4 \rangle$ can be found in ref. [7,13].

Doing the inverse Fouriertransform of eq. (5.27) we get the correlation function $\langle U_i(t) U_i(0) \rangle$. These results are presented in fig. 16-22 of part 5.6.

5.6 DISCUSSION OF RESULTS

Only a few papers have been written about the motion of a linear molecule in a cubic potential. Brot et al. [40,41] did work on the rotational motion of rotators with two degrees of freedom. In their first paper [40] they used a $\sin^2\theta$ potential (cylindrical symmetry). We will not compare with their results, because we are interested in potentials with cubic symmetry. In their second publication they used a cubic potential. The method is identical to the method of Lassier et al. [31] described in our chapter 4. A comparison of Brot's results and our results does not show principal difference. A quantitative comparison of Brot's results and our results is not possible. We cannot extract numerical values from their figures to compare the results. Another interesting former work about twodimensional

rotators has been done by de Raedt [13,37]. It is described in part 5.5 of this work. De Raedt has also performed a Monte-Carlo-Simulation of the problem [36]. The basic idea of this method is described in part 5.4. Both his calculations are for systems without friction, they should be compared with the limit $\Gamma^* \rightarrow 0$ of our results from the simulation of Langevin-equation. The results are given in Fig. 16-18. Fig. 16 shows the results for the correlation function $\langle r(t)r(0) \rangle$. Fig. 17 shows the correlation function $E_g^{(2)}(t)$ and Fig. 18 the correlation function $T_{2g}^{(2)}(t)$. The solid lines are the data from the simulation of the Langevin-equation, the dashed lines are the Monte-Carlo-results, and the dotted lines are de Raedt's results from Ref. [13,37]. These figures show the results with the positive sign of the potential ($s = +1$).

The results with negative sign of the potential ($s = -1$) is given in Fig. 19 for the correlation function $E_g^{(2)}(t)$ and $T_{2g}^{(2)}(t)$. The results for $\langle r(t)r(0) \rangle$ are not given, because they are similar to the results with positive sign of the potential.

The main difference between the two signs of the potential is the exchange in the behaviour of the correlation functions. $E_g^{(2)}(t)$ and $T_{2g}^{(2)}(t)$. From the different behaviour of these correlation functions we can learn how important it is to use symmetry adapted functions. If these functions have their maximum in the minima of the potential the correlation function will describe the oscillatory motion in the potential minimum. If the maxima of a certain symmetry adapted function are at saddle points of the potential, the corresponding

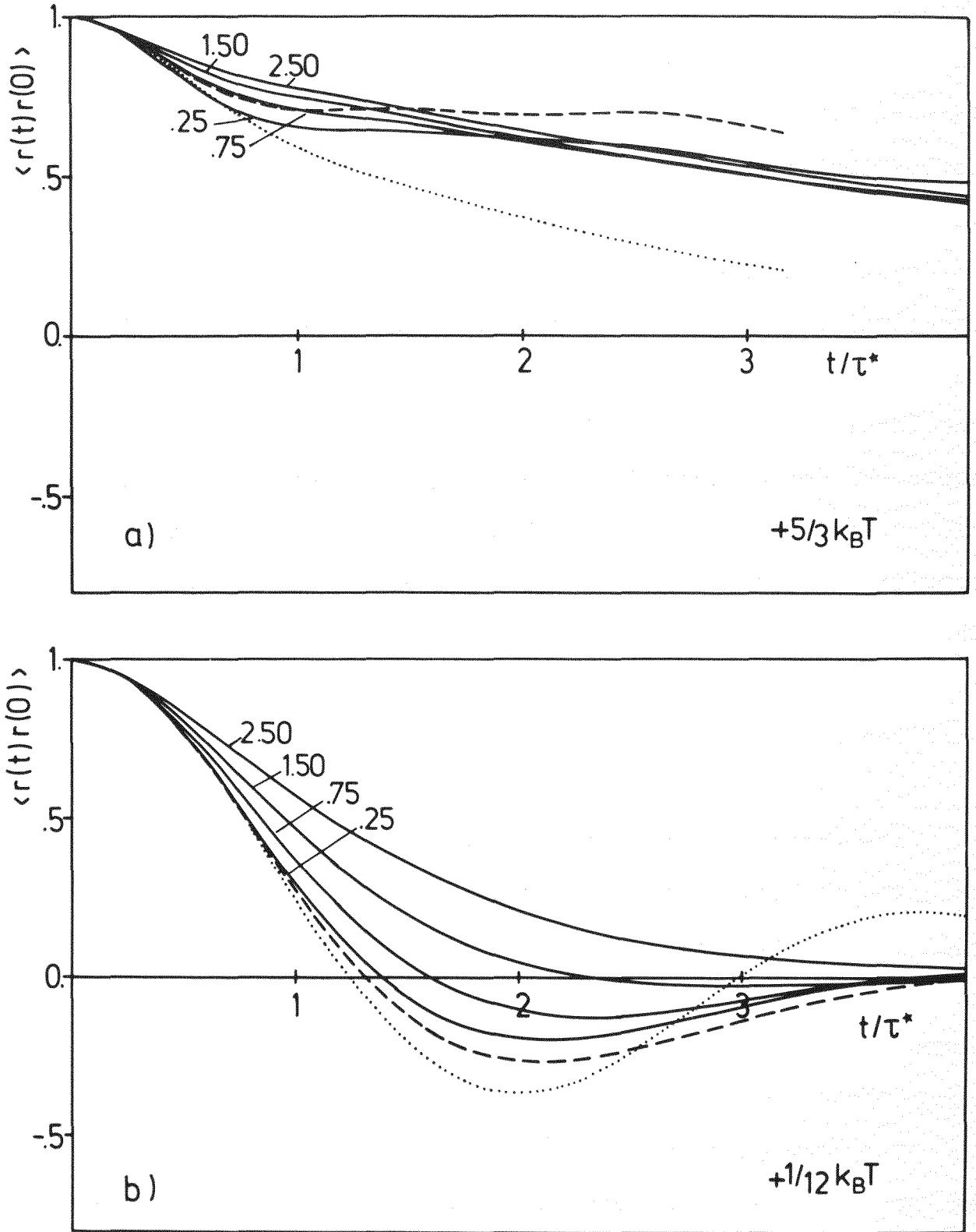


Fig. 16: The figure shows the results for the correlation function $\langle r(t)r(0) \rangle$ for different friction parameters as indicated. The dashed line is the result from the Monte-Carlo-calculation [36]. The dotted line is taken from Ref. [13, 37].
a) The results for the saddle point height $5/3 k_B T$ and positive sign of the potential.
b) The results for the saddle point height $1/12 k_B T$ and positive sign of the potential.

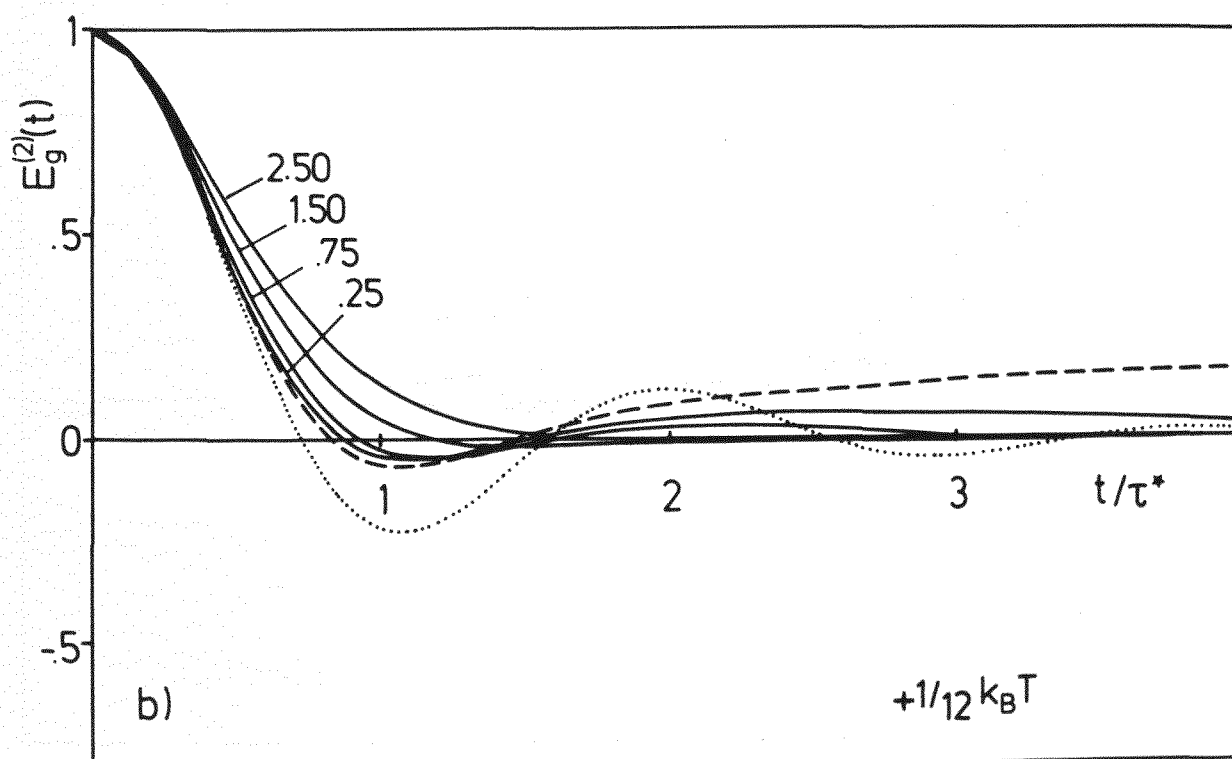
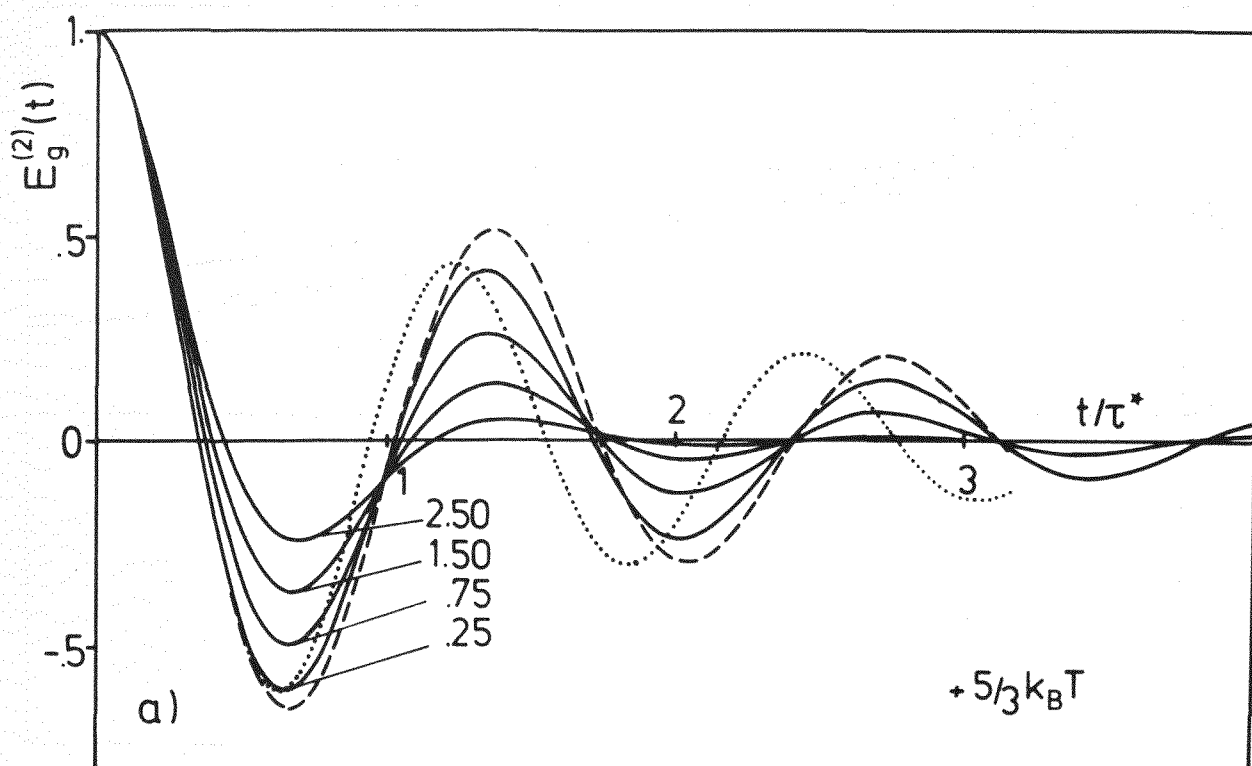


Fig. 17: The results for the correlation function $E_g^{(2)}(t)$.
Some convention as in Fig. 16a and 16b.

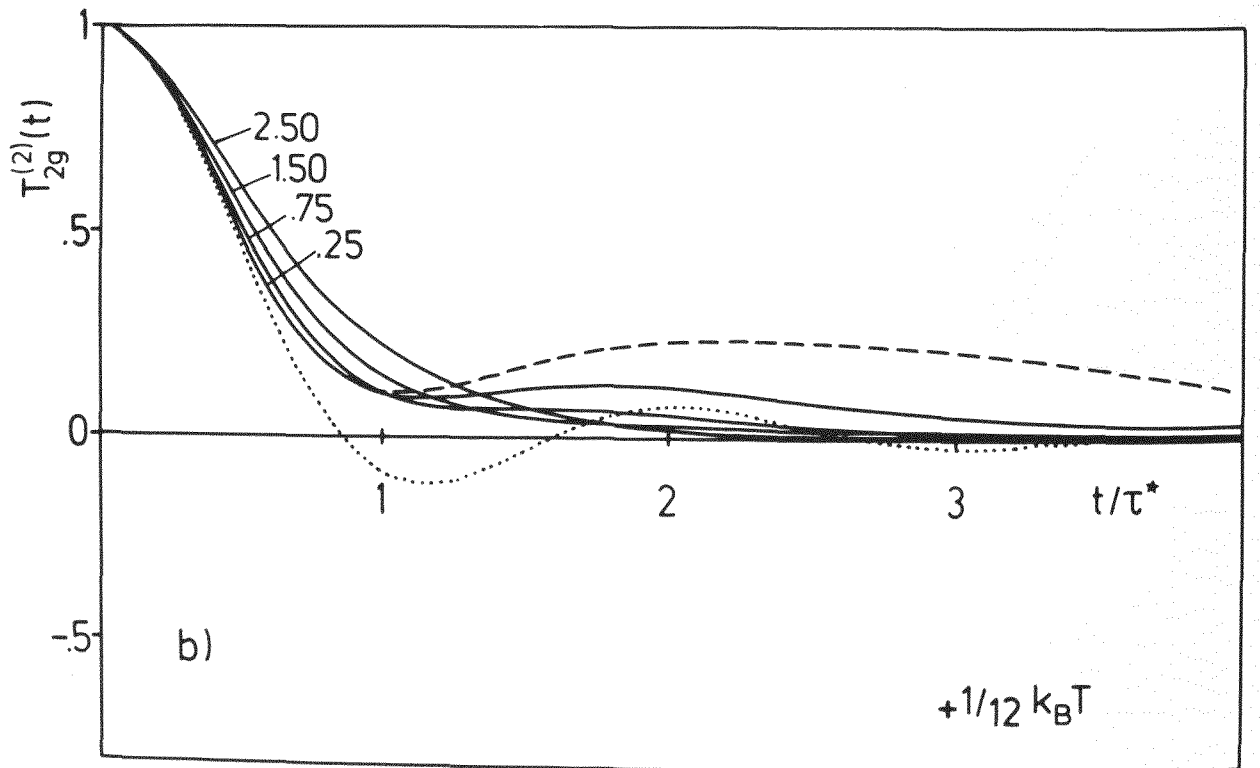
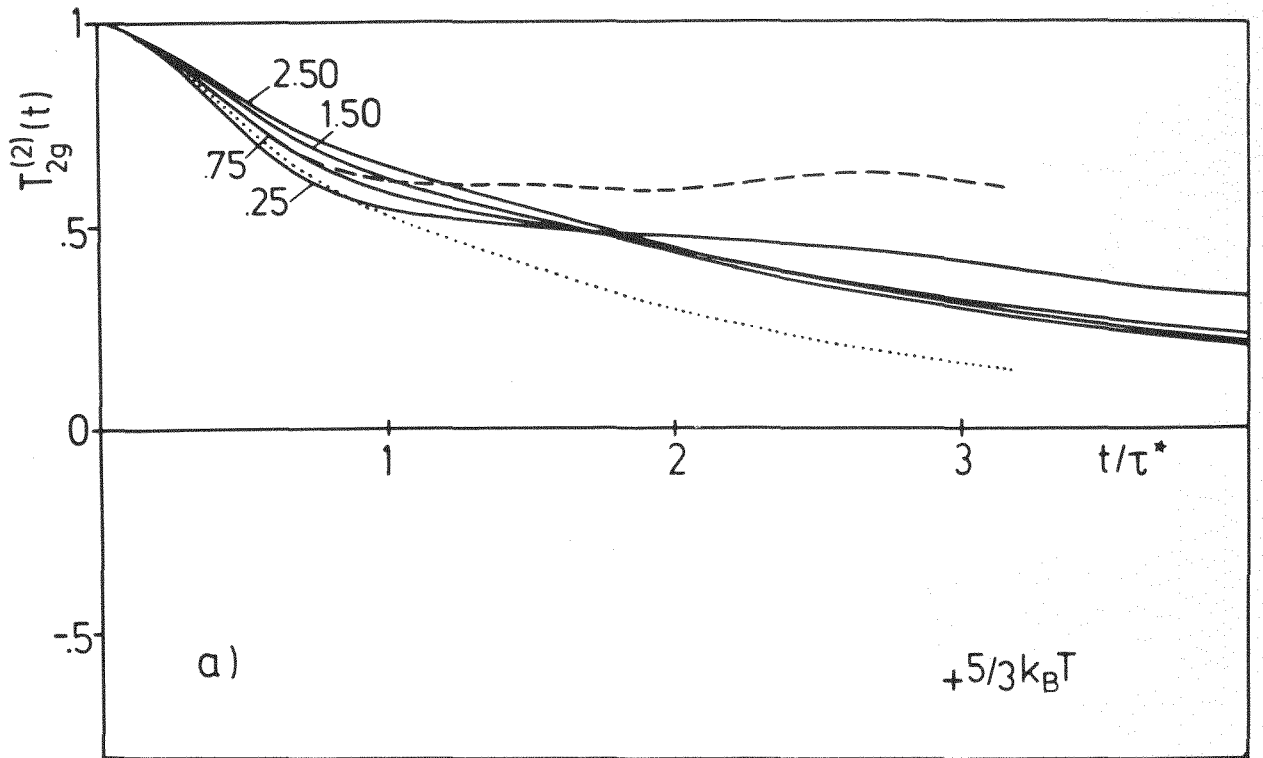


Fig. 18: The results for the correlation function $T_{2g}^{(2)}(t)$.
Some convention as in Fig. 16a and 16b.

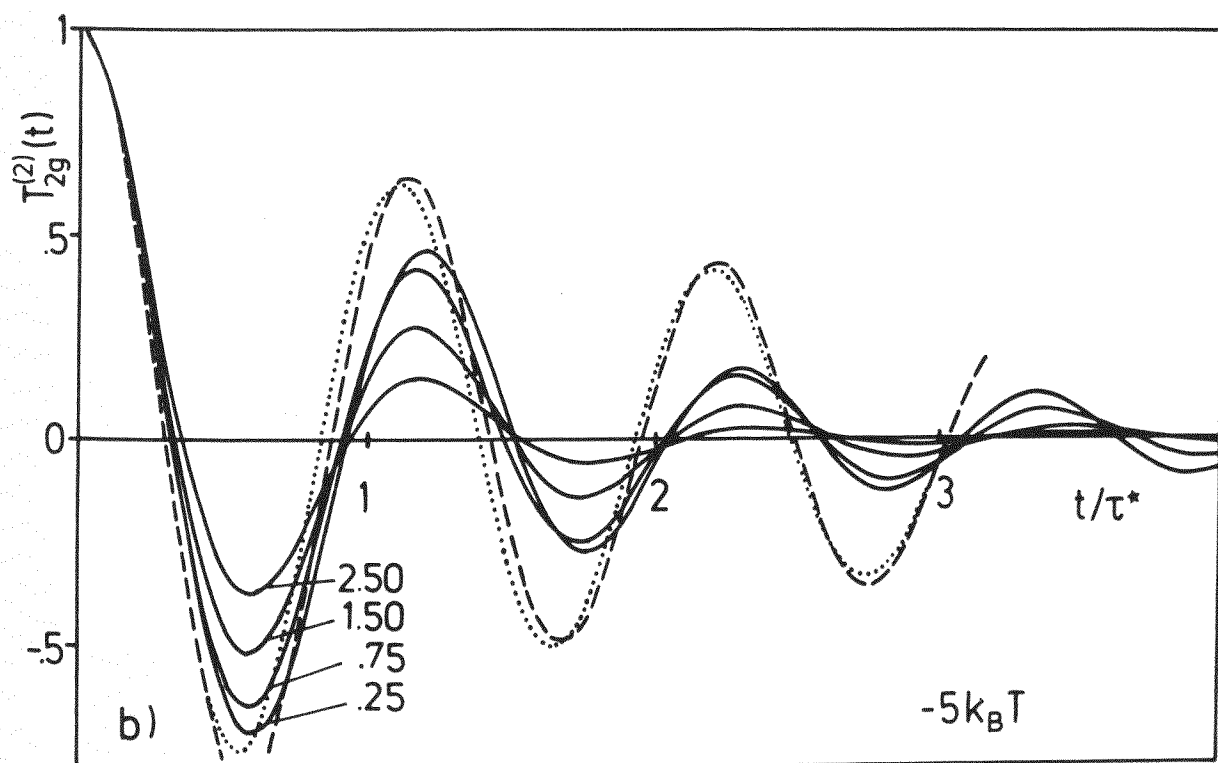
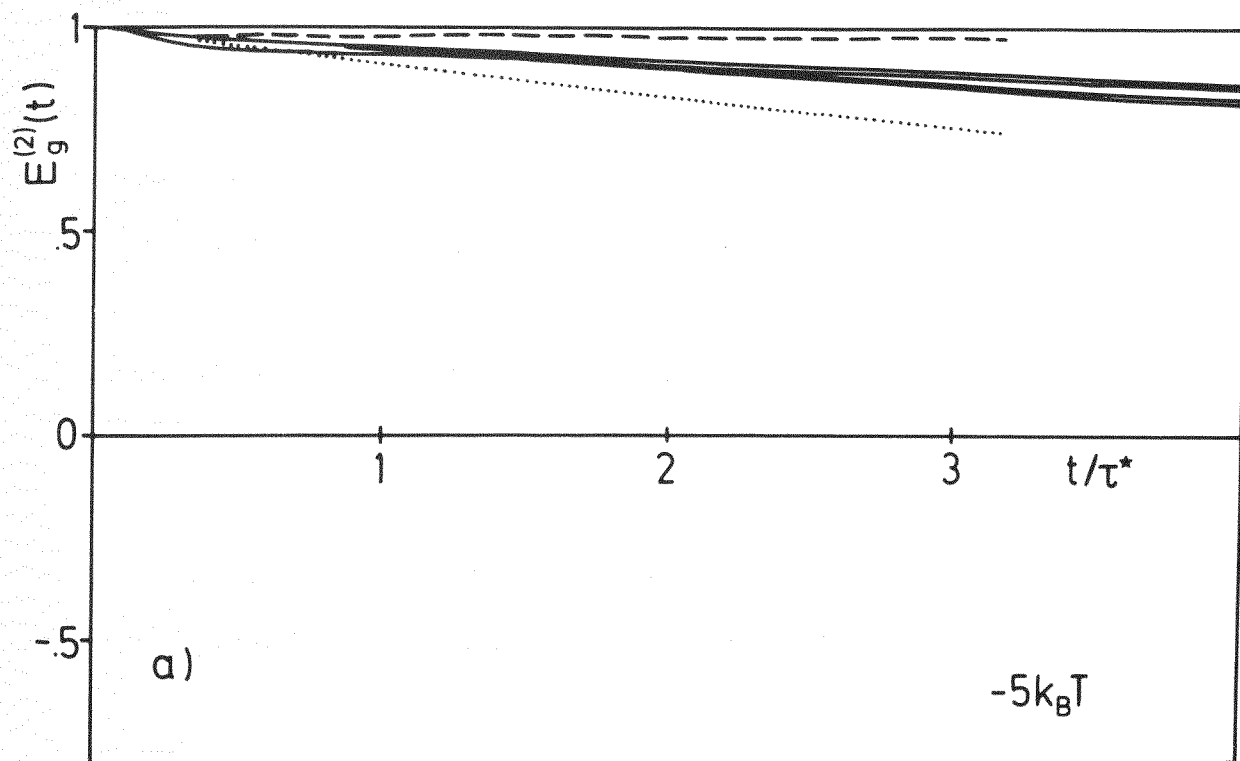


Fig. 19: a) The results for the correlation function $E_g^{(2)}(t)$ in the case of negative sign of the potential. The barrier height is $5 k_B T$. All other conventions as in Fig. 16.

b) The results for the correlation function $T_{2g}^{(2)}(t)$. Same potential as in Fig. 19a.

correlation function will describe the jumps from one minimum to the other. The decay of these correlation functions comes from the motion from one minimum to all other minima.

In the case of positive sign $E_g^{(2)}(t)$ shows the damped oscillatory behaviour. This correlation function describes the oscillatory motion in the potential minima. The correlation function $T_{2g}^{(2)}(t)$ describes mainly the decay of the correlation by the jumps from one minimum to another.

Comparing the results for both signs of the potential one has to take into account that for positive s , the potential barrier, i.e. the difference between the saddle point and the potential minimum, is $1/6 \gamma$. In the case of negative s the barrier height is $1/2 \gamma$ that is three times as high.

The results of our Langevin simulation converge for small friction parameter to results of the Monte Carlo simulation. The earlier results of de Raedt show the same behaviour (oscillatory behaviour in the one case, decay in the other case) as the Langevin-results. But the limit $\Gamma^* \rightarrow 0$ is not reproduced.

Fig. 20 shows the results for the correlation function $T_{2g}^{(2)}(t)$ for two different frictions ($\Gamma^* = .25$ and $\Gamma^* = 2.50$). The parameter in the figure is the barrier height of the potential. The dashed line shows the results of the harmonic approximation of the potential. Fig. 21 shows the same for the correlation function $E_g^{(2)}(t)$.

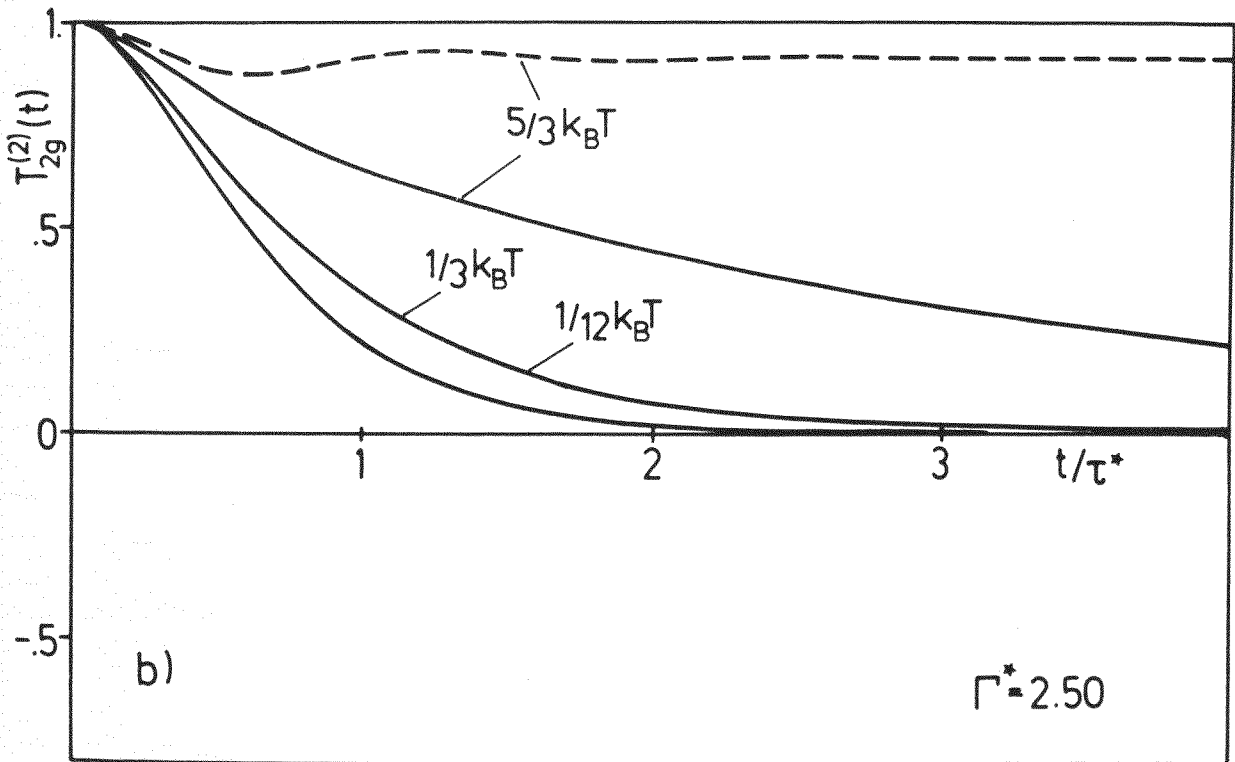
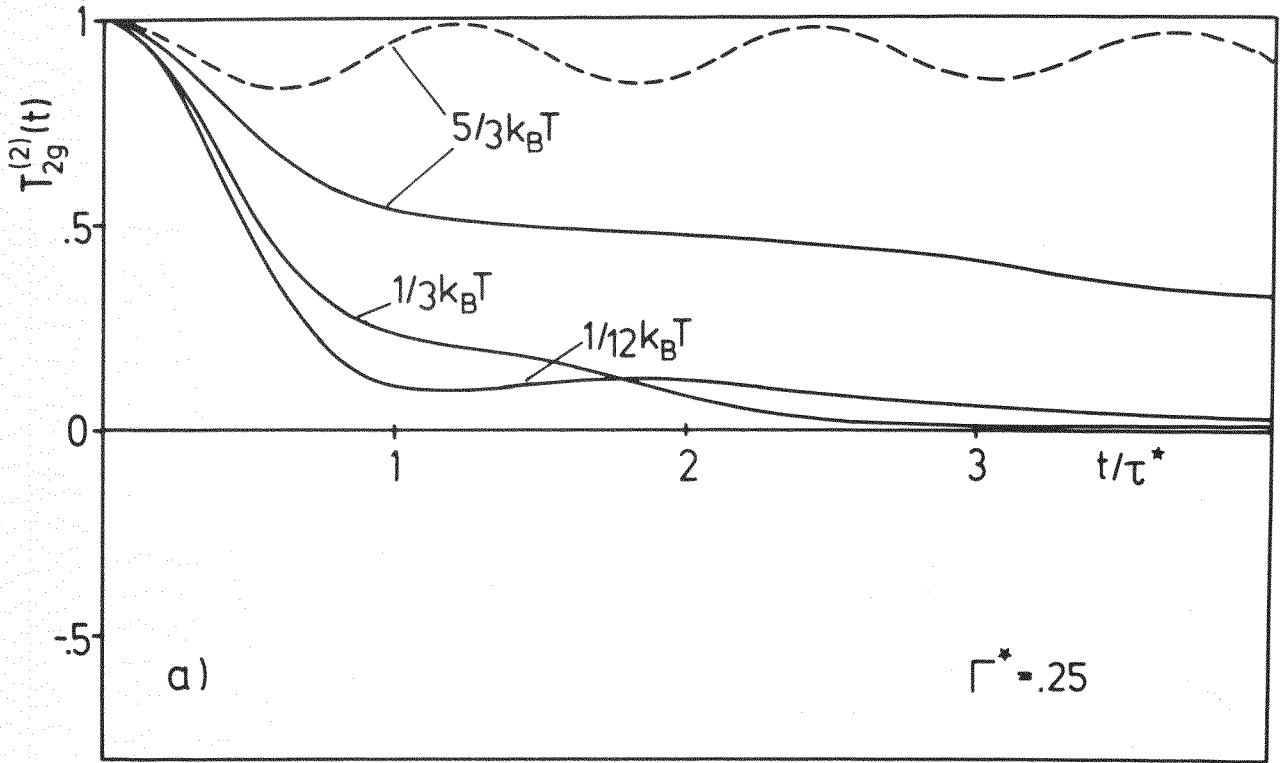


Fig. 20: The correlation function $T_{2g}^{(2)}(t)$ for different potential parameters as indicated. The dashed line is the solution of the stochastic harmonic oscillator with the data of the largest potential.

a) Friction parameter $\Gamma^* = .25$

b) Friction parameter $\Gamma^* = 2.50$

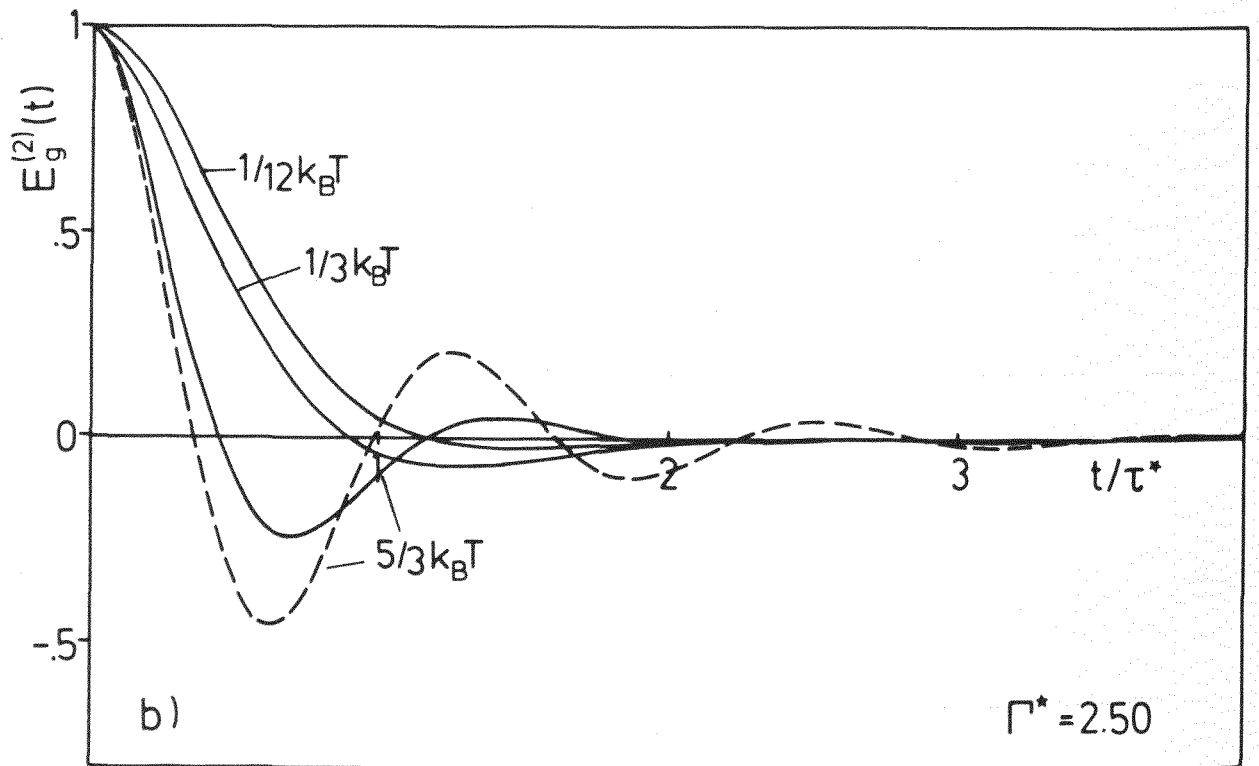
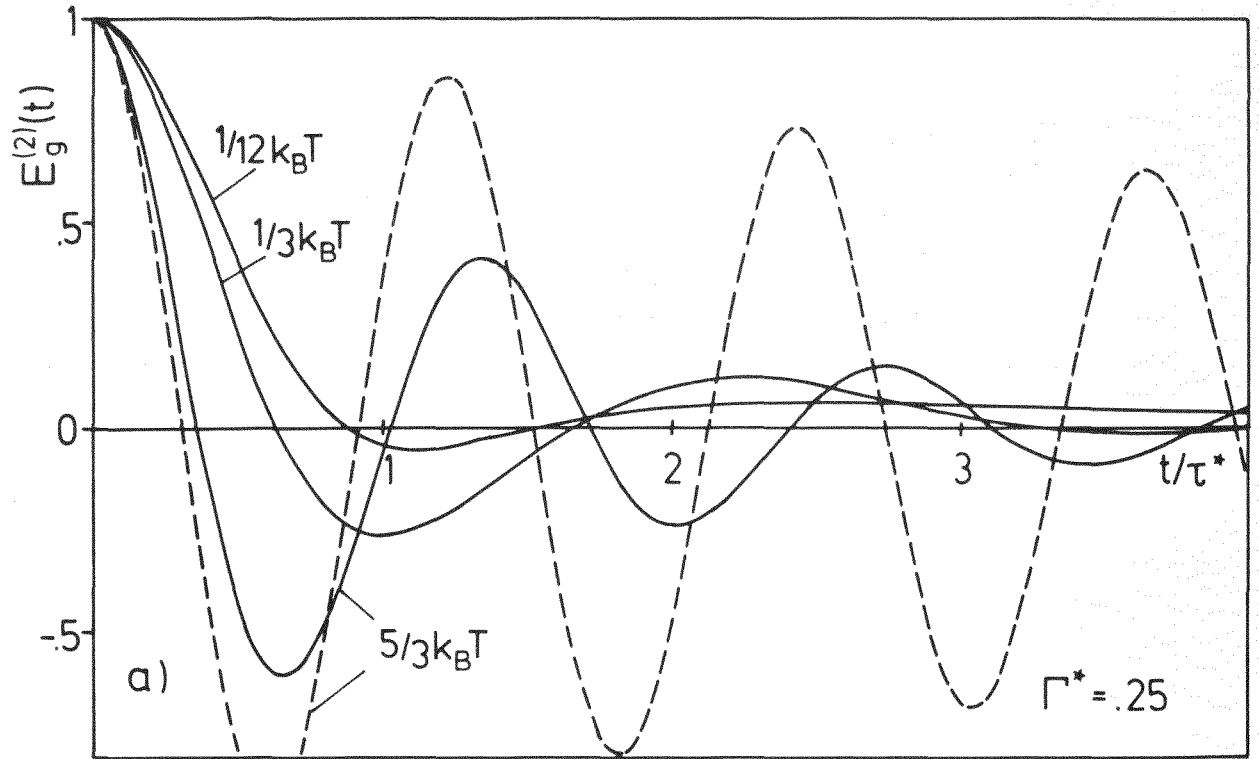


Fig. 21: Results for the correlation function $E_g^{(2)}(t)$.
Same convention as in Fig. 20.

In the case of a harmonic approximation the only damping factor is the friction. There is no decay of the correlation from the potential (non ergodicity of harmonic potentials). From eq. (4.20) we know that the damping factor is $\Gamma^*/2$. Thus in the case of Fig. 21a the damping time is $8\tau^*$.

Fig. 20 shows the correlation function which describes the jump-decay of the correlation. Because in the harmonic potential the barrier height is infinite, no jumps are possible. The correlation function will not tend to zero as t goes to infinity.

In the figures all the correlation functions are normalized in that way that they are unity for time equal zero. The annormalized values of the correlation functions $E_g^{(2)}(t)$ and $T_{2g}^{(2)}(t)$ are given in tables 7 and 8. The column denoted by theory gives the theoretical values which are calculated from

$$\langle U^2(0) \rangle = \frac{1}{Z} \int_{\text{sphere}} U^2(x_0) e^{-\beta V(x_0)} d^3x_0 \quad (5.28)$$

The function U denotes K_{11} or K_{12} in the case $E_g^{(2)}(t)$ respective K_{13} , K_{14} or K_{15} in the case $T_{2g}^{(2)}(t)$. Z is a normalization factor. The integration in (5.28) was done by a numerical integration technique [13,37]. The values in the column M.C. are from the Monte-Carlo-calculation and the values in h.a. are the results from the harmonic approximation. One gets the results for the harmonic approximation if one inserts Eq. (5.19) into Eq. (5.15) respectively (5.16). The results are

	γ	$\Gamma^* = .25$	$\Gamma^* = .75$	$\Gamma^* = 1.50$	$\Gamma^* = 2.50$	h. a.	M. C.	theory
E_g	.5	.076	.076	.076	.076	-	.076	.075
	1.	.070	.071	.072	.071	-	-	.071
	2.	.065	.064	.064	.063	-	-	.063
	4.	.052	.052	.052	.051	.075	-	.051
	10.	.034	.033	.032	.032	.030	.031	.031
T_{2g}	.5	.082	.082	.082	.082	-	.082	.082
	1.	.086	.085	.085	.085	-	-	.085
	2.	.090	.090	.090	.090	-	-	.090
	4.	.098	.098	.098	.099	.099	-	.033
	10.	.110	.111	.111	.112	.112	.112	.112

Table 7 The values of the correlation functions $E_g^{(2)}(t)$ and $T_{2g}^{(2)}(t)$ for $t=0$ and positive sign of the potential

	γ	$\Gamma^*= .25$	$\Gamma^*= .75$	$\Gamma^*= 1.50$	$\Gamma^*= 2.50$	h.a.	M.C.	theory
E_g	.5	.084	.084	.084	.084	-	.085	.084
	1.	.089	.089	.090	.090	-	-	.089
	2.	.098	.098	.099	.099	-	-	.099
	4.	.117	.119	.119	.120	.087	-	.120
	10.	.149	.158	.160	.162	.154	.162	.163
T_{2g}	.5	.077	.076	.076	.076	-	.076	.077
	1.	.074	.074	.073	.073	-	-	.073
	2.	.067	.067	.067	.066	-	-	.067
	4.	.054	.053	.053	.053	.050	-	.053
	10.	.033	.027	.026	.025	.020	.024	.024

Table 8 Same as table 8 but for negative sign of the potential.

$$E_g^{(2)}(t) = \frac{15}{16\pi} \cdot \frac{1}{\gamma} \quad s = +1 \quad (5.29)$$

$$E_g^{(2)}(t) = \frac{5}{8\pi} \left(1 - \frac{3}{2} \cdot \frac{1}{\gamma} \right) \quad s = -1$$

$$T_{2g}^{(2)}(t) = \frac{5}{12\pi} \left(1 - \frac{3}{2} \cdot \frac{1}{\gamma} \right) \quad s = +1 \quad (5.30)$$

$$T_{2g}^{(2)}(t) = \frac{5}{8\pi} \cdot \frac{1}{\gamma} \quad s = -1$$

The values for finite friction are extracted from the different simulations of the Langevin-equation. The agreement of the different methods is very good. This is one possibility to check the simulation data.

To understand the inelastic scattering law $S(Q, \omega)$ we want to discuss its qualitative behaviour in the harmonic approximation. For a quantitative discussion one has to perform the Fouriertransformation of the computer experiments numerically. That is not possible with our present data which have not been calculated over a sufficiently long time range.

In the low temperature case the harmonic approximation is rather good. Therefore we use its solution to discuss our result. To perform the Fouriertransformation we write

$$\begin{aligned} \frac{\langle \varepsilon \varepsilon_o \rangle}{\langle \varepsilon_o^2 \rangle} = :g(t) &= \frac{\omega' + \Gamma/2}{2\omega'} \exp\left\{ - \left(\frac{\Gamma}{2} - \omega' \right) |t| \right\} \\ &- \frac{\omega' - \Gamma/2}{2\omega'} \exp\left\{ - \left(\frac{\Gamma}{2} + \omega' \right) |t| \right\} \end{aligned} \quad (5.31)$$

where $\omega' = \sqrt{\frac{\Gamma^2}{4} - \omega_0^2}$. ω_0 is the frequency of the undamped harmonic oscillator. The total intermediate scattering law has the form

$$I(\vec{Q}, t) = A_0(\vec{Q}, \vec{r}) + A_1(\vec{Q}, \vec{r}) g(t) \quad (5.32)$$

in the harmonic approximation.

The incoherent scattering law is a combination of a δ -function (first term of Eq. (5.32)) and the Fouriertransformed of $\langle \varepsilon \varepsilon_0 \rangle$. To perform it we have to consider three different cases (periodic: ω' imaginary, aperiodic $\omega'=0$, and overdamped ω' real) independently.

If we denote a Lorentzian $a/(a^2 + \omega^2)$ by $L(a/\omega)$ and the Fouriertransformed of $g(t)$ by $f(\omega)$ we can write in the overdamped case

$$\pi \cdot f(\omega) = \frac{\omega' + \Gamma/2}{2\omega'} L\left(\frac{\Gamma}{2} - \omega'/\omega\right) + \frac{\omega' - \Gamma/2}{2\omega'} L\left(\frac{\Gamma}{2} + \omega'/\omega\right) \quad (5.33)$$

It is a linear combination of two Lorentzians with different width.

In the aperiodic case (5.31) simplifies to

$$\frac{\langle \varepsilon \varepsilon_0 \rangle}{\langle \varepsilon_0^2 \rangle} = \left(1 + \frac{\Gamma}{2} |t|\right) e^{-\Gamma/2 |t|} \quad (5.34)$$

The Fouriertransformation of this is [42]

$$\pi \cdot f(\omega) = L\left(\frac{\Gamma}{2} / \omega\right) + \frac{\Gamma}{2} \frac{\left(\frac{\Gamma}{2}\right)^2 \omega^2}{\left(\left(\frac{\Gamma}{2}\right)^2 + \omega^2\right)^2} \quad (5.35)$$

And in the periodic case we get [42]

$$\begin{aligned} \pi \cdot f(\omega) = & \frac{1}{2} L\left(\frac{\Gamma}{2} / \omega - \omega_1\right) + \frac{1}{2} L\left(\frac{\Gamma}{2} / \omega + \omega_1\right) \\ & + \frac{\Gamma}{2} \frac{\left(\frac{\Gamma}{2}\right)^2 + \omega_1^2 - \omega^2}{\left[\frac{\Gamma^2}{4} + (\omega_1 + \omega)^2\right] \left[\frac{\Gamma^2}{4} + (\omega_1 - \omega)^2\right]} \end{aligned} \quad (5.36)$$

where ω_1 is defined by $\omega_1^2 = -\omega'^2$. Eq. (5.36) has a double peak structure: one peak at $\omega = \omega_1$ and the other one $\omega = -\omega_1$.

In the high temperature case where we neglect the potential only in the cases $\Gamma = 0$ and $\Gamma \gg 1$ an analytic expression can be given.

From Eq. (3.5) one sees that $I(\vec{Q}, t)$ is a linear combination of expressions of the form $\langle \cos n\omega t \rangle_\omega$, where ω is the angular velocity. The result can be expressed in terms of the degenerate hypergeometric function (see publication part III.B). The result of Fourier transformation is a linear combination of terms

$$\psi(\omega) = \frac{\tau^{*2}}{2} \frac{|\omega|}{n^2} \exp\left\{-\frac{\tau^{*2}\omega^2}{2n^2}\right\} \quad (5.37)$$

which has a double peak structure. The peaks are at $\omega = \pm \frac{n}{\tau^*}$.

In the case of large friction, the diffusion equation is valid. We know that in the case of the diffusion equation correlation functions decay exponentially. Therefore the scattering law is a combination of Lorentzians centered at $\omega = 0$.

The Langevin-equation in the intermediate temperature range (thermal energy and potential of same magnitude) interpolates between the two limiting cases. This can be seen from the time dependent correlation functions which converge to the two limiting cases.

In the intermediate temperature range the width of the peaks is much larger, than in the high-temperature range. Because of the nonergodicity of the harmonic potential all decay of the correlations in the low temperature range is due to the friction (and stochastic force). This is expressed by the fact that the width of the peaks is $\Gamma/2$. In the intermediate temperature range the anharmonic terms of the potential will make an additional decay. This leads to a broadening of the peaks.

6. THREEDIMENSIONAL ROTATIONAL MOTION IN A POTENTIAL

In this chapter we want to discuss the rotational motion with three degrees of freedom, i.e. threedimensional rotators. We want to be much more specific as in the previous chapters. Of course the method is general enough to treat any molecule in a potential. We will restrict the numerical calculation to one specific example: NH_4Cl . If possible we discuss the problem in a general way, but all parameters are chosen with respect to NH_4Cl . Furthermore we want to discuss the motion of the particle in some detail, because the advantage of solving the Langevin-equation (instead of Fokker-Planck-equation) is that one can look at details of the motion. In the first part of this chapter we want to discuss the potential in some detail.

6.1 THE POTENTIAL

Hüller and Kane [43] used an electrostatic model to calculate the rotational potential of the ammonium ion in the cubic field of the surrounding halide ions and in the field of the surrounding ammonium ions. The structure of NH_4Cl can be seen in fig. 22.

The rotational potential of the ammonium ion is expanded in terms of symmetry adapted functions. In this case that functions are the cubic rotator functions $H_{\mu\nu}^{(\ell)}(\xi, \eta, \zeta)$ [41]. The expansion reads:

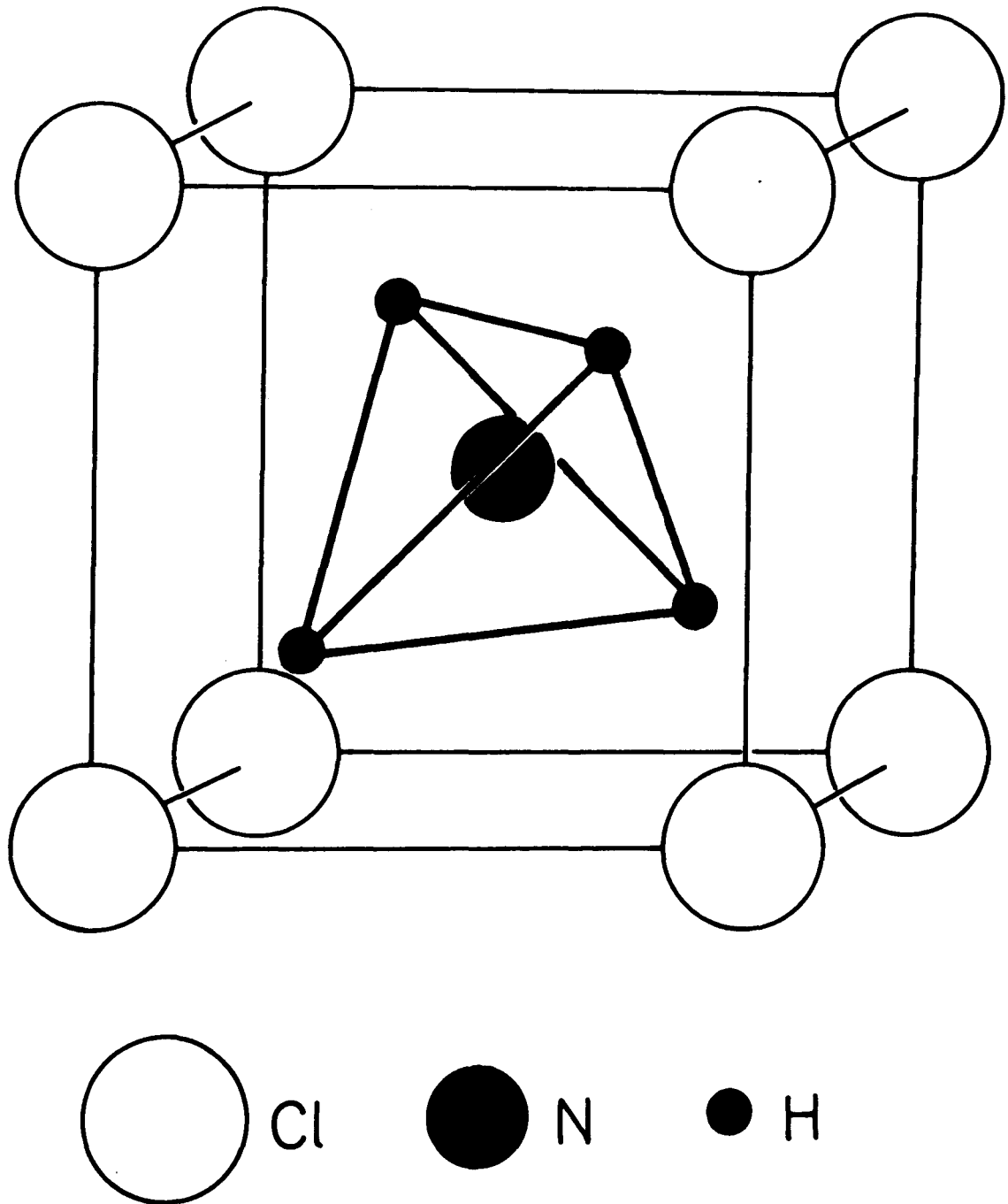


Fig. 22: The structure of NH_4Cl . The Cl^- ions perform a cubic structure. The NH_4^+ ions are a tetrahedron. The figure shows one of the two equilibrium orientations. One gets the other one by a rotation around a four fold axis by $\frac{\pi}{2}$.

$$V_{\text{rot}}(\xi, \eta, \zeta) = \sum_{\ell=0}^{\infty} \sum_{\mu, \nu=1}^{2\ell+1} B_{\mu\nu}^{(\ell)} H_{\mu\nu}^{(\ell)}(\xi, \eta, \zeta) \quad (6.1)$$

ξ, η, ζ are the Euler angles which describe the orientation of the NH_4^+ ion relative to the crystal frame. For a tetrahedron at a site of tetrahedral symmetry most of $B_{\mu\nu}^{(\ell)}$ vanish. The only coefficients which are different from zero are $B_{11}^{(0)}, B_{11}^{(3)}, B_{11}^{(4)}, B_{11}^{(6)}, \dots$. If the symmetry of the site is cubic $B_{11}^{(3)}$ vanishes, too.

The cubic rotator functions have a relatively simple form if expressed in terms of quaternions instead of Euler angles. For details about quaternions see Appendix B of the publication. The transformation from Euler angles to quaternions is

$$\begin{aligned} \tau_1 &= \sin \frac{1}{2} \eta \sin \frac{1}{2} (\xi - \xi) \\ \tau_2 &= \sin \frac{1}{2} \eta \cos \frac{1}{2} (\xi - \xi) \\ \tau_3 &= \cos \frac{1}{2} \eta \sin \frac{1}{2} (\xi + \xi) \\ \tau_4 &= \cos \frac{1}{2} \eta \cos \frac{1}{2} (\xi + \xi) \end{aligned} \quad (6.2)$$

The cubic rotator functions $H_{\mu\nu}^{(\ell)}(\tau_1, \tau_2, \tau_3, \tau_4)$ are polynomials of order 2ℓ . Librational frequencies calculated with a potential (6.1) up to order $\ell=6$ are in satisfactory agreement with experiments [43]. Therefore we want to restrict our calculations on terms up to order $\ell=6$. The rotational potential now reads

$$V_{\text{rot}}(\vec{\tau}) = B_{11}^3 H_{11}^3(\vec{\tau}) + B_{11}^4 H_{11}^4(\vec{\tau}) + B_{11}^6 H_{11}^6(\vec{\tau}) \quad (6.3)$$

The coefficients could be determined from model calculations and experiments. The model calculations [43] took into account

- (i) direct interaction ammonium ion-halide ion
- (ii) polarizability of the halide ion
- (iii) direct and indirect interaction of the ammonium ions.

The point (iii) discriminates between the ordered phase (orientational order of the ammonium ions) and the disordered phase (ammonium ions randomly orientated in the two minimum orientations). The coefficients for NH_4Cl are given in table 9.

	ordered phase	disordered phase
B_{11}^3	-323.20	-
B_{11}^4	-2221.38	-2213.90
B_{11}^6	-367.81	-354.28

Table 9 The coefficients of the potential for NH_4Cl .
They are given in units of Kk_B . From ref. [43].

The cubic rotator functions are defined by

$$\begin{aligned}
 H_{11}^3 &= 16 \Sigma^6 - 20 \Sigma^4 + 5 \\
 H_{11}^4 &= \frac{80}{3} \Sigma^8 - \frac{560}{9} \Sigma^6 + \frac{140}{3} \Sigma^4 + \frac{2240}{3} \tau_1^2 \tau_2^2 \tau_3^2 \tau_4^2 - \frac{91}{9} \\
 H_{11}^6 &= \frac{2464}{3} \Sigma^{12} - 2464 \Sigma^{10} + 2520 \Sigma^8 - \frac{2240}{3} \Sigma^6 \\
 &\quad - 210 \Sigma^4 + \frac{4928}{3} (\tau_1^6 \tau_2^6 + \tau_1^6 \tau_3^6 + \tau_1^6 \tau_4^6 + \tau_2^6 \tau_3^6 + \tau_2^6 \tau_4^6 + \tau_3^6 \tau_4^6) \\
 &\quad - 3360 \tau_1^2 \tau_2^2 \tau_3^2 \tau_4^2 + \frac{241}{3}
 \end{aligned} \tag{6.4}$$

where the abbreviation

$$\Sigma^n = \sum_{i=1}^4 \tau_i^n \tag{6.5}$$

has been used.

The potential V_{rot} has 48 minima which correspond to the 24 minimum orientations of the tetrahedron. The factor 2 comes from the fact that two quaternions (the antipodes) describe the same rotation. Table 10 gives the minima of the potential and the type of jumps when the tetrahedron rotates from one minimum to another. Note that one quadrupole stands for all possible permutations and changes of sign.

Another important quantity is the height of the rotational barrier for the different rotations. In fig. 23 to 25 you can see the rotational potential for rotations around a (100), a (110) and a (111) axis. To get this we used the following interpretation

Minima →		0 0 0 1 (8)	$\frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2}$ (16)	$\frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} 0 0$ (24)
rotation angle	rotation axis			
90°	100	$\pm \frac{1}{\sqrt{2}} 0 0 \frac{1}{\sqrt{2}}$ (6)	$\frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} 0 0$ (6)	1 0 0 0 (2) $\frac{1}{2} \frac{1}{2} \pm \frac{1}{2} \pm \frac{1}{2}$ (4)
120°	111	$\pm \frac{1}{2} \pm \frac{1}{2} \pm \frac{1}{2} \frac{1}{2}$ (8)	0 0 0 1 (4) $-\frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2}$ (4)	$\frac{1}{\sqrt{2}} 0 \pm \frac{1}{\sqrt{2}} 0$ (8)
180°	110	$\pm \frac{1}{\sqrt{2}} + \frac{1}{\sqrt{2}} 0 0$ (12)	$-\frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} 0 0$ (12)	$-\frac{1}{2} \frac{1}{2} \pm \frac{1}{2} \pm \frac{1}{2}$ (8) 0 0 0 ± 1 (4)
180°	100	$\pm 1 0 0 0$ (6)	$-\frac{1}{2} - \frac{1}{2} \frac{1}{2} \frac{1}{2}$ (6)	0 0 $\pm \frac{1}{\sqrt{2}} + \frac{1}{\sqrt{2}}$ (4) $-\frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} 0 0$ (2)
120°	111	$\pm \frac{1}{2} \pm \frac{1}{2} \pm \frac{1}{2} - \frac{1}{2}$ (8)	0 0 0 -1 (4) $-\frac{1}{2} - \frac{1}{2} - \frac{1}{2} \frac{1}{2}$ (4)	-1 0 0 0 (2) $-\frac{1}{2} - \frac{1}{2} \pm \frac{1}{2} \pm \frac{1}{2}$ (4)
90°	100	$\pm \frac{1}{\sqrt{2}} 0 0 - \frac{1}{\sqrt{2}}$ (6)	$-\frac{1}{\sqrt{2}} - \frac{1}{\sqrt{2}} 0 0$ (6)	-1 0 0 0 (2) $-\frac{1}{2} - \frac{1}{2} \pm \frac{1}{2} \pm \frac{1}{2}$ (4)
0°	-	0 0 0 -1 (1)	$-\frac{1}{2} - \frac{1}{2} - \frac{1}{2} - \frac{1}{2}$ (1)	$-\frac{1}{\sqrt{2}} - \frac{1}{\sqrt{2}} 0 0$ (1)

Table 10 The 48 minima of the potential and all possible 47 rotations to another minimum. Every coordinate stands for a group of minima. The number in brackets denotes the quantity of the members of each group.

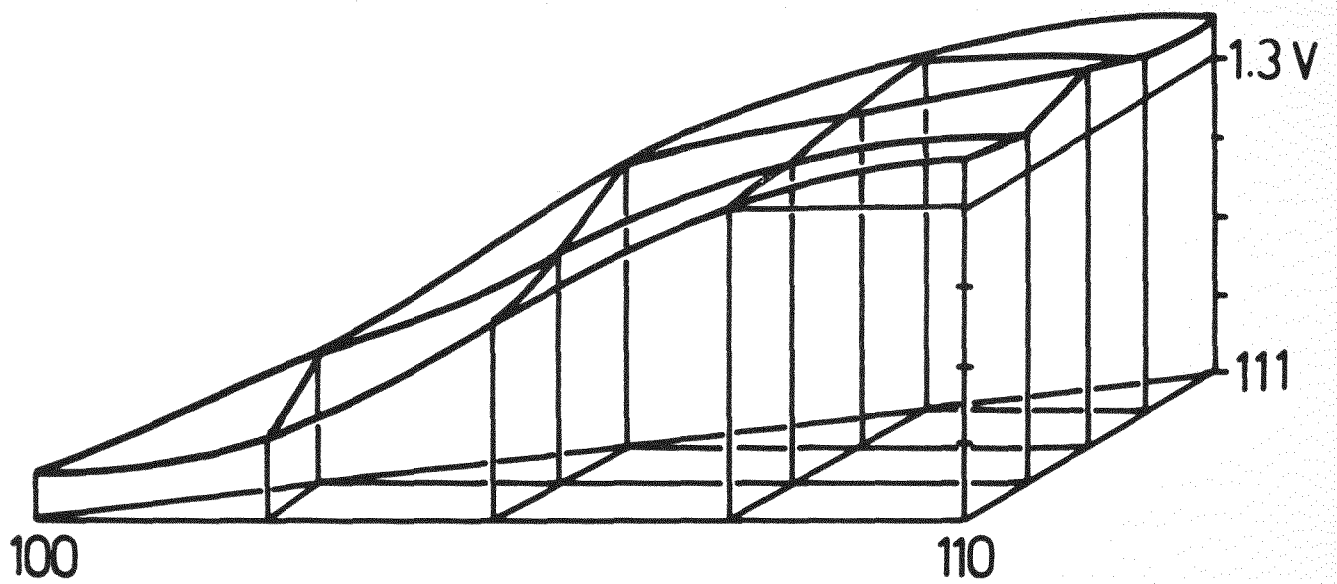


Fig. 23: The figure shows the height of potential barrier for different rotation axis. The basis plane is at .9 V and the plane at 1.3 V is indicated.
 $V = B_{11}^4 + B_{11}^6$. Disordered phase.

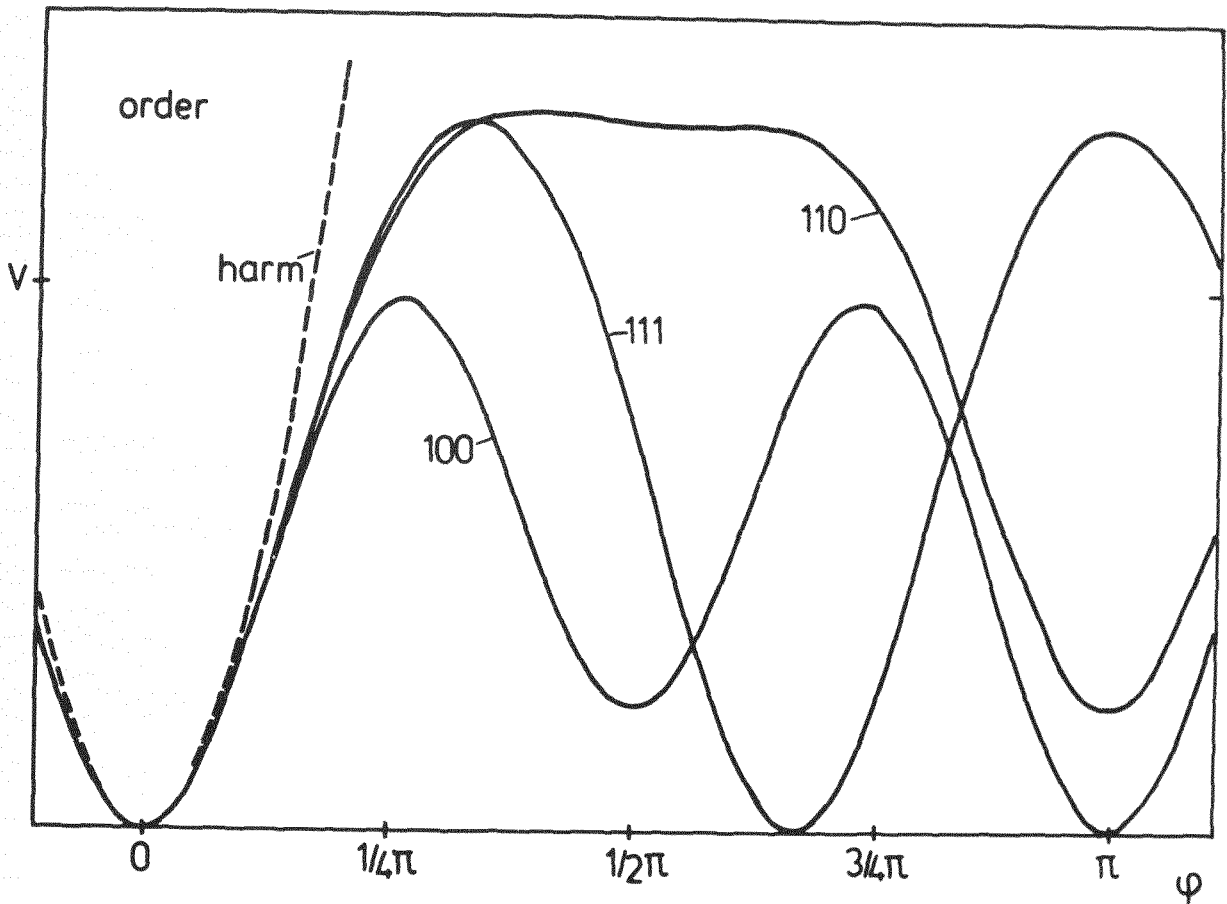


Fig. 24: The rotational potential from eq. (6.3) for different rotation axis as indicated. The harmonic approximation is also given. Ordered phase.

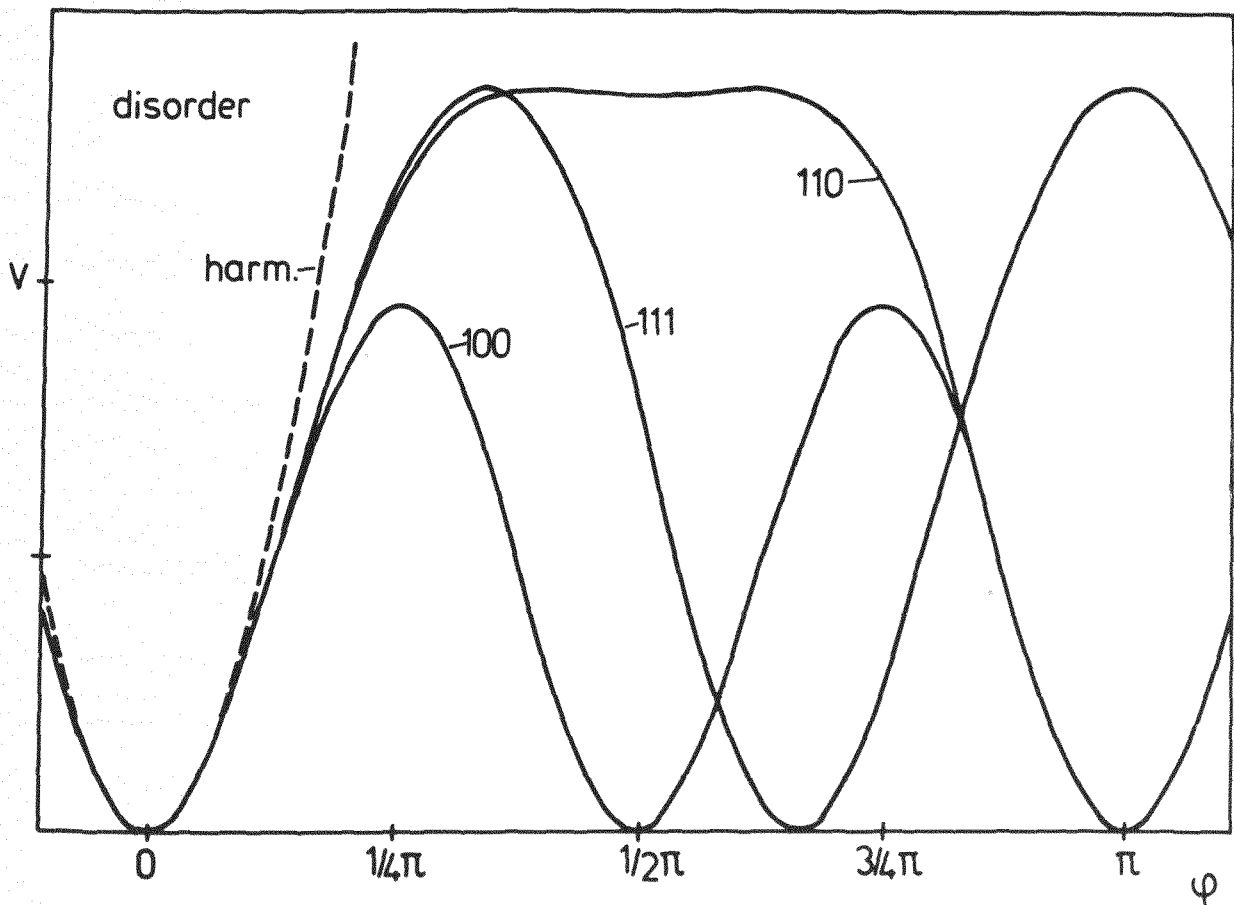


Fig. 25: Same as in fig. 24. Disordered phase.

$$\begin{aligned}
 \tau_1 &= n_x \sin \frac{\varphi}{2} \\
 \tau_2 &= n_y \sin \frac{\varphi}{2} \\
 \tau_3 &= n_z \sin \frac{\varphi}{2} \\
 \tau_4 &= \cos \frac{\varphi}{2}
 \end{aligned}
 \tag{6.6}$$

of the quaternions (see Appendix B of the publication). $\vec{n}$ is the unit vector of the rotation axis, and φ is the rotation angle.

6.2 NEUTRON SCATTERING LAW

With incoherent neutron scattering we observe the motion of single particles. In the case of NH_4Cl one looks at the motion of the hydrogen atoms at the corners of a tetrahedron. The neutron scattering law can be expanded in the same way as in chapter 5.2. Because the Cl-ions form a cubic structure, we can also use the cubic harmonics K_{lm} . We finally arrive at the same correlation functions as in chapter 5.2. The time-dependence of these correlation functions is, however, completely different, because the dynamics of a tetrahedron and a linear molecule are quite different.

We want to calculate the same correlation functions as in the previous chapter.

6.3 LANGEVIN-EQUATION

The most convenient coordinates to describe the rotational motion of a tetrahedron are the quaternions [45,46]. The Langevin-equation is then given by Eq. (2.28). The potential is given in Eq. (6.3). The only important quantity for the calculation is the ratio of potential strength and temperature. We prefer to work at constant temperature and to change the potential. Therefore we multiply the potential by a prefactor γ , so that we can change the height of the barrier without changing the temperature. Then the Langevin equation reads

$$\ddot{\vec{\tau}} = -\frac{\gamma}{4I} \text{grad}_{\vec{\tau}} V - \dot{\Gamma} \dot{\vec{\tau}} - |\dot{\vec{\tau}}|^2 \vec{\tau} + \frac{G^{1/2}}{4I} \vec{F}(t) \quad (6.7)$$

This equation describes the motion of a pseudoparticle with mass $4I$ on the four-dimensional unit sphere. With the full potential from Eq. (6.3) this equation can not be solved analytically. Therefore we will first look at the low temperature limit.

6.3.1 $T \ll V$

In this limit the potential can be expanded around a minimum into a harmonic potential. We get then three decoupled harmonic oscillators. Because they are all equivalent, it is sufficient to solve one of them. The harmonic approximation is [43]

$$V(\epsilon) = -(8 B_{11}^3 + \frac{40}{3} B_{11}^4 + 28 B_{11}^6) \epsilon^2 \quad (6.8)$$

where ε is the displacement of the harmonic oscillator from the potential minimum.

One problem is, that the equation of motion is in quaternion space and the correlation functions are in real space. Therefore we must express the correlation functions in real space in terms of quaternion correlation functions. The time dependent space vector is given by

$$\mathbf{x}_i(t) = \sum_{j=1}^3 D_{ij}(t) \cdot \hat{\mathbf{x}}_j \quad (6.9)$$

where $\hat{\mathbf{x}}_j$ is the position vector of one of the protons of the tetrahedron. The $D_{ij}(t)$ are the elements of the rotation matrix which is given in the Appendix of the publication. For the different types of minima the quaternions must be expressed in terms of ε . E.g. in the the case of the minimum $(0,0,0,1)$ the three orthogonal rotations are:

$$\begin{aligned} & \frac{1}{\sqrt{1+\varepsilon^2}} (\varepsilon, 0, 0, 1) \\ & \frac{1}{\sqrt{1+\varepsilon^2}} (0, \varepsilon, 0, 1) \\ & \frac{1}{\sqrt{1+\varepsilon^2}} (0, 0, \varepsilon, 1) \end{aligned} \quad (6.10)$$

The displacements ε obeys the equation of motion:

$$\ddot{\varepsilon} = - \frac{\omega^2}{4I} \varepsilon - \Gamma \dot{\varepsilon} + \frac{G^{1/2}}{4I} F(t) \quad (6.11)$$

where the oscillator frequency is given by

$$\omega^2 = 2\gamma \left(8 B_{11}^3 + \frac{40}{3} B_{11}^4 + 28 B_{11}^6 \right) \quad (6.12)$$

As an example we will calculate the correlation function $\langle r(t)r(0) \rangle$ to show how to calculate correlation functions. One gets the correlation function from

$$\langle r(t)r(0) \rangle = \sum_{i=1}^3 \langle x_i(t)x_i(0) \rangle \quad (6.13)$$

The vector components x_i are given in Eq. (6.9). Putting this into Eq. (6.13) we get

$$\langle r(t)r(0) \rangle = \sum_{i=1}^3 \sum_{\ell,k=1}^3 \frac{1}{4} \sum_{n=1}^4 \langle D_{i\ell}(t)D_{ik}(0) \rangle (\hat{x}_\ell^{(n)} \hat{x}_k^{(n)}) \quad (6.14)$$

The sum over n runs over the four protons which build up the tetrahedron. Putting (6.10) into the rotation matrix, expanding the matrix up to second order in ε one gets from (6.14)

$$\langle r(t)r(0) \rangle = 1 - \frac{8}{3} \langle \varepsilon^2 \rangle + \frac{8}{3} \langle \varepsilon(t)\varepsilon(0) \rangle \quad (6.15)$$

In a similar way we get

$$E_g^{(2)}(t) = \frac{20}{3\pi} \langle \varepsilon(t)\varepsilon(0) \rangle \quad (6.16)$$

$$T_{2g}^{(2)}(t) = \frac{5}{4\pi} \left(\frac{1}{3} - \frac{8}{3} \langle \varepsilon^2 \rangle + \frac{4}{3} \langle \varepsilon(t)\varepsilon(0) \rangle \right) \quad (6.17)$$

Then we calculate the correlation functions in the same way as in part 5.3.1. The results of these harmonic expansion are given in Figs. 33 and 34.

6.3.2. NUMERICAL SIMULATION

We simulated Eq. (6.7) on a computer and extracted from the simulation data various correlation functions and information about the jump dynamics.

The simulation was performed in the case of the ordered and the disordered phase. The parameters which were changed for the different simulations are the friction Γ ($\Gamma = .25, .75, 1.50, 2.50$ and 3.75), and the strength γ of the potential. Table 11 shows the height of the barriers for different parameters γ . The simulations are performed with $\gamma = .1, .15, .25$, and $.40$ in the case of ordered phase, and with $\gamma = .35, .70$, and 1.40 in the case of disordered phase.

Each simulation was done over 250 000 time steps and repeated 10 times with different random numbers. The cpu-time used for these $2.5 \cdot 10^6$ time steps is of the order 800 seconds on an IBM-3033.

6.4 JUMP-DYNAMICS

The solution of the Langevin-equation has the advantage that one very easily gets information about the detailed dynamics of the jumps from one minimum to another minimum. We did the analysis of data for five different potentials. Table 11 shows the corresponding parameters and barrier heights.

γ	.25	.40	.35	.70	1.4
V_{120°	2.4	3.8	3.0	6.1	12.2
V_{90°	1.8	2.8	2.2	4.3	8.6
phase	order	order	disorder	disorder	disorder

Table 11 The table shows the height of potential barriers for 120° and 90° jumps in units of the thermal energy.

The motion of the pseudoparticle with a parameter γ less than .25 is not analyzed, because the motion is more diffusive in that case than jump like. We wrote a computer program which analyses the jumps.

The 48 minima of the potential are labeled from 1 to 48. All simulations started in the minimum (0,0,0,1) which got the label 1. The association of a label with a certain minimum is arbitrary.

A computer program is written, which asks if the particle is in a minimum or not. The distance of the particle from a certain minimum can be plotted versus time. Fig. 26 and 27 show typical results. At the bottom of each figure the time is written in units of 10Δ (Δ = time-step of simulation). In the line above the time also the label of the minimum is given (see figure-caption for details). Fig. 26a and 26b show the result for small friction ($\Gamma^* = .25$). The motion in the potential minimum is nearly oscillatory. Fig. 26c shows the results for

Fig. 26: The figure shows the square of the distance of the pseudo particle from the minimum. One number labels the time steps in units of 10Δ . The other number denotes the minimum.

a) Here the particle oscillates in the minimum with label 4. The label 4 denotes the minimum $(1,0,0,0)$. If the distance is larger than .05 a J (for jump) occurred. The three events do not correspond to jumps, because the pseudo particle falls back into the minimum where it started. The friction parameter is 0.25, which means small friction. The motion is oscillatory.

b) Same as a). The maximum distance which is indicated is .10.

c) The label 24 denotes the minimum $(-1/2; 1/2; -1/2; -1/2)$. The friction parameter is now 2.50. There is no oscillatory motion left.

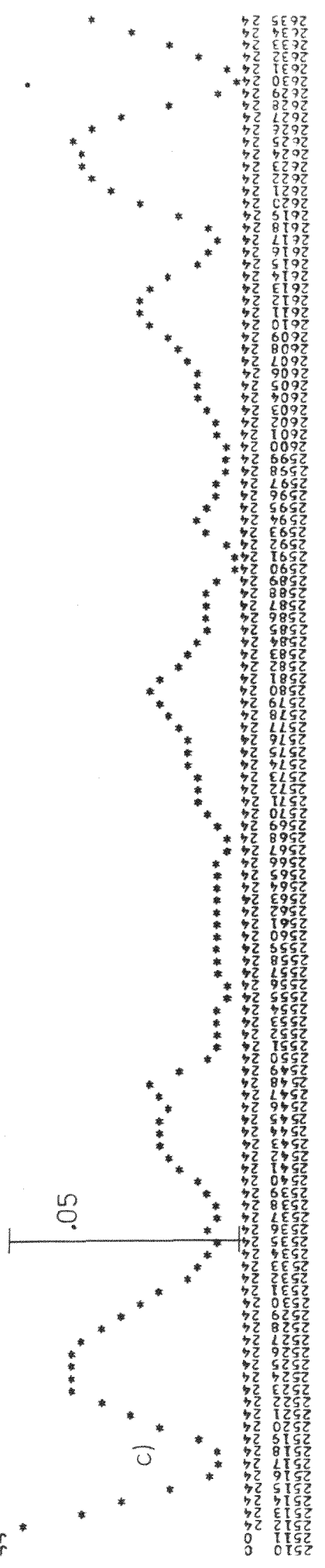
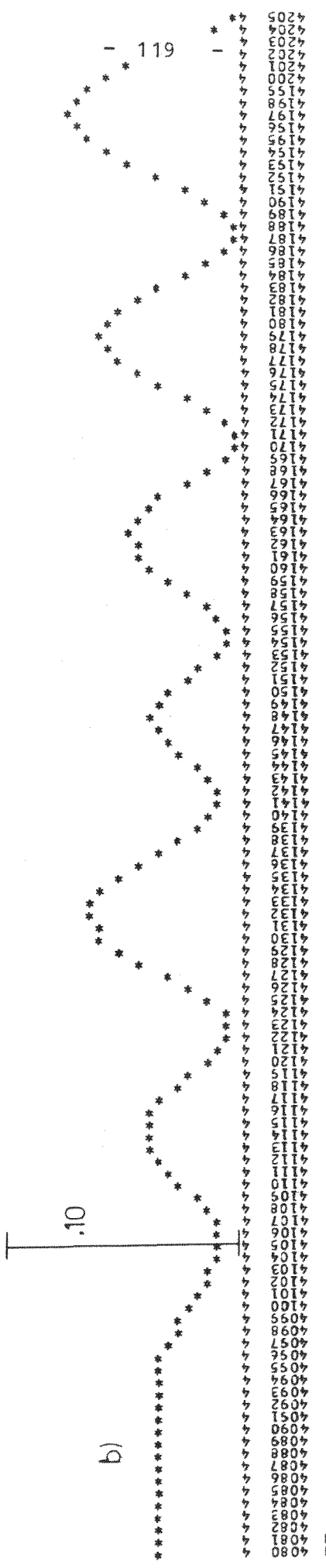
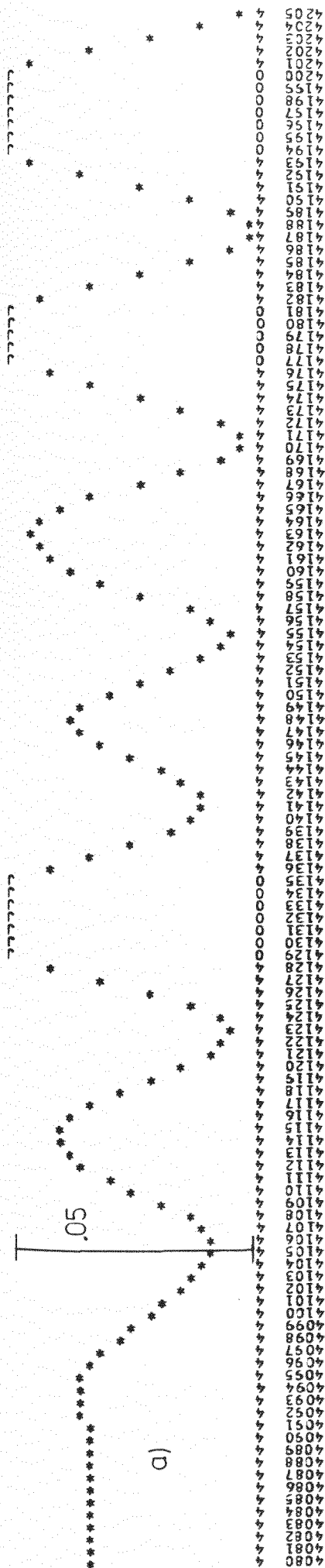


Fig. 27: Now the figure shows a multiple jump

a) The minima are:

$$43 \cong \left(-\frac{1}{\sqrt{2}} \quad -\frac{1}{\sqrt{2}} \quad 0 \quad 0 \right)$$

$$23 \cong \left(-1/2 \quad -1/2 \quad -1/2 \quad 1/2 \right)$$

$$36 \cong \left(0 \quad 0 \quad -\frac{1}{\sqrt{2}} \quad \frac{1}{\sqrt{2}} \right)$$

$$11 \cong \left(1/2 \quad 1/2 \quad -1/2 \quad 1/2 \right)$$

All three jumps are 90° jumps around a (100) axis. The friction is 0.25.

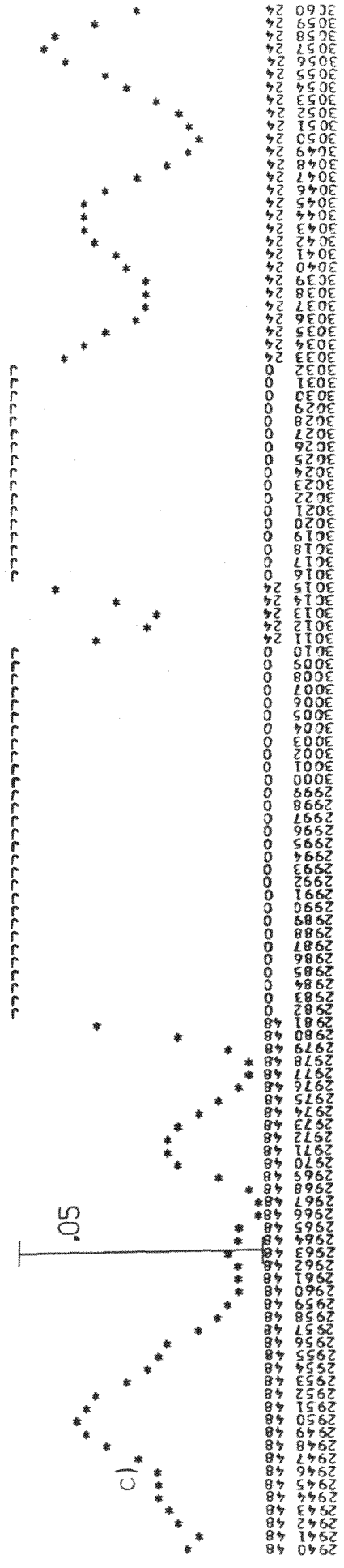
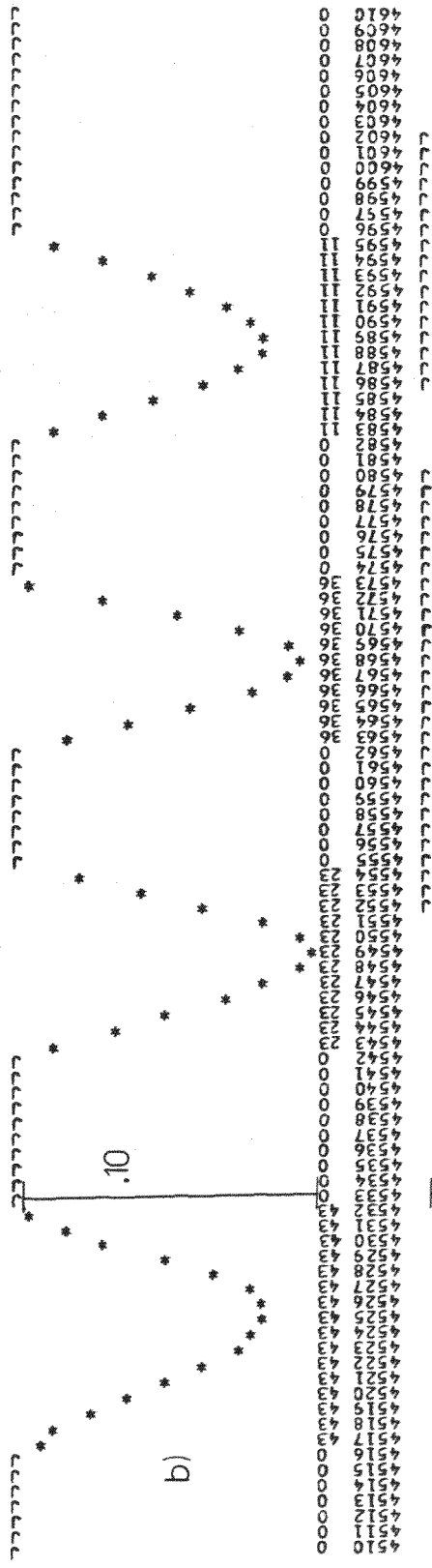
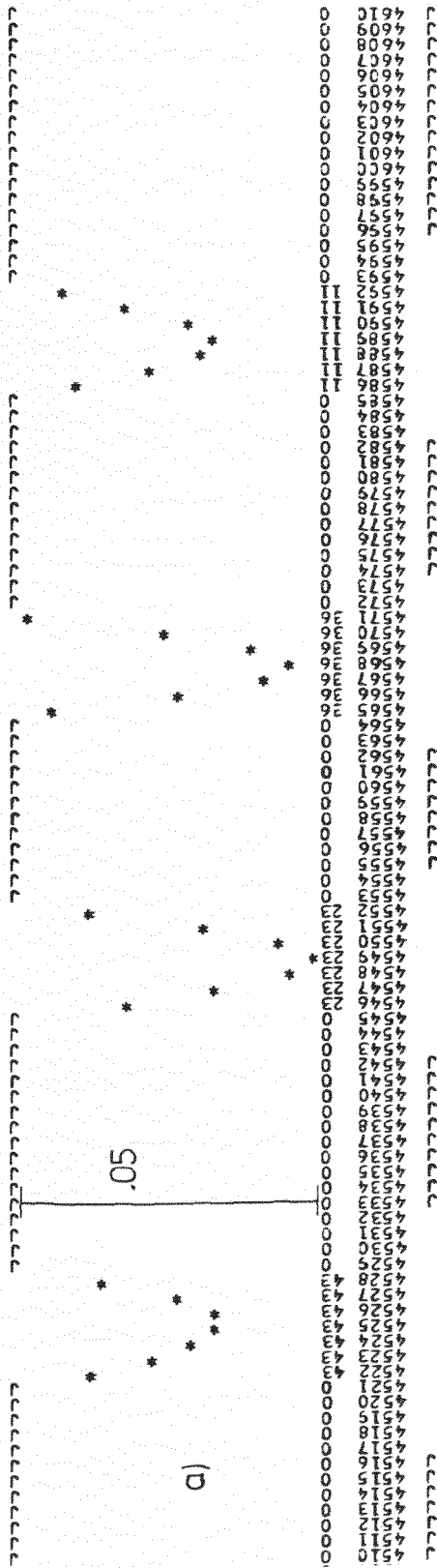
b) Same as a) with a different scale for the ordinate.

c) This figure shows a single jump. The minima are:

$$48 \cong \left(0 \quad 0 \quad -\frac{1}{\sqrt{2}} \quad -\frac{1}{\sqrt{2}} \right)$$

$$24 \cong \left(-1/2, -1/2, -1/2, -1/2 \right)$$

The jump is around a (100) axis by 90° . The friction is now 2.50.



a friction which is ten times larger ($\Gamma^* = 2.50$). Now we cannot see any oscillatory behaviour.

Fig. 27 shows jumps. The Figs. 27a and 27b show a multiple jump where the particle leaves one minimum and goes through several other minima before it is again captured and Fig. 27c shows a single jump. To get more information about jumps another program lists all jumps, which occur during the experiments. Fig. 28 shows the output of such a program. The first and the second column give the residence time of the particle in a minimum, respective the jump-time. The next two columns gave the labels of the minimum from which and to which the particle jumps. The last two columns give the type of the jump and the number of jumps which make a multiple jump.

To decide if a particle has performed a jump or not we look at the distance between the particle and the minimum. If this distance is less than $\sqrt{.20}$ we say, the particle is in the minimum. (In the program we compare the square of distance with .20). When the particle changes the minimum to which it belonged we say that a jump has happened. A sequence of jumps is finished (the particle is caught by a minimum) if the total energy of a particle is less than the lowest barrier (barrier for 90° -jumps). Because in that case the particle cannot leave the minimum without any further agitation from the stochastic-force. This is a well defined criterion to decide if a jump-sequence is finished or not and to discriminate between single and multiple jumps. The criterion with the distance is not so well defined, because the choice of the distance (in our case

residence time	jump time	from	to	type	multi- plicity
895	2	1	29	90	1
146	7	29	25	120	1
82	45	25	1	180	3
23	21	1	18	120	2
192	318	18	40	90	17
228	89	40	6	90	5
713	379	6	39	180	22
159	199	39	33	0	6
604	30	33	30	120	2
47	217	30	7	180	11
186	297	7	27	180	10
104	0	27	9	90	1
44	9	9	10	120	1
912	76	10	8	120	4
49	361	8	32	90	18
417	66	32	4	90	5
724	371	4	38	90	23
1053	15	38	37	120	1
407	11	37	17	90	1
459	79	17	7	120	2
106	47	7	30	180	3
332	0	30	9	90	1
196	56	9	43	90	3
2018	0	40	24	90	1
303	40	24	38	180	3
76	17	38	27	120	2
521	10	27	35	120	1
210	172	35	41	0	10
302	0	41	16	90	1
67	0	16	42	90	1
282	0	42	15	90	1
844	4	15	39	90	1
390	240	39	11	180	8
135	2	11	40	90	1
109	8	40	36	120	2
617	0	36	1	90	1
51	0	1	29	90	1
571	281	29	12	180	17
543	68	12	43	180	4
60	212	43	23	90	9
60	14	23	1	120	1
1037	175	1	21	120	8
400	1	21	45	90	6
19	278	45	6	180	6
89	20	6	3	180	2
2062	0	3	25	90	1
102	67	25	39	120	4
247	19	39	25	120	2
77	91	25	33	120	4
63	0	33	19	90	1
345	188	19	22	120	9
133	78	22	11	0	4

Fig. 28: All the information about the jumps during one experiment. The time in the two left columns is in units of 10Δ . In the right column the length of a jump sequence is given. The parameters are $\gamma = .70$ and $\Gamma = .25$.

.20) is more or less arbitrary. We tried several values (from 0.05 up to 0.4) the one we finally used seems to be quite a good one.

From the output which is shown in Fig. 28 we can discriminate between the different types of jumps (90° , 120° , 180°) and whether the jump is a single jump or a multiple one.

Table 12 and Table 13 show the proportions of the different jump types. The two different types of 180° jumps (see Table 10) are not discriminated. Table 12 shows the results for single jumps, and Table 13 for multiple jumps. The proportion for each jump type depends neither on the friction nor on the potential strength in the region of parameters we looked at. The ratio of single jumps to multiple jumps depends on both the friction as well as the potential strength. Fig. 29 shows the proportion of the single jumps as a function of the friction parameter.

Toepler et al [47,48] measured the jump rate around 3-fold and 4-fold axis separately. They started from a jump model with two different jump rates ν_3 and ν_4 . (ν_3 = jump rate for 120° jumps, ν_4 = jump rate for 90° jumps). This jump model can be solved analytically. The result for the incoherent scattering law is a linear combination of three Lorentzians. The width of these Lorentzians depends on the jump rates ν_3 and ν_4 . Fitting the experiment they get values for the jump rates ν_3 and ν_4 . They found that above the phase transition (in the disordered phase) approximately $\nu_4 \approx 2\nu_3$.

$\Gamma \backslash \gamma$	.25	.75	1.50	2.50	3.75
.25 (o)	.82	.83	.83	.85	.87
.40 (o)	.87	.87	.88	.86	.87
.35 (d)	.87	-	.86	.87	.89
.70 (d)	.92	.90	.90	.92	.91
1.40 (d)	.97	-	.92	.91	-

90°

$\Gamma \backslash \gamma$	.25	.75	1.50	2.50	3.75
.25 (o)	.16	.17	.17	.15	.13
.40 (o)	.13	.13	.12	.14	.13
.35 (d)	.13	-	.14	.13	.10
.70 (d)	.08	.10	.08	.08	.09
1.40 (d)	-	-	-	-	-

120°

Table 12 The proportion of 90° and 120° jumps in the case of single jumps. The 180° jumps are less than .01 in all cases.

$\Gamma \backslash \gamma$	.25	.75	1.50	2.50	3.75
.25 (o)	.30	.26	.27	.29	.29
.40 (o)	.29	.28	.25	.31	.31
.35 (d)	.29	-	.28	.28	.30
.70 (d)	.28	.29	.28	.26	.27
1.40 (d)	.32	-	-	-	-

90°

$\Gamma \backslash \gamma$	.25	.75	1.50	2.50	3.75
.25 (o)	.24	.38	.38	.38	.42
.40 (o)	.35	.35	.43	.41	.45
.35 (d)	.35	-	.36	.41	.43
.70 (d)	.34	.39	.38	.44	.42
1.40 (d)	.42	-	-	-	-

120°

$\Gamma \backslash \gamma$	.25	.75	1.50	2.50	3.75
.25 (o)	.34	.35	.34	.32	.29
.40 (o)	.34	.36	.32	.28	.25
.35 (d)	.34	-	.35	.31	.27
.70 (d)	.35	.31	.34	.30	.31
1.40 (d)	.28	-	-	-	-

180°

Table 13 The proportions of 90° , 120° and 180° jumps in the case of multiple jumps. In the case of $\gamma = 1.40$ no results could be extracted from the simulation data, because too few jumps occur.

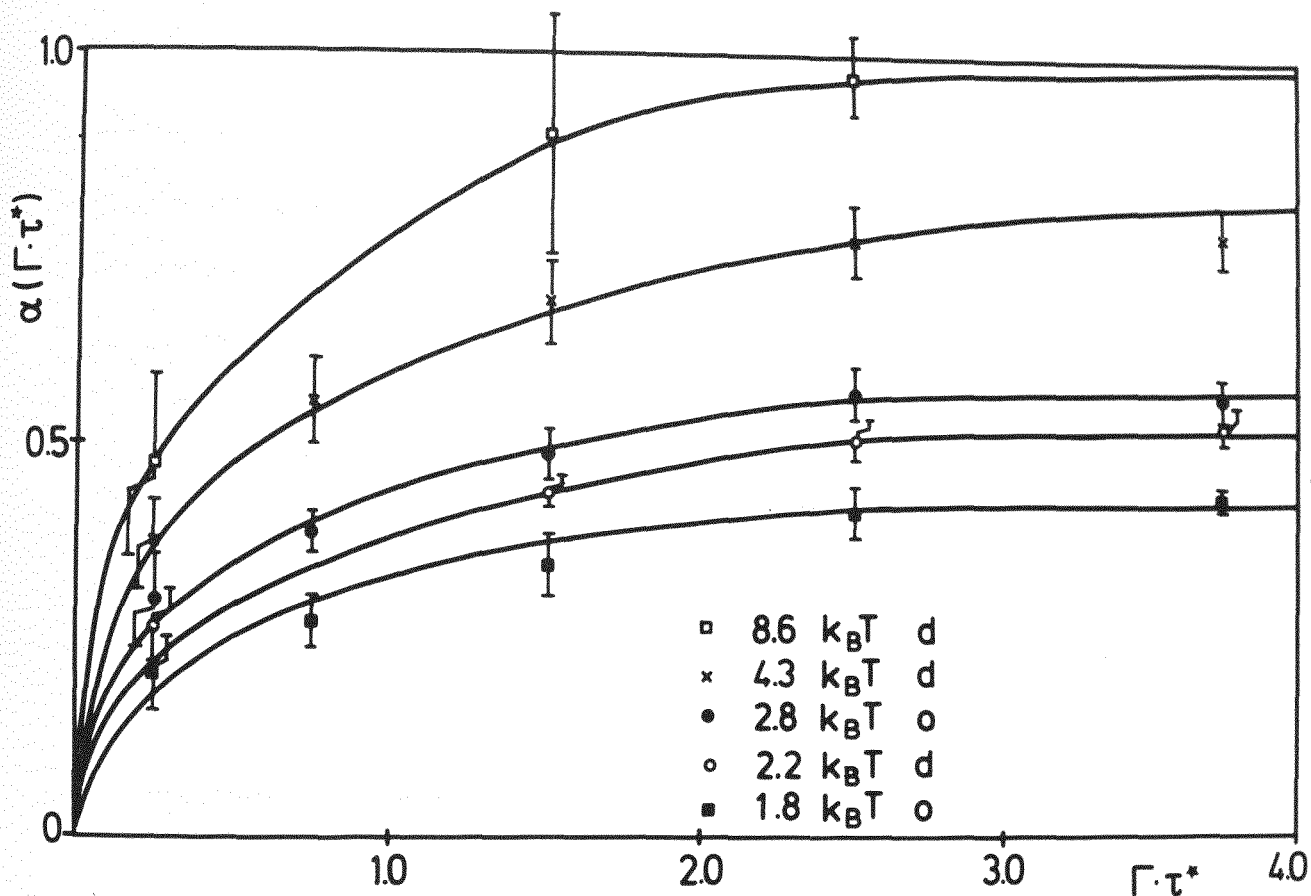


Fig. 29: The figure shows the proportion α of single jump as a function of friction parameter Γ . The height of the barrier for 90° jump is given in units of $k_B T$.

That means, that 90° jumps happen twice as often as 120° jumps. From Tables 12 and 13 we know the probability of 90° and 120° degree-jumps in the case of single and multiple jumps.

From Table 12 and 13 it is seen that the proportions of 90° , 120° , and 180° jumps do not depend on the friction or on the potential strength. Therefore we can average over the proportions.

$$P_S^{90} = 0.88$$

$$P_S^{120} = 0.13$$

$$P_M^{90} = 0.29$$

$$P_M^{120} = 0.40$$

If we denote by α the probability that a certain jump is a single jump, α can be determined from the experimental result $v_4 = 2v_3$.

$$\begin{aligned} 0.88 \alpha + 0.29 (1-\alpha) &= 2\bar{v} \\ 0.13 \alpha + 0.40 (1-\alpha) &= \bar{v} \end{aligned} \quad (6.18)$$

The solution for α is

$$\alpha = 0.43 \quad (6.19)$$

43% for all jumps are single jumps and 57% are multiple jumps.

The experiments in the disordered phase have been performed in a range of temperatures around 245 °K. The barrier height V_{90} is at this temperature $10.1 k_B T$, which corresponds to $\gamma = 1.63$. Because jumps become increasingly rare with such high potentials we will compare with the upper most curve in Fig. 29, which is for $V_{90} = 8.6 k_B T$. The curve for $V_{90} = 10.1 k_B T$ is a little bit above the curve for $V_{90} = 8.6 k_B T$. From $\alpha = 0.43$ we determine the friction constant Γ .

$$0.1 \frac{1}{\tau^*} < \Gamma < 0.4 \frac{1}{\tau^*} \quad (6.20)$$

That is the region of small friction.

The quantity τ^* which makes the time dimensionless is

$$\begin{aligned} \tau^* &= \left(\frac{I}{k_B T} \right)^{1/2} \\ &= 1.86 \cdot 10^{-12} (T)^{-1/2} \end{aligned} \quad (6.21)$$

where the temperature T must be put in [$^{\circ}\text{K}$]. One important approximation has been made: all the 180° jumps are neglected inspite of the fact that one should not neglect them because they amount to approximately 19% of all jumps when $\alpha = 0.43$.

From the comparison between the experimental results with our numerical simulation we have been able to determine the microscopic friction parameter of the rotational motion of NH_4^+ -tetrahedrons in NH_4Cl .

6.5 DISCUSSION OF RESULTS

To our knowledge there does not exist any theoretical work on the rotational motion of a tetrahedron in a potential with the exception of jump models [47-50]. From the jump models the incoherent scattering law can be calculated. It is in that case a linear combination of Lorentzians.

In the case of our numerical simulation a Fourier transformation is not possible, because the simulation times are too short. The qualitative discussion of the scattering law given in part 5.6 of this work is valid, because the structure of the correlation function is the same as in the two-dimensional case.

Fig. 30 to 34 show the correlation functions extracted from the simulation data in the case of the disordered phase. In the case of the ordered phase there is only a quantitative difference, qualitatively it is the same. We have the same

behavior as in the case $s = +1$ of the rotation with two degrees of freedom, because the minima of the potential are also in the 111-direction of the crystal.

Fig. 30, 31, and 32 show the correlation functions $\langle r(t)r(0) \rangle$, $E_g^{(2)}(t)$ and $T_{2g}^{(2)}(t)$ respectively in the case of potential parameter $\gamma = .7$ ($V_{90} = 4.3 k_B T$) for three different frictions. Fig. 33 and 34 show the correlation function $\langle r(t)r(0) \rangle$ for different potential parameters in the case of small and large friction. Also the analytic solution of harmonic approximation is shown.

In the case of a jump model the scattering law is a linear combination of two Lorentzians. Töpler et al. [47,48] measured the width of each of them. For a certain choice of the momentum $\vec{Q}$ the prefactor of one or the other of the Lorentzians is zero. With $\vec{Q} // (100)$ and $Q_x = 2.67 \text{ \AA}^{-1}$ they get one Lorentzian and with $\vec{Q} // (111)$ and $Q_x = 2.64 \text{ \AA}^{-1}$ they get the other one. Their results for the width as a function of temperature is given in Fig. 36. The dots are experimental points for $\vec{Q} // (111)$ and the crosses for $\vec{Q} // (100)$.

We can check if our simulation leads to a width of the same magnitude.

A quantitative comparison of our data which have been obtained in the time domain with the neutron scattering law given as a function of momentum and energy transfer is difficult. For a Fourier transform from the time domain into the frequency domain the long time behavior must be known,

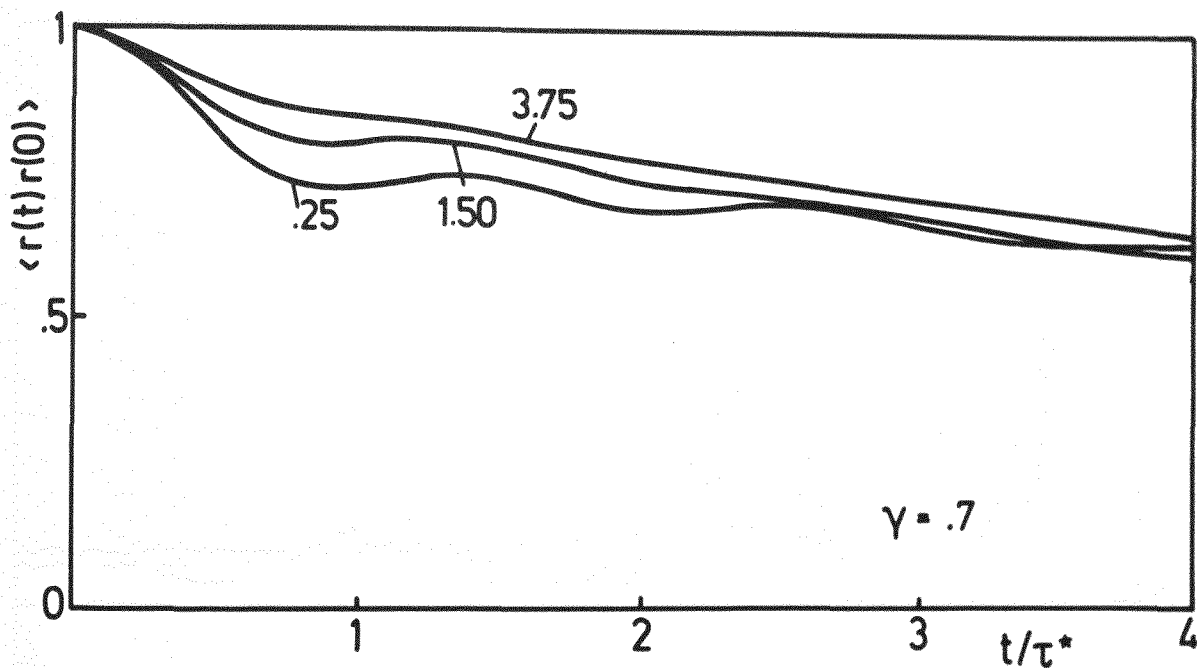


Fig. 30: The correlation function $\langle r(t)r(0) \rangle$ for a potential parameter $\gamma = .7$ ($V_{90} = 4.3 k_B T$). The friction parameter Γ^* is .25, 1.50, and 3.75 from bottom to top. Disordered phase.

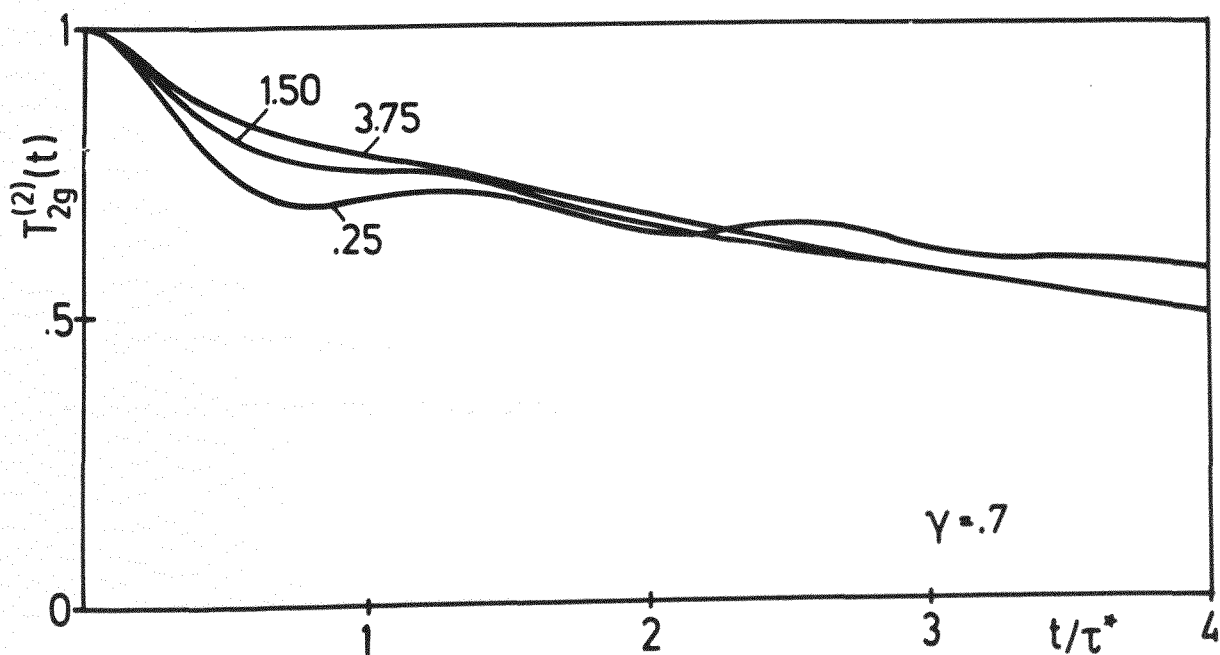


Fig. 31: The correlation function $T_{2g}^{(2)}(t)$. Same parameters as in Fig. 31.

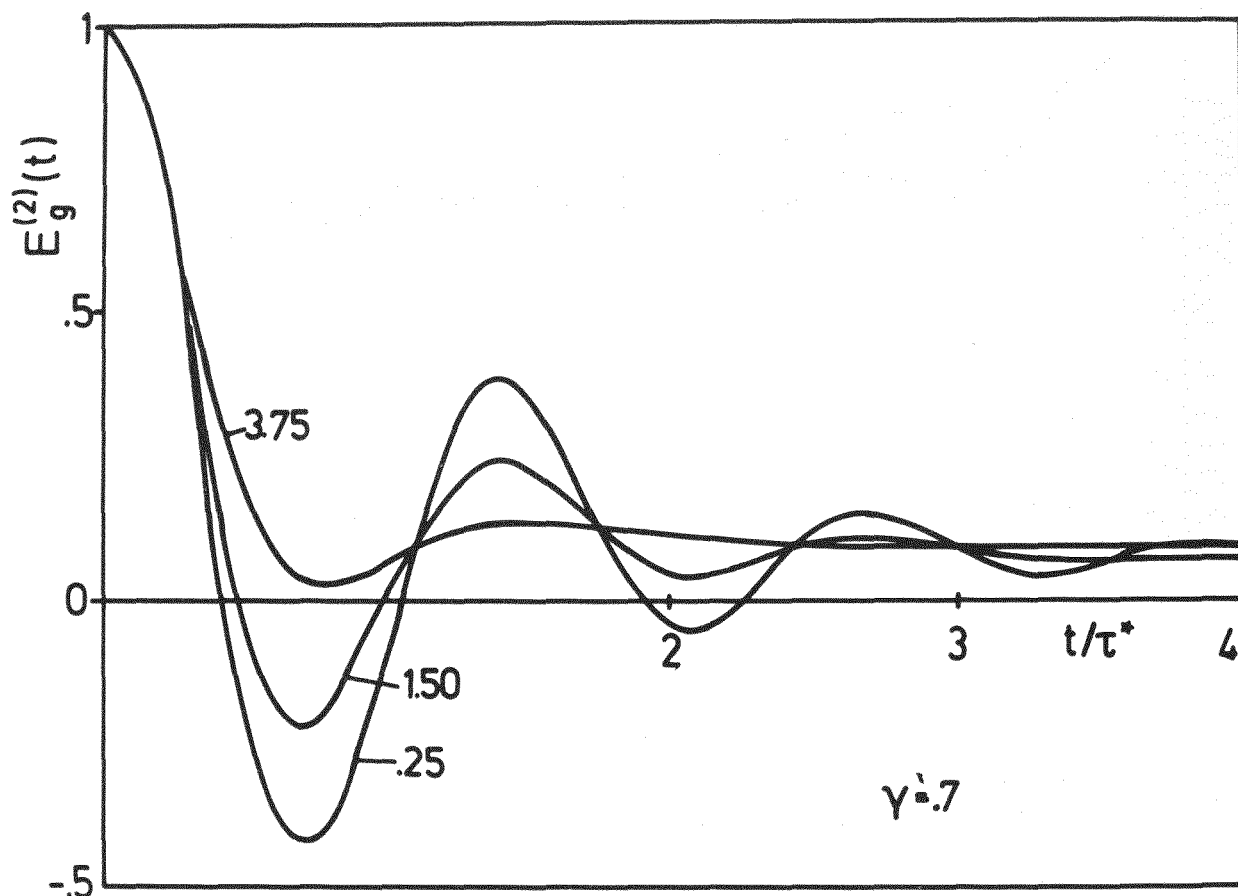


Fig. 32: The correlation function $E_g^{(2)}(t)$. Same parameters as in Fig. 31. In the case $\Gamma = .25$ the amplitude is largest.

but the computer experiments for such a program are prohibitively expensive. Therefore the comparison can only be semi-quantitative.

The geometrical details of the experiment and the question which correlation functions have been measured at the momentum transfers will be reserved for further work. The main result of the study of NH_4Cl in this paper is that 75% of the 120° jumps around the threefold symmetry axis of the tetrahedron are multiple 90° jumps around two-fold symmetry axes.

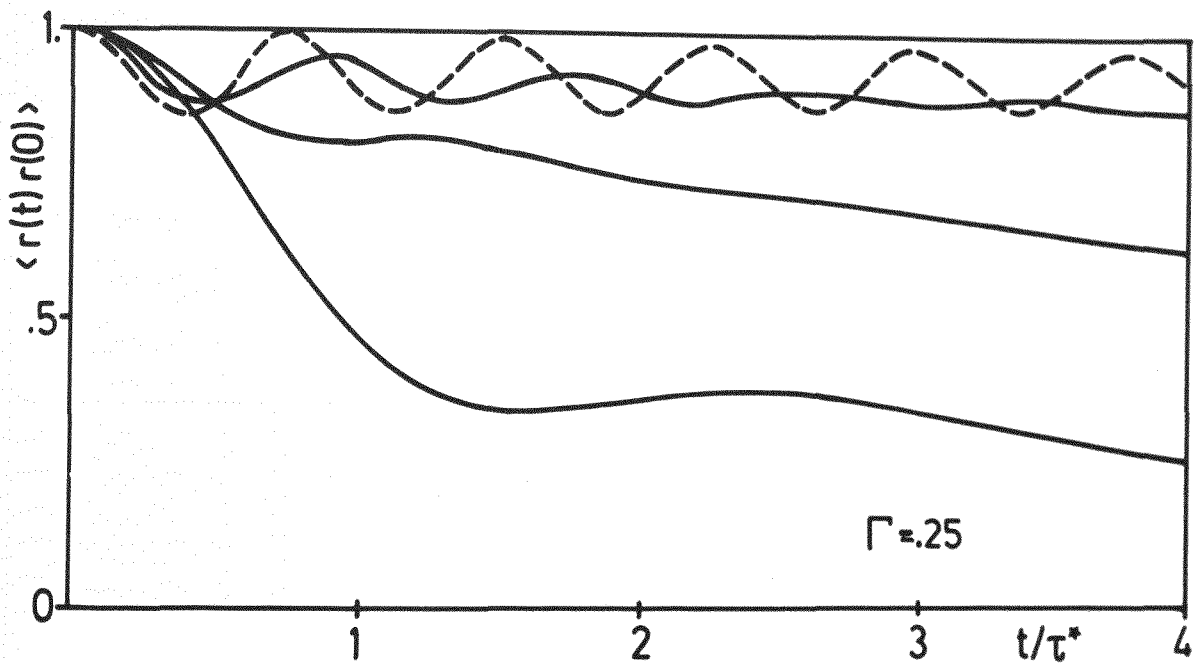


Fig. 33: The correlation function $\langle r(t)r(0) \rangle$ in the case of small friction ($\Gamma = .25$) and for different potential parameters ($\gamma = .35, .70, 1.40$ from bottom to top). The dashed line is the result from harmonic approximation with $\gamma = 1.40$.

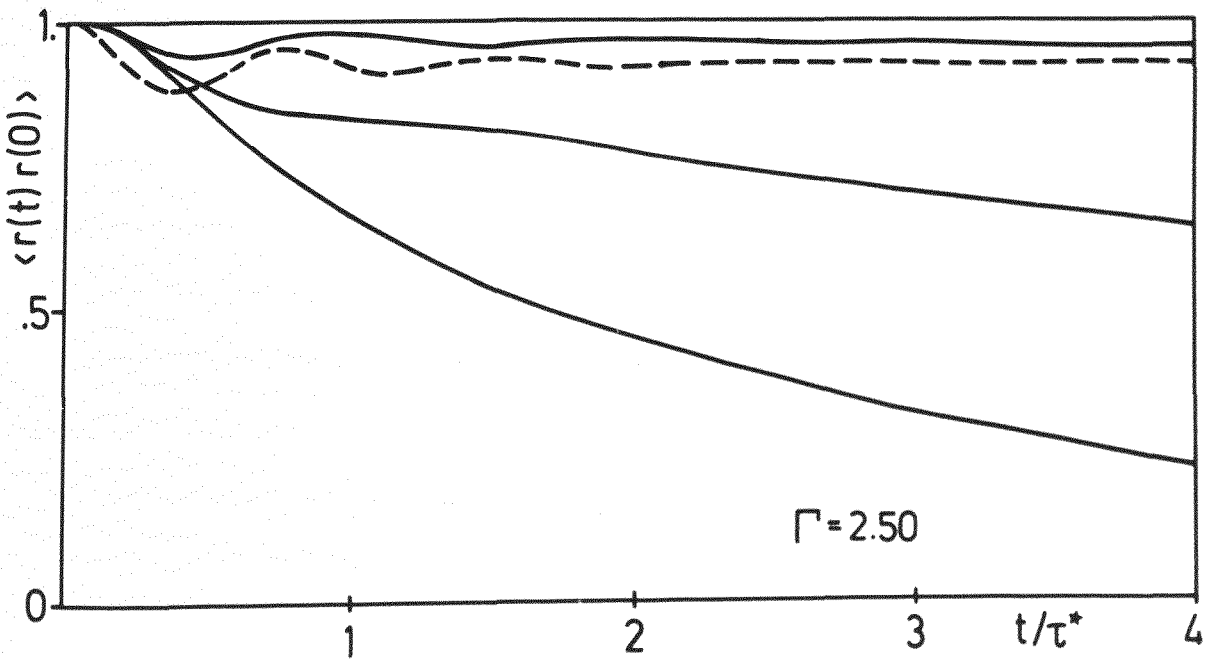


Fig. 34: Same as in Fig. 34, but ten times larger friction. $\Gamma = 2.50$.

Γ γ	.25	.75	1.50	2.50	3.75	$[\text{sec}^{-1}]$
	in units of τ^*					
1.40	(.013)	-	.003	.003	-	$2.7 \cdot 10^{10}$
.70	.08	.09	.08	.09	.08	$1.2 \cdot 10^{12}$
.35	.26	-	.39	.40	.32	$6.7 \cdot 10^{12}$
.40			.305	.306	.242	$4.8 \cdot 10^{12}$
.25	-	-	.475	.592	.374	$1.0 \cdot 10^{13}$
.15			.926	.574	-	$2.1 \cdot 10^{13}$
.10	-	-	1.178	.708	-	$3.2 \cdot 10^{13}$

Table 14 The time constant of the exponential which can be fitted to the long time behavior of the correlation function $\langle r(t)r(0) \rangle$. The last column gives the value which is used for further calculations. In the first line .013 is obvious to large.

This result makes it clear that both types of jumps must have almost identical activation energies. The width of the quasielastic neutron scattering should not depend very much on the direction of $\vec{Q}$ and on geometric details. In the following we will compare the quasielastic line-width with the decay of $\langle r(t)r(0) \rangle$ which is the slowest of all correlation functions studied.

From the Arrhenius law one can extrapolate using a linear regression routine into the experimental temperature range.

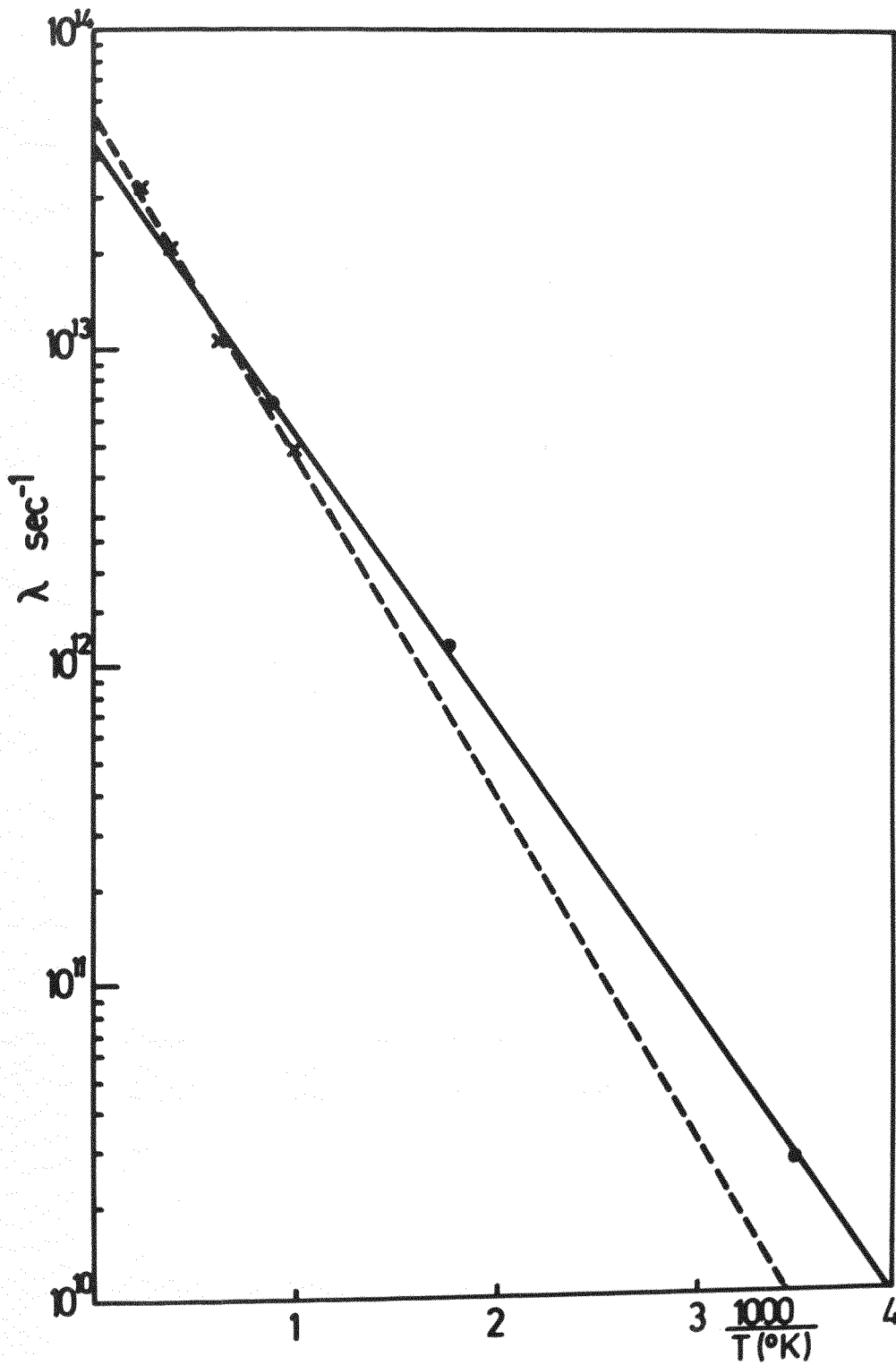


Fig. 35: Arrhenius plot for the width λ of the Lorentzian as determined from the computer simulation. The circles are the disordered phase and the crosses are the ordered phase. The lines are determined by linear regression.

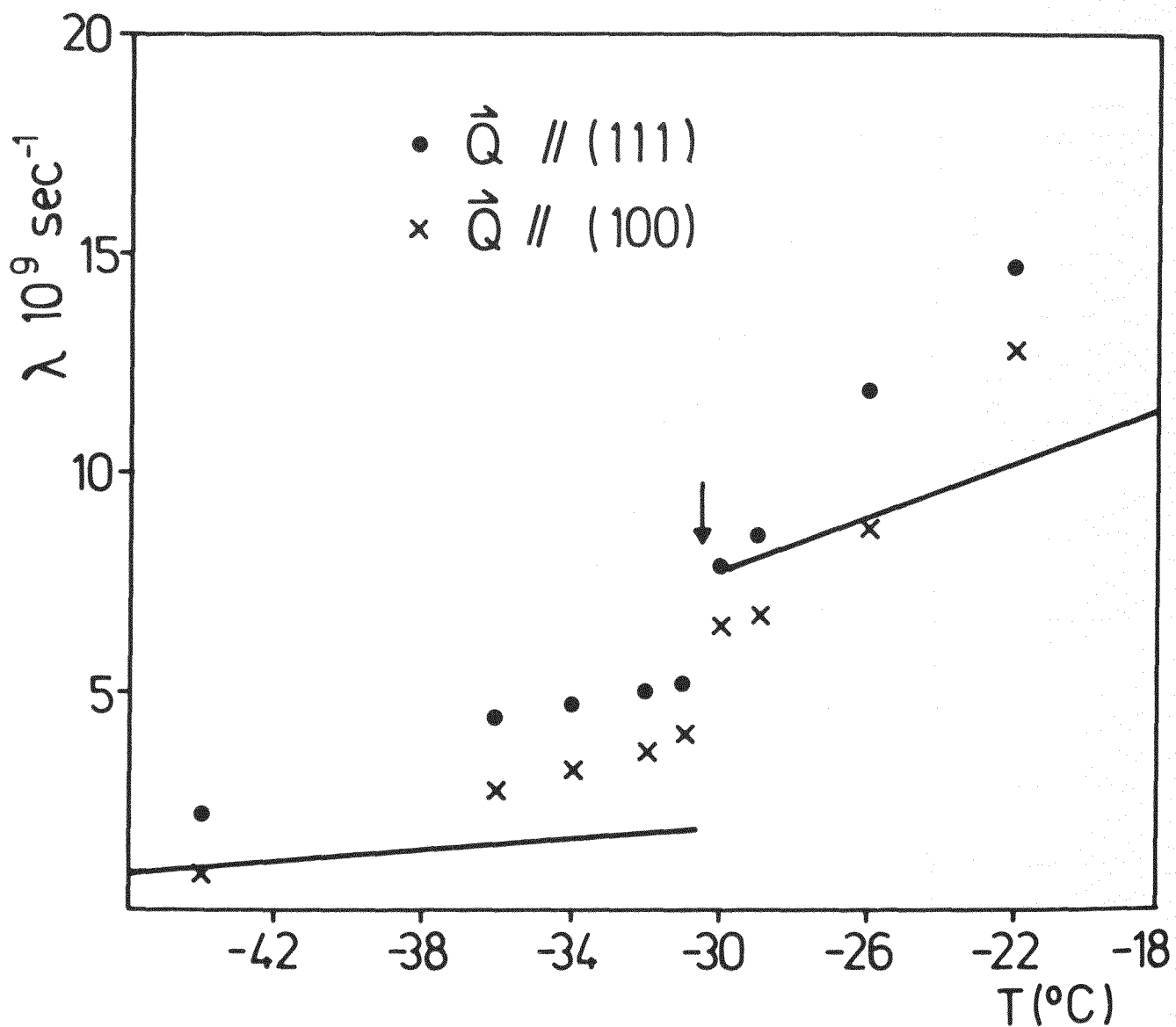


Fig. 36: The width λ of the Lorentzians as function of temperature. The points are from experimental data [47]. The lines are from the numerical simulation. The lines are calculated from the corresponding Arrhenius plot. The arrow indicates the phase transition temperature.

Fig. 36 shows the resulting width compared with the experimentally measured points. The agreement is good. It is worthwhile to say that there is no fitting parameter involved. The only input used is the Hüller-Kane-potential [43], which is completely determined from the libration frequencies.

The discrepancy between experimental and theoretical values for temperatures close to and below the phase transition can be understood. The theoretical results are calculated for complete orientational order, and that is obviously not the case close to the phase transition. Incomplete order leads to a larger width.

The Arrhenius law which has been found is

$$\lambda = 4.38 \cdot 10^{13} e^{-\frac{181}{k_B T}} [\text{sec}^{-1}] \quad T > T_C \quad (6.22)$$

$$\lambda = 5.49 \cdot 10^{13} e^{-\frac{214}{k_B T}} [\text{sec}^{-1}] \quad T < T_C \quad (6.23)$$

where the thermal energy $k_B T$ must be inserted in [meV]. The activation energies 181 meV ($T > T_C$) and 214 meV ($T < T_C$) agree satisfactorily with experimental work [48] and the results of Hüller and Kane [43]. Table 15 shows the results of the different works.

	Activation energy $T < T_C$ [meV]	Activation energy $T > T_C$ [meV]
Töpler et al. [48]	$E_3 = 197$ $T = T_C - 1 \text{ } ^\circ\text{K}$ $E_4 = 212$	$E_3 = 197$ $T = T_C + 1 \text{ } ^\circ\text{K}$ $E_4 = 188$
Hüller/Kane [43]	$E_4 = 212$	$E_4 = 184$
present work	$E = 214$	$E = 181$

Table 15 The activation energies from different works.
Töpler et al. measured the activation energies
for 90° and 120° separately.

Summing up we can say, that the classical Langevin-model of rotational motion is able to describe the experiments very well. We got the width of the scattering law without a fitting parameter in good agreement with experimental work. The friction parameter can be used to fit the ratio between 90° jumps and 120° jumps. From this ratio we get a value for the microscopic friction parameter, which shows that we are in the small friction regime. From the studies of the jump dynamics we know, that for small friction parameters multiple jumps happen quite often. 75% of 120° jumps are multiple 90° jumps and consequently the activation energy for both types of jumps must be quite similar. Besides we learnt that 180° jumps around

110-axis may not be neglected in a jump model.

Future work should run over larger simulation times so that the correlation functions can be Fourier transformed. Then the neutron scattering law can be compared directly with experimental work.

7. APPENDICES

A: GENERALIZED DIANOUX-VOLINO-FORMALISM

We start with the generalized diffusion equation

$$\frac{1}{D} H_t G = \frac{\partial}{\partial \varphi} \left[\frac{\partial G}{\partial \varphi} + \frac{1}{k_B T} \left(\frac{dV}{d\varphi} \right) G \right] \quad (\text{A.1})$$

$G(\phi, \phi_0, t)$ is the probability of finding the particle at ϕ at time t if it was at ϕ_0 at time zero and H_t is an operator given by the series

$$H_t = \sum_{i=0}^{\infty} f_i(t) \frac{\partial^i}{\partial t^i} \quad (\text{A.2})$$

where the $f_i(t)$ are arbitrary functions of time. The operator is considered as an expansion of a memory function around $t=0$. Following Dianoux and Volino [11] we define $c_n(t)$ and $\tilde{c}_n(t)$ such that

$$c_n(t) = \langle \cos n\varphi \rangle_{\varphi} = \int_0^{2\pi} d\varphi \cos n\varphi G(\varphi, \varphi_0, t) \quad (\text{A.3})$$

$$\tilde{c}_n(t) = c_n(t) - c_n(\infty) \quad (\text{A.4})$$

The $\tilde{c}_n(t)$ fulfill the following relations:

$$\begin{aligned} \tilde{c}_0(t) &= 0 \\ \tilde{c}_n(\infty) &= 0 \\ \tilde{c}_n(t) &= \tilde{c}_{-n}(t) \\ c_n(0) &= \cos n\varphi_0 - \frac{I_k\left(\frac{V}{2k_B T}\right)}{I_0\left(\frac{V}{2k_B T}\right)} \delta_{n,kN} \end{aligned} \quad (\text{A.5})$$

The first three relations follow from definition of $\tilde{c}_n$ and from the symmetry of the cosine function. The fourth relation can be understood from the calculation of the order parameter in chapter 5.6.

Multiplication of (A.1) by $\cos n\phi$ from the left side and integration over ϕ yields:

$$\frac{1}{D} H_t c_n(t) = \int_0^{2\pi} d\phi \cos n\phi \frac{\partial}{\partial \phi} \left[\frac{\partial G}{\partial \phi} + \frac{1}{k_B T} \left(\frac{dV}{d\phi} \right) G \right] \quad (A.6)$$

Integration by parts and manipulation of trigonometric identities leads to

$$-\frac{1}{D} H_t c_n(t) = n^2 c_n(t) + \frac{nNV}{2k_B T} [c_{n+N}(t) - c_{n-N}(t)] \quad (A.7)$$

Where we have made use of the fact that the potential has the form

$$V(\phi) = -\frac{V}{2} \cos N\phi$$

In the case $n \neq kN$ (k arbitrary integer) the $\tilde{c}_n$ are identical to the c_n and obey therefore eq. (A.7). For the case $n = kN$ c_n and $\tilde{c}_n$ are not identical. Then one has to use the identity [22,33] to show that the $\tilde{c}_n$ obey eq. (A.7)

$$I_{k+1}(x) - I_{k-1}(x) = -\frac{2k}{x} I_k(x) \quad (A.8)$$

$I_k(x)$ is the modified Bessel-function of order k . With the use of third relation of (A.5) equation (A.7) reads

$$-\frac{1}{D} H_t \tilde{c}_n = n^2 \tilde{c}_n + \frac{nNV}{4k_B T} [\tilde{c}_{n+N} - \tilde{c}_{|n-N|}] \quad (A.9)$$

This equation can be written in matrix form:

$$-\frac{1}{D} H_t \vec{\tilde{C}}(t) = M \cdot \vec{\tilde{C}}(t) \quad (A.10)$$

Where the matrix M is given by

$$M_{m,n} = m^2 \delta_{m,n} + \frac{mNV}{4k_B T} [\delta_{m+N,n} - \delta_{|m-N|,n}] \quad (A.11)$$

and the n^{th} component of the vector $\vec{\tilde{C}}(t)$ is the function $\tilde{c}_n(t)$.
The matrix M is diagonalized by the unitary transformation

$$\Lambda = U^{-1} M U \quad (A.12)$$

The transformed vector

$$\vec{D}(t) = U^{-1} \vec{\tilde{C}}(t) \quad (A.13)$$

obeys the equation of motion:

$$-\frac{1}{D} H_t \vec{D}(t) = \Lambda \vec{D}(t) \quad (A.14)$$

Because Λ is a diagonal matrix, the components $d_p(t)$ of $\vec{D}(t)$ are uncoupled. For further calculations we want to write the solution of (A.14) in the way

$$d_p(t) = d_p(0) f_p(t) \quad (A.15)$$

where the new function $f_p(t)$ is determined by

$$f_p(0) = 1$$

and

$$H_t f_p(t) = -\lambda_p D f_p(t) \quad (A.16)$$

The λ_p are the diagonal elements of the matrix Λ . The average $\langle \cos(\varphi - \varphi_0) \rangle$ can be divided into two parts

$$\begin{aligned} \langle \cos(\varphi - \varphi_0) \rangle &= \langle \cos \varphi \cos \varphi_0 \rangle + \\ &+ \langle \sin \varphi \sin \varphi_0 \rangle \end{aligned} \quad (A.17)$$

Dianoux and Volino have shown that $\langle \cos \varphi \cos \varphi_0 \rangle$ is given by

$$\begin{aligned} \langle \cos \varphi \cos \varphi_0 \rangle &= \frac{I_K^2 \left(\frac{V}{2k_B T} \right)}{I_O^2 \left(\frac{V}{2k_B T} \right)} \delta_{m,KN} + \\ &+ \sum_p U_{mp} T_{pm} f_p(t) \quad K=0,1,2,\dots \end{aligned} \quad (A.18)$$

U_{mp} are elements of the matrix U and the T_{pm} are elements of a matrix T which is defined by

$$T = U^{-1} \Omega^C \quad (A.19)$$

Ω^C is a matrix, given by

$$\begin{aligned} \Omega_{n,m}^C &= \frac{1}{2} \frac{I_K}{I_O} \delta_{n-m,KN} + \frac{1}{2} \frac{I_K}{I_O} \delta_{n+m,K'N} - \\ &- \frac{I_K I_{K''}}{I_O^2} \delta_{n,K''N} \delta_{m,K'''N} \end{aligned} \quad (A.20)$$

For clarity the arguments $\frac{V}{2k_B T}$ of the modified Bessel functions I_K have been dropped.

In a similar manner one gets an equation for $\tilde{s}_n(t)$, which is identical with the equation for $\tilde{c}_n(t)$ if the cosine function is replaced by a sine function. The only important difference concerns parity which is odd for sine functions but even for cosine functions. Corresponding to M one obtains a matrix N, defined by

$$N_{n,m} = m^2 \delta_{n,m} + \frac{mNV}{4k_B T} (\delta_{m+N,n} - \frac{(m-N)}{|m-N|} \delta_{|m-N|,n}) \quad (A.21)$$

The matrix N has eigenvalues μ_p and is diagonalized by an eigenvector matrix W. Now one obtains a similar result for the sine-correlation-function.

$$\langle \sin m\phi \sin n\phi_o \rangle = \sum_p W_{np} S_{pn} g_p(t) \quad (A.22)$$

The functions $g_p(t)$ are obtained on replacing the eigenvalue λ_p in eq. (A.16) by μ_p . The S_{pn} are the elements of the matrix $W^{-1} \Omega^S$, where Ω^S is given by

$$\Omega_{n,m}^S = \frac{1}{2} \frac{I_K}{I_O} \delta_{n-m,KN} - \frac{1}{2} \frac{I_{K'}}{I_O} \delta_{n+m,K'N} \quad (A.23)$$

Adding the results of equation (A.18) and (A.22) we have the correlation function $\langle \cos m(\phi - \phi_o) \rangle$. The only problem which is left is the solution of (A.1), which constitutes a set of uncoupled differential equations. For some simple forms of the operator H_t an analytic solution can be given. But in more

general cases one has to solve (A.16) by numerical methods. A considerable amount of computing time is required for this solution because (A.16) represents a large number of order 100 differential equations.

B: GENERATION OF NORMALLY DISTRIBUTED RANDOM NUMBERS

To perform a numerical solution of the Langevin-equation we have to use random numbers to simulate the stochastic force term. From the central limit theorem we know that each stochastic process will be Gaussian after N stochastic events when N is a large number. For the case of the Langevin equation that means that after a large number of impulses of the stochastic force the result of the calculation becomes independent of the distribution function obeyed by the stochastic force. To get a quick convergence and reliable results for short observation times we used a stochastic force which obeys a Gaussian distribution.

During the first part of our simulation (without potential, one degree of freedom with potential) we used the method of summing equally distributed random numbers. Let $X_1, X_2, \dots, X_N$ be a sequence of N uniform distributed random numbers. Then

$$\eta = \sum_{i=1}^N \left(X_i - \frac{N}{2} \right) \left(\frac{N}{12} \right)^{-1/2} \quad (\text{B.1})$$

will be asymptotically distributed as a normal random number, with zero mean and variance $\frac{N}{12}$. With $N=12$ we get unit variance. In that case the maximum error ϵ from the normal

distribution is [22] less than 1% for $|\eta| < 2$ and of the order 90% for $2 \leq |\eta| \leq 3$. In the latter interval the distribution function is too small, that this large error will be important. And there is, of course, a cutoff at $|\eta| = 6$. With this method we cannot produce random numbers which have a magnitude larger than 6. For the second part of our simulations (two and three degrees of freedom with potential) we used another method, which is known as the method of Box and Muller [51].

If X_1 and X_2 are independent equally distributed random numbers one gets by

$$\eta_1 = (-2 \ln X_1)^{1/2} \cos(2\pi X_2)$$

$$\eta_2 = (-2 \ln X_1)^{1/2} \sin(2\pi X_2)$$

a pair of independent normally distributed random numbers η_1 and η_2 , with zero mean and unit variance.

The latter procedure is much more convenient than the first one. The Box-Muller-procedure is an exact one whereas the other is an approximation. Besides the Box-Muller-procedure needs less (about 5% on an IBM 3033) cpu-time, than the addition-method.

And last not least the Box-Muller-procedure makes a better use of the uniformly distributed random numbers. It uses only 2 uniform random numbers mean-while the other method uses 24 to generate a pair normally distributed random numbers.

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