Quasielastic neutron scattering from anharmonic oscillators subject to weak frictional forces

C. A. Condat
Department of Physics, University of Puerto Rico, Mayagüez, Puerto Rico 00681

J. Jäckle
Fakultät für Physik, Universität Konstanz, 78434 Konstanz, Germany
(Received 30 January 1995; revised manuscript received 24 May 1995)

A Fokker-Planck approach is used to calculate the quasielastic line in the dynamic structure factor for a one-dimensional anharmonic oscillator subject to weak frictional forces. The problem is reduced to solving a diffusion equation in energy space. A general eigenfunction method of solution is developed using the exact solution to the harmonic oscillator as a guide. It is shown that energy relaxation speeds up, inducing a broadening of the quasielastic line, if a small positive anharmonic term is added to the harmonic potential. The method is then applied to analyze a model embodying essential properties of the soft potentials used in the study of glasses and undercooled liquids.

I. INTRODUCTION

Quasielectric neutron scattering is a major source of experimental information regarding slow dynamic processes in supercooled liquids and glasses, as well as in other complex, disordered systems.[1,2] For the physical interpretation of such information, relatively simple models of general type can be useful. We have shown recently that one-dimensional particle motion in anharmonic potentials subject to weak frictional forces generally yields a quasielastic line in the dynamic structure factor $S(k,\Omega)$, even for single-well potentials.[3] The coordinate of the one-dimensional motion may in fact be a generalized coordinate describing a slow mode of collective motion within a small spatial region.[4] Our result is based on the observation that for strictly Hamiltonian motion without friction the intensity of the elastic line is generally larger than that given by the Debye-Waller factor. The difference is found in the intensity of the quasielastic line when frictional forces are added. The result was applied to the soft-potential model[5,6] for glasses by Bhattacharya *et al.*,[7] who found that the intensity of the quasielastic line is of observable magnitude. The purpose of the present paper is to calculate the *width* of this quasielastic line and to establish its relation with energy relaxation.[6]

We follow the method of Dykman and coworkers[8,9] of transforming the Fokker-Planck equation in the energy-phase representation. The Fokker-Planck equation describes the one-dimensional motion of a particle subject to an anharmonic potential and weak frictional and stochastic forces. It is shown that the quasielastic component of the dynamic structure factor is obtained from the solution of a generalized diffusion equation in energy space. This solution can be calculated as an expansion in Laguerre polynomials, the resulting quasielastic line being a superposition of Lorentzians. This expansion will enable us to obtain general results for the quasielastic line width, and to answer such questions as whether the quasielastic line widens or narrows when a small anharmonic term is added to a harmonic potential.

Nonzero damping always generates a quasielastic peak in $S(k,\Omega)$. The situation is different if we consider the spectral distribution $S(\Omega)$ of the position-position correlation function. Since it determines the susceptibility for systems in thermal equilibrium, the function $S(\Omega)$ has been studied in great detail for systems subject to weak stochastic forces.[8] It has been shown that, for single-minimum potentials, the quasielastic peak appears only if the potential contains an asymmetry, so that the oscillator equilibrium position shifts with frequency. For two-minima potentials, there is an exponentially narrow quasielastic peak caused by fluctuational transitions between the minima.

We are aware of only two previous calculations of the dynamic structure factor for particles subject to both potential and frictional forces. In a model for superioinic conductors, Dieterich *et al.* treated the Brownian motion of a particle in periodic potentials.[10,11] Here the dynamic structure factor consists of a quasielastic part related to diffusion and an inelastic part due to oscillatory particle motion. On the other hand, Volino and Dianoux considered a cosine potential in their study of diffusion through smectic layers.[12]

This paper is organized as follows: In Sec. II a heuristic derivation is given for the formula for the quasielastic component in the presence of weak friction. The Fokker-Planck equation in energy-phase space is derived and the low friction approximation introduced in Sec. III. Section IV contains an analysis of the diffusion equation in energy space. This equation is exactly solved in Sec. V for a harmonic-oscillator potential. The general method of solution for anharmonic potentials is presented in Sec. VI, where we analyze the relation between anharmonicity and the quasielastic linewidth.

II. QUASIELASTIC LINE AND ENERGY RELAXATION

Here we give a heuristic argument to show that the quasielastic component of the dynamic structure factor for one-dimensional motion in single-well potentials is

 ©1995 The American Physical Society

determined by energy relaxation in the case of weak friction. The intermediate scattering function is defined as

$$F(k,t)=\langle e^{ik[q(t)-q(0)]}\rangle \ , \tag{1}$$

where k is the momentum transfer, $q(t)$ the oscillator coordinate at the time t, and the angular brackets represent an average over the initial conditions and over the realizations of the stochastic force, which is required to balance the frictional force. We may choose the energy E and the phase Ψ as the variables over which to perform the averages. Since the quasielastic component of $S(k,\Omega)$ is directly related to the long-time part of $F(k,t)$, and at long times the value of the phase is uncorrelated with the initial conditions, we can separately average over the initial and final phases and write,

$$\begin{aligned} F(k,t) &\simeq \int dE \int dE_0 \langle e^{ikq(t)}\rangle_E P(E,t|E_0,0)\langle e^{-ikq(0)}\rangle_{E_0} P_{\rm eq}(E_0) \\ &= \int_0^\infty dE P_0(E,t)\langle e^{ikq(t)}\rangle_E \ , \end{aligned} \tag{2}$$

where $P_{\rm eq}$ is the equilibrium distribution for the energy, $P(E,t|E_0,0)$ the transition probability density between the energies E_0 and E, and $P_0(E,t)$ is given by

$$P_0(E,t)=\int dE_0 P(E,t|E_0,0)P_{\rm eq}(E_0)\langle e^{-ikq(0)}\rangle_{E_0} \ . \tag{3}$$

The function $P_0(E,t)$ is a weighted average of the transition probability density $P(E,t|E_0,0)$ over the initial energy. It describes energy relaxation. The brackets in Eqs. (2) and (3) indicate that we have integrated over a cycle while keeping the energy constant (for weak friction the energy changes very little over a period). Since

$$P(E,0|E_0,0)=\delta(E-E_0) \ , \tag{4}$$

the initial condition for $P_0(E,t)$ is,

$$P_0(E,0)=P_{\rm eq}(E)\langle e^{-ikq}\rangle_E \ . \tag{5}$$

This argument leading to Eq. (2) will be corroborated in Sec. III by a systematic treatment of the Fokker-Planck equation that yields a differential equation for $P_0(E,t)$. This equation is identical to Kramers' generalized diffusion equation for diffusion along the energy axis.

III. FOKKER-PLANCK DESCRIPTION

To compute dynamical averages of properties associated with the scatterer we need the probability density $W(p,q,t|p_0,q_0,0)$ that at time t its generalized coordinate and momentum are q and p, given that at $t=0$ their values were q_0 and p_0, respectively. The initial condition satisfied by W is

$$W(p,q,0|p_0,q_0,0)=\delta(p-p_0)\delta(q-q_0) \ . \tag{6}$$

Once W is known, we can compute the time-dependent correlation function for a dynamic variable $g[q]\,(\equiv g[q(t)])$ as follows:

$$\langle g[q(t)]g^*[q_0]\rangle=\frac{1}{Z}\int dqdp\int dq_0dp_0 g[q]g^*[q_0]W(p,q,t|p_0,q_0,0)e^{-H(p_0,q_0)/T} \ , \tag{7}$$

where Z is the partition function and $H(p_0,q_0)$ the Hamiltonian. We assume the particle has unit mass and take the Boltzmann constant equal to unity.

The spectral distribution of the correlation function (7) is given by

$$S_{g,g}(\Omega)=\frac{1}{\pi}\,{\rm Re}\int_0^\infty dt e^{i\Omega t}\langle g[q(t)]g^*[q_0]\rangle \ . \tag{8}$$

In the special case $g[q(t)]=e^{ikq(t)}$, Eqs. (7) and (8) yield the intermediate scattering function $F(k,t)$ and the dynamic structure factor, respectively. We now make the transformation $(p,q)\rightarrow(E,\Psi)$ to energy and phase variables. The intermediate scattering function then reads

$$F(k,t)=\int_0^\infty dE\int_0^{2\pi} d\Psi e^{ikq(E,\Psi)}P(E,\Psi;t) \ , \tag{9}$$

where the function

$$P(E,\Psi;t)=\frac{1}{\omega(E)Z}\int dq_0dp_0e^{-ikq_0}W[p(E,\Psi),q(E,\Psi),t|p_0,q_0,0]e^{-E(p_0,q_0)/T} \tag{10}$$

is, apart from the factor $[\omega(E)]^{-1}$, the average of the transition probability density times $\exp(-ikq_0)$ over the initial conditions. Here $\omega(E)$, the energy-dependent oscillation frequency in the absence of noise, is the inverse of the transformation Jacobian.

An equation for W that incorporates the simultaneous influences of potential and stochastic forces on the scatterer motion is the Fokker-Planck (or Kramers) equation,[13,15]

$$\frac{\partial W}{\partial t}=-p\frac{\partial W}{\partial q}+\frac{\partial U}{\partial q}\frac{\partial W}{\partial p}+\Gamma\frac{\partial}{\partial p}\left[p+T\frac{\partial}{\partial p}\right]W\ , \tag{11}$$

where $U(q)$ is the potential energy and Γ is the friction coefficient. The time-dependent correlation function, Eq. (7), can be rewritten as

$$\langle g[q(t)]g^*[q_0\rangle=\int dqdpg[q]\hat{W}(p,q;t)\ , \tag{12}$$

where the function

$$\hat{W}(p,q;t)=\frac{1}{Z}\int dq_0dp_0g^*[q_0]W(p,q,t|p_0,q_0,0)e^{-H(p_0,q_0)/T}\ , \tag{13}$$

satisfies the same Fokker-Planck equation as W. From Eq. (6) it is clear that the initial condition for $\hat{W}$ is

$$\hat{W}(p,q,0)=\frac{1}{Z}g^*[q]e^{-H(p,q)/T}\ . \tag{14}$$

Since we are interested in the low-friction case, for which the energy changes very little during an oscillation, we make the transformation $(p,q)\rightarrow(E,\Psi)$. The derivatives in Eq. (11) are transformed according to the rules[9]

$$\frac{\partial}{\partial p}\rightarrow p\frac{\partial}{\partial E}-\omega(E)q_E\frac{\partial}{\partial\Psi} \tag{15}$$

and

$$\frac{\partial}{\partial q}\rightarrow\frac{\partial U}{\partial q}\frac{\partial}{\partial E}+\frac{\omega(E)}{p}\left[1-q_E\frac{dU}{dq}\right]\ , \tag{16}$$

where $q_E=\partial q/\partial E$. The Fokker-Planck equation for $\hat{W}(E,\Psi)$ reads

$$\frac{\partial\hat{W}}{\partial t}=-\omega(E)\frac{\partial\hat{W}}{\partial\Psi}+2\Gamma L\hat{W}\ , \tag{17}$$

with

$$L=\left[p\frac{\partial}{\partial E}-\omega(E)q_E\frac{\partial}{\partial\Psi}\right]\times\left[p\left[1+T\frac{\partial}{\partial E}\right]-T\omega(E)q_E\frac{\partial}{\partial\Psi}\right]\ . \tag{18}$$

We could have also derived Eq. (17) by first transforming the usual Langevin equation pair for the variables p and q into a pair of Langevin equations for E and Ψ,[9] and then evaluating the corresponding Kramers-Moyal coefficients.[15] For future reference we give the Langevin equation for the energy

$$\dot{E}=-2\Gamma p^2+pf(t)\ , \tag{19}$$

where $f(t)$ is the stochastic force.

Since the functions $P(E,\Psi)$, $q(E,\Psi)$ and, consequently, $\hat{W}(E,\Psi;t)$ are periodic in Ψ, we follow Refs. 7 and 8 and expand $\hat{W}$ in a Fourier series,

$$\hat{W}(E,\Psi;t)=\sum_{m=-\infty}^{\infty}W_m(E,t)e^{im\Psi}\ . \tag{20}$$

From Eqs. (17) and (20) we obtain a set of coupled equations for the W_m's,

$$\frac{\partial W_m}{\partial t}+im\omega(E)W_m=2\Gamma\sum_n L_{mn}W_n\ , \tag{21}$$

where

$$L_{mn}=\frac{1}{2\pi}\int_0^{2\pi}d\Psi e^{-im\Psi}Le^{in\Psi}\ . \tag{22}$$

We have made no approximations up to this point. For low friction, i.e., $\Gamma\ll\omega(E)$ for all E that are likely to be visited at a given temperature ($E\lesssim T$), there is little mixing between the different components W_m. We can then uncouple Eqs. (21) and analyze each component separately. In the following, we will consider the region $\Omega\ll\omega(E)$, for which only the $m=0$ component contributes.

The probability density in (E,Ψ) space is given by

$$P(E,\Psi)=\frac{1}{\omega(E)}\hat{W}(E,\Psi)\ . \tag{23}$$

To investigate the behavior of $S_{g,g}(\Omega)$ in the quasielastic region, it suffices to know the zeroth-order component of $P(E,\Psi)$, $P_0(E)$, which, after the uncoupling of Eqs. (21), can be shown to satisfy the continuity equation,

$$\frac{\partial P_0}{\partial t}(E,t)+\frac{\partial j}{\partial E}(E,t)=0\ . \tag{24}$$

The current density j along the energy axis is given by

$$j(E,t)=-2\Gamma\frac{\overline{p^2}(E)}{\omega(E)}\left[1+T\frac{\partial}{\partial E}\right]\omega(E)P_0(E,t)\ . \tag{25}$$

Note that the effects of the potential $U(q)$ appear only through the frequency $\omega(E)$ and the average of the kinetic energy over a cycle,

$$\overline{p^2}(E)=\frac{1}{2\pi}\int_0^{2\pi}d\Psi p^2(E,\Psi)\ . \tag{26}$$

These two magnitudes are related by the equation

$$\overline{p^2}(E)=\omega(E)\int_0^E \frac{dE'}{\omega(E')} . \tag{27}$$

The current density, Eq. (25), satisfies the boundary conditions

$$j(0,t)=j(\infty,t)=0 , \tag{28}$$

if the energy origin is chosen so that the potential minimum is at $E=0$. If the potential has two or more minima, it can be separated into domains.[3,16,17] In this case, we must impose the condition that the current is continuous across the domain-separating energies.

With expansion (20) and the uncoupling approximation, we can express the intermediate scattering function, Eq. (1), as the superposition

$$F(k,t)=\sum_{m=-\infty}^{\infty} F_m(k,t) , \tag{29}$$

where

$$F_m(k,t)=\int_0^\infty dE \frac{W_m(E,t)}{\omega(E)} \int_0^{2\pi} d\Psi e^{ikq(E,\Psi)} e^{im\Psi} , \tag{30}$$

with $q(E,\Psi)$ being the solution to the Hamiltonian equation of the motion. In particular, $F_0(k,t)$ is precisely the result obtained heuristically in Sec. II. The quasielastic component of the dynamic structure factor can be obtained by substituting $F_0(k,t)$ into Eq. (8),

$$S_0(k,\Omega)=\frac{1}{\pi}\,\mathrm{Re}\int_0^\infty dt\, e^{i\Omega t} F_0(k,t) . \tag{31}$$

In the following section we analyze the differential equation satisfied by the probability density component P_0.

IV. THE DIFFUSION EQUATION IN ENERGY SPACE

The differential equation for the probability density component $P_0(E,t)$,

$$\frac{\partial P_0}{\partial t}-\frac{\partial}{\partial E}\left[2\Gamma\frac{\overline{p^2}}{\omega}\left[1+T\frac{\partial}{\partial E}\right]\omega P_0\right]=0 , \tag{32}$$

describes, as it was first pointed out by Kramers,[13] diffusion along the E coordinate. Together with the boundary conditions (28), it contains the information we need for our analysis of the quasielastic region. An equation of this type was also obtained by Carmeli and Nitzan in their theory of non-Markovian activated rate processes.[14] The initial condition for P_0 can be obtained from Eqs. (14), (20), and (23). These yield

$$P_0(E,0)=\frac{1}{2\pi\omega(E)Z}\int_0^{2\pi} d\Psi g^*[q(E,\Psi)]e^{-E/T} . \tag{33}$$

The equilibrium solution of Eq. (32) is

$$P_{\mathrm{eq}}(E)=\frac{1}{\omega(E)Z}e^{-E/T} . \tag{34}$$

Conditions (28) ensure that this is the only allowed steady-state solution. To investigate its nonequilibrium solutions, it is convenient to rewrite Eq. (32) in the Sturm-Liouville form.[18] Defining

$$P_0(E,t)=e^{\lambda t}y(E) , \tag{35}$$

$$A(E)=2\Gamma T\overline{p^2}(E) , \tag{36}$$

and

$$B(E)=2\Gamma\overline{p^2}(E)\left[1+\frac{T}{\omega}\frac{d\omega}{dE}\right] , \tag{37}$$

Eq. (32) is transformed into

$$Ky(E)=\lambda y(E) \tag{38}$$

with

$$K=\frac{d}{dE}\left[A(E)\frac{d}{dE}+B(E)\right] \tag{39}$$

being a self-adjoint operator in the sense that

$$\int_0^\infty dE G(E)y_1(E)Ky_2(E) = \int_0^\infty dE G(E)y_2(E)Ky_1(E) . \tag{40}$$

In order to satisfy Eq. (40) and the boundary conditions (28), the weight function $G(E)$ must be chosen as

$$G(E)=\exp\left[\int_0^E dx\, A^{-1}(x)B(x)\right] =\frac{1}{\omega(0)ZP_{\mathrm{eq}}(E)} . \tag{41}$$

We remark that the low-energy limit $\omega(0)$ of the oscillation frequency must be finite. We will therefore require that the potential bottom be harmonic, a condition generally satisfied by physically meaningful potentials. Condition (40) ensures the orthogonality of solutions corresponding to different values of λ.

It is interesting to observe that the current density, Eq. (25), can be decomposed into diffusive (j_d) and drift (j_f) components,

$$j_d=-D(E)\frac{\partial P_0}{\partial E} \tag{42}$$

and

$$j_f=V(E)P_0 , \tag{43}$$

where the magnitude of the energy-dependent diffusion coefficient,

$$D(E)=2\Gamma T\overline{p^2}(E) , \tag{44}$$

increases with the average kinetic energy and the frictional forces. The magnitude of the "drift velocity,"

$$V(E)=-2\Gamma\overline{p^2}(E)\left[1+\frac{T}{\omega}\frac{d\omega}{dE}\right] , \tag{45}$$

can become very large in energy regions where $|d\omega/dE|$ is large and ω is small. This occurs at energies close to a rounded potential maximum. An example is the "ϕ^4" potential (see Fig. 1 in Ref. 2). The functions $D(E)$ and $V(E)$ control energy relaxation; both are proportional to the kinetic energy averaged over a cycle.

V. THE HARMONIC OSCILLATOR

In this section we consider the simple harmonic oscillator, for which Eq. (32) admits an exact analytical solution. This solution can be used as a starting point to treat the more complicated cases to be discussed in Sec. VI. The potential energy for the harmonic oscillator is

$$U(q)=\tfrac{1}{2}\omega_0^2 q^2 . \tag{46}$$

Some simple results follow easily,

$$\overline{p^2}=E , \tag{47}$$

$$q(E,\Psi)=\frac{(2E)^{1/2}}{\omega_0}\cos(\Psi) , \tag{48}$$

and

$$P_{\rm eq}(E)=\frac{e^{-E/T}}{2\pi T} . \tag{49}$$

Inserting Eq. (48) into Eq. (30) we see that $F_0(k,t)$ can be written as

$$F_0(k,t)=2\pi\int_0^\infty dE P_0(E,t)J_0\left[\frac{k}{\omega_0}\sqrt{2E}\right] , \tag{50}$$

where J_0 is a Bessel function of the first kind. We next calculate $P_0(E,t)$. Defining $\xi=-E/T$, Eq. (38) reads

$$\xi\frac{d^2y}{d\xi^2}+(1-\xi)\frac{dy}{d\xi}-\left[1-\frac{\lambda}{2\Gamma}\right]y=0 . \tag{51}$$

This is Kummer's equation, whose solutions are confluent hypergeometric functions. Eliminating the solution that does not satisfy regularity requirements at the origin and using Kummer's transformation[19] we find

$$y(E)\sim M(\lambda/2\Gamma,1,E/T)e^{-E/T} , \tag{52}$$

with M defined as in Ref. 19. If we further demand that the current density decays exponentially as $E/T\to\infty$, the allowed values of λ must be restricted to

$$\lambda_m=-2m\Gamma , \tag{53}$$

with m a non-negative integer. Other values of λ would imply an unphysical power-law decay of $j(E)$ as $E/T\to\infty$. [Note the inaccuracy of Eq. (13.1.4) in Ref. 19: M must be a polynomial if its first argument is a negative integer.] If $\lambda=-2m\Gamma$, the hypergeometric function reduces to a Laguerre polynomial, $M(-m,1,x)=L_m(x)$. The Laguerre polynomials are orthonormal, with the weight factor e^{-x}.

Since the weight function (41) required to satisfy the self-adjoint property is $G(E)=e^{E/T}$, the particular solutions of Eq. (51) must be chosen as

$$y_m(E)=T^{-1/2}L_m(E/T)e^{-E/T} . \tag{54}$$

These satisfy the normalization condition

$$\int_0^\infty dE y_m(E)y_n(E)G(E)=\delta_{mn} . \tag{55}$$

The probability density component P_0 can be expanded in terms of the set $\{y_m(E)\}$,

$$P_0(E,t)=\sum_{m=0}^\infty \gamma_m y_m(E)e^{\lambda_m t} , \tag{56}$$

where the coefficients γ_m are determined using the initial condition (33). After some algebra, we obtain

$$P_0(E,t)=\frac{1}{2\pi T}\sum_{m=0}^\infty \frac{\Theta^m}{m!}e^{-\Theta}e^{-E/T}L_m(E/T)e^{-2\Gamma mt} , \tag{57}$$

with $\Theta=(T/2)(k/\omega_0)^2$. The sum can be carried out exactly.[20] Using Eqs. (31) and (50) we obtain

$$S_0(k,\Omega)=e^{-2\Theta}\delta(\Omega)+\frac{e^{-2\Theta}}{\pi}\sum_{j=1}^\infty \frac{\Theta^{2j}}{j!}\frac{2j\Gamma}{(2j\Gamma)^2+\Omega^2} . \tag{58}$$

The first term in Eq. (58) is the elastic component, whose intensity is given by the Debye-Waller factor $e^{-2\Theta}$. The quasielastic component, which is formed by a superposition of Lorentzians of increasing width, is also affected by the Debye-Waller factor. There are a few points worth noting.

(1) If we take the $\Gamma\to 0$ limit, the quasielastic component disappears and we obtain the well-known result for the elastic component in the absence of friction.[21]

(2) The total intensity i_Q scattered in the quasielastic region can be obtained by integrating Eq. (58) over Ω. We obtain

$$i_Q=e^{-2\Theta}[I_0(2\Theta)-1] , \tag{59}$$

with I_0 being a modified Bessel function. By adding the elastic intensity in the presence of friction, $e^{-2\Theta}$, we recover the total elastic intensity in the absence of friction. The total quasielastic intensity i_Q is independent of Γ, since the quasielastic structure is associated with the disappearance of long-time correlations, which are destroyed by any nonzero value of Γ. What remains of the correlation as $t\to\infty$ is due to the confinement and does not depend on Γ. This residual correlation is responsible for what is left of the elastic component in the presence

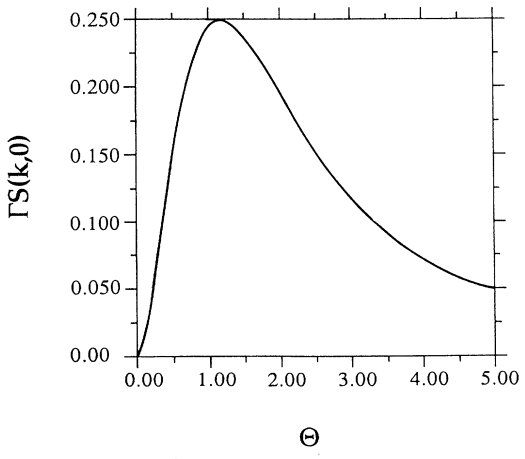

FIG. 1. Quasielastic peak height times the friction constant for the harmonic oscillator as a function of $\Theta=(T/2)(k/\omega_0)^2$.

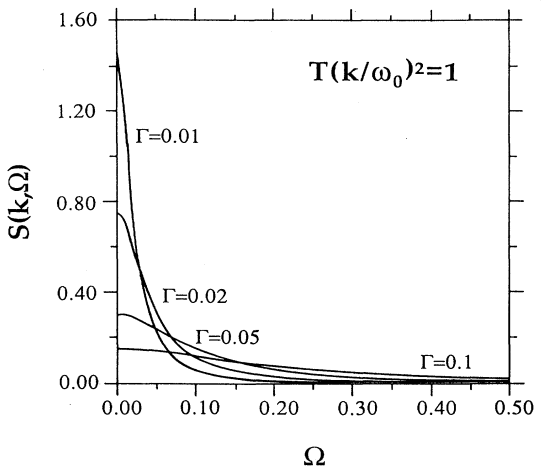

FIG. 2. Evolution of the quasielastic peak for the harmonic oscillator with increasing Γ. Here Θ=0.5 and the units are arbitrary.

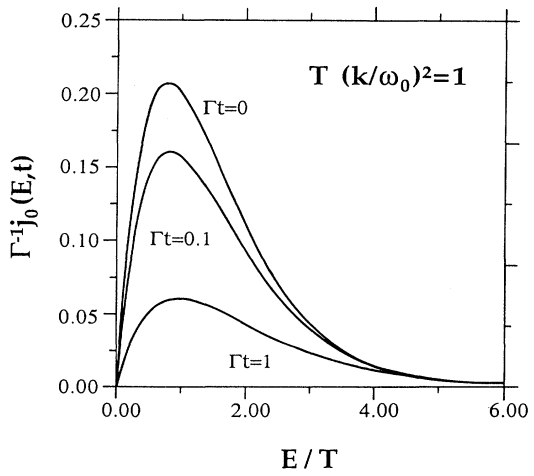

FIG. 4. Current density along the energy axis for the harmonic oscillator as a function of E/T. Here $\Theta=0.5$ and the times are indicated next to the corresponding curves.

of noise.

(3) The quasielastic peak height can be obtained directly from Eq. (58). It is plotted in Fig. 1. It goes to zero for very small and very large values of Θ, but shows a well-defined maximum at $\Theta\approx 1.1$.

The series (58) can be easily evaluated, even for large Θ. It is depicted in Fig. 2 for $\Theta=0.5$ and several values of Γ. We have used arbitrary units to show more clearly the rapid flattening of the peak with increasing Γ. In Fig. 3, we show the changes in the quasielastic peak shape with increasing Θ. Since we have plotted $\Gamma S(k,\Omega)$ vs Ω/Γ, this figure is valid for arbitrary values of Γ in the region $\Gamma \ll \omega_0$ [this condition guarantees the validity of the uncoupling of Eqs. (21)]. For small values of the temperature and the momentum transfer, i.e., for small values of Θ, a one-Lorentzian representation is sufficient: for $\Theta=0.2$ we get an accuracy better than 1% using a single Lorentzian. For higher values of T and k more Lorentzians are required, as it can be seen from Fig. 3 for the case $\Theta=2.5$.

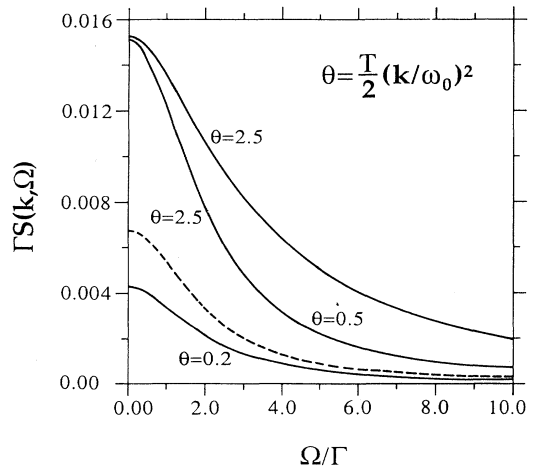

FIG. 3. Evolution of the quasielastic peak for the harmonic oscillator with increasing Θ as a function of the dimensionless variables Ω/Γ. The dashed line is the contribution of the leading Lorentzian for $\Theta=2.5$

By taking $\hbar\omega_0=k_B T$ we can estimate realistic values of Θ. If $T\sim 300$ K, $k=1$ (Å)$^{-1}\kappa$, and the effective mass of the scatterer is $M_e=NM_H$, where M_H is the mass of the hydrogen atom, $\Theta\approx 0.08\kappa^2/N$. For $N\sim 1$ and high values of the momentum transfer, say, $\kappa=8$, $\Theta\approx 5$ and many Lorentzians will be needed. For massive scatterers ($N\gg 1$) or low values of the momentum transfer ($\kappa\leq 2$), on the other hand, the one-Lorentzian approximation will generally suffice.

The present method permits the direct analysis of diffusion along the energy axis. Using Eq. (25), we obtain an analytical expression for the current density, $j(E,t)$, which turns out to be proportional to $\Gamma e^{-\Gamma t}$. This indicates that the current is driven by the frictional forces and that it decays exponentially at long times. The current density also decays exponentially at high energies. It is represented in Fig. 4 as a function of E/T for several values of the product Γt and $\Theta=0.5$. It is largest at $t=0$ and then decreases monotonously with time. The current density is responsible for the evolution of the probability density component $P_0(E,t)$ from its $t=0$ form (which corresponds to the undamped system) to its equilibrium value, $P_0(E,\infty)=P_{\rm eq}(E)$. The frictional forces provide the mechanism through which equilibrium is achieved.

VI. ANHARMONIC POTENTIALS

A. General solution method

In this section we will be concerned with arbitrary single-minimum, harmonically bottomed potentials. We

know from Sec. IV that our fundamental equation is self-adjoint in the sense of Eq. (40) for potentials in this class. Since the solution for purely harmonic potentials is given by a linear combination of Laguerre polynomials, it is natural to expand the solution for anharmonic potentials in terms of Laguerre polynomials. The harmonic-oscillator solution can thus be used as a benchmark for the analysis of anharmonic problems. We write the general solution to Eq. (38) in the form

$$y_\lambda(E)=\sum_{m=0}^{\infty}\frac{B_{\lambda,m}}{\sqrt{T}}\frac{\omega(0)}{\omega(E)}e^{-E/T}L_m(E/T)\ . \tag{60}$$

Substituting $y(E)$ into Eq. (38), using Laguerre's differential equation,[19] and remembering that the weight factor $G(E)=[\omega(E)/\omega(0)]e^{E/T}$ must be used for the inner product of the solutions, we obtain the system of algebraic equations,

$$\sum_{m=0}^{\infty}[\alpha_{nm}-\beta_{nm}-(\lambda/2\Gamma)\kappa_{nm}]B_{\lambda,m}=0 \tag{61}$$

with

$$\alpha_{nm}=m\int_0^\infty d\zeta\frac{e^{-\zeta}}{\zeta\omega(\zeta)}\left[1-\frac{\overline{p^2}}{T\zeta}-\frac{\overline{p^2}}{T}\right]L_n(\zeta)L_m(\zeta)\ , \tag{62}$$

$$\beta_{nm}=m\int_0^\infty d\zeta\frac{e^{-\zeta}}{\zeta\omega(\zeta)}\left[1-\frac{\overline{p^2}}{T\zeta}\right]L_n(\zeta)L_{m-1}(\zeta)\ , \tag{63}$$

and

$$\kappa_{nm}=\int_0^\infty d\zeta\frac{e^{-\zeta}}{\omega(\zeta)}L_n(\zeta)L_m(\zeta)\ . \tag{64}$$

Here $\zeta=E/T$. The allowed values of λ can be obtained by truncating the equation system and applying the compatibility condition. Once the λ's are determined, the coefficients B_m can be found with the usual methods of linear algebra. The next step is to write the probability density component as a linear combination of the allowed solutions y_λ,

$$P_0(E,t)=\sum_\lambda e^{\lambda t}\rho_\lambda y_\lambda(E)\ , \tag{65}$$

where the coefficients ρ_λ are determined using the initial condition, Eq. (33). We have therefore a program to compute the function $P_0(E,t)$ and, consequently, the intermediate scattering function and the dynamic structure factor. This program will be fully implemented in a separate publication.

Since $\alpha_{n0}=\beta_{n0}=0$, $\lambda=0$ (corresponding to the elastic line) is always a solution. A calculation of ρ_0 and $y_0(E)$ would then suffice to obtain the Debye-Waller factor.

From Eqs. (30), (31) and (65), we see that the quasielastic line can be expressed as a sum of Lorentzian components. This is not surprising, since these components arise from diffusional modes (see Sec. 6.2 and 7.6 in Ref. 2). In the rest of the paper we use Eq. (61) to obtain some general results for the width of the quasielastic Lorentzians.

B. Weakly anharmonic systems

We next seek an answer to the following question: What happens to the width of the quasielastic peak if a small anharmonic term is added to the potential in Eq. (46)? Let us try the symmetrical form

$$U(q)=\frac{\omega_0^2}{2}q^2+\frac{2\alpha\omega_0^4}{3}q^4\ . \tag{66}$$

If $\alpha>0$, the potential is "hardened" by the quartic term and the oscillation frequency $\omega(E)$ is an increasing function of E. If the anharmonic term is small, $|\alpha|T\ll 1$, we can write approximately[9,22]

$$\omega(E)\cong\omega_0(1+2\alpha E)\ . \tag{67}$$

Using Eq. (27) and eliminating terms of $O(\alpha^2)$ and higher, we readily find that the average of the square momentum over an orbit is

$$\overline{p^2}(E)\cong E(1+\alpha E)\ . \tag{68}$$

The matrix elements in Eq. (61) can now be easily calculated, and we obtain the following system:

$$\sum_{m=0}^{\infty}\left[\left[m(2m\alpha T-1)-\frac{\lambda}{2\Gamma}+\frac{(2m+1)\alpha T\lambda}{\Gamma}\right]\delta_{nm}-\alpha T\left[m(m-1)+\frac{m\lambda}{\Gamma}\right]\delta_{n,m-1}-\alpha T\left[m(m+1)+\frac{(m+1)\lambda}{\Gamma}\right]\delta_{n,m+1}\right]B_{\lambda,m}=0 \tag{69}$$

By keeping only terms with $m,n<3$, we find the following compatibility condition:

$$\left[\frac{\lambda}{2\Gamma}\right]^2+(3+16\alpha T)\left[\frac{\lambda}{2\Gamma}\right]+2(1+10\alpha T)=0\ . \tag{70}$$

The solutions to this equation, whose magnitudes yield directly the widths of the first Lorentzians in $S_0(k,\Omega)$, are

$$\begin{aligned}\lambda_0&=0\ ,\\ \lambda_1&=-2\Gamma(1+4\alpha T)\ ,\\ \lambda_2&=-4\Gamma(1+6\alpha T)\ .\end{aligned} \tag{71}$$

Of course, λ_0 corresponds to the elastic component.

From Eqs. (71) we find that the width of the quasielastic Lorentzians *increases* if a small positive anharmonic term is included in the potential. This broadening of the quasielastic peak is due to the speeding up of energy relaxation that takes place when the average kinetic energy is increased. According to the Langevin equation for the energy, Eq. (19), the frictional terms become more efficient with increasing p. Equations (44) and (45) also indicate that energy diffusion and drift are faster at higher values of the average kinetic energy.

In the approximation we used here, the orthonormal set of basis functions $\{y_\lambda\}$ is given by

$$y_0(E)=\frac{1-2\alpha E}{\sqrt{T}}e^{-E/T}L_0(E/T)\ , \tag{72}$$

$$y_1(E)=\frac{e^{-E/T}}{\sqrt{T}}[-2\alpha T L_0(E/T) +(1-2\alpha E)L_1(E/T) +2\alpha T L_2(E/T)]\ , \tag{73}$$

and

$$y_2(E)=\frac{e^{-E/T}}{\sqrt{T}}[-6\alpha T L_1(E/T) +(1-2\alpha E)L_2(E/T)]\ . \tag{74}$$

The function $P_0(E,t)$ can now be expanded in terms of these functions, the coefficients being determined from the initial conditions.

C. Strongly anharmonic system

As we mentioned in the Introduction, the soft-potential model has become an important tool in glass physics.[5,6] A key feature of these models is the frequency reduction at intermediate energies due to potential softening. The conventional forms for the potential can be used, but the resulting functions $\omega(E)$ and $\overline{p^2}(E)$ are exceedingly complicated. It is therefore convenient to model directly the frequency as a function of E. We choose the form

$$\omega(E)=\omega(0)\left[1-\frac{aE}{1+E^2}\right]\ , \tag{75}$$

with $0\le a\le 2$. If $a=0$, we recover the harmonic oscillator, but if $a\neq 0$, Eq. (75) corresponds to oscillations in a potential whose low- and high-energy regions are harmonic, but which exhibits a softening at intermediate energies. The magnitude of this softening and the ensuing energy reduction increases with growing a. With the units chosen in Eq. (75), $\omega(E)$ has a minimum at $E=E_M=1$. [We must avoid the $a\to 2$ limit, however, since $\omega(E)$ would then grow too slowly after vanishing at $E=1$. On the other hand, $\omega(E)=0$ would imply a zero range of validity for our approximation.]

Using Eq. (27), we can now calculate $\overline{p^2}(E)$. At first, this function decreases below the value corresponding to the harmonic oscillator: the softening of the potential corresponds to a decrease in the average kinetic energy which becomes stronger with increasing a. At higher values of E, $\overline{p^2}(E)$ grows faster than for the harmonic oscillator due to the hardening of the potential.

From our discussion in Sec. VI B, we expect that at low temperatures, i.e., $T\ll E_M$, the width of the quasielastic peak will decrease with increasing temperatures because the oscillator records the potential softening. At higher temperatures, i.e., $T\gtrsim E_M$, the peak width should grow as many oscillators in the ensemble record the potential hardening at $E>1$. That this is indeed the case can be seen from Fig. 5, where we show the widths of the first three Lorentzians as functions of the temperature. These widths were calculated following the procedure developed in Sec. VI A. The ratio between the initial slopes $|\lambda_2|$ and $|\lambda_1|$ is 3, in agreement with Eq. (71). This was to be expected, because at low temperatures the scatterer can only reach weakly anharmonic regions. The minimum width becomes more marked and shifts to lower temperatures with increasing order. Following a wide maximum, the Lorentzian widths decay to the harmonic-oscillator values at high temperatures (this is not shown in Fig. 5). Increasing the magnitude of a the curves preserve their general shapes, although the minima become deeper and the maxima higher.

The preceding argument indicates that a signature of a "softening" potential at low temperatures would be a narrowing of the quasielastic line when the temperature is increased at fixed momentum transfer. At high temperatures the line should widen with increasing temperature if the potential "hardens" again at high energies.

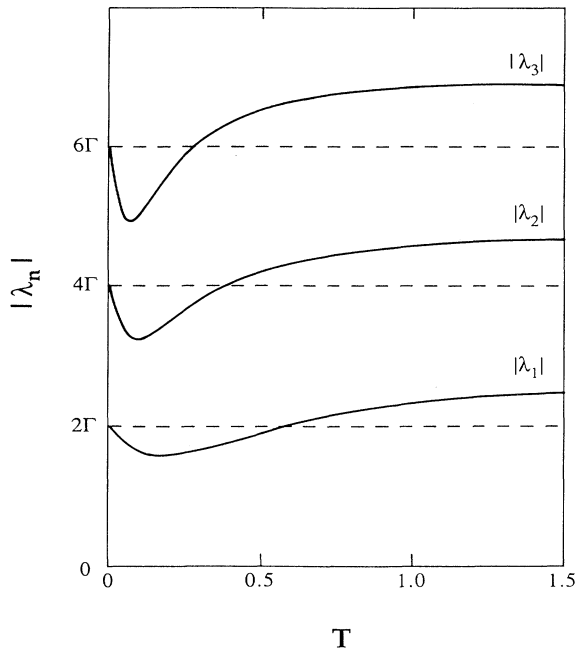

FIG. 5. Temperature dependence of the width of the first three Lorentzians for a strongly anharmonic potential. The energy dependence of the oscillation frequency is given by Eq. (75) with $a=1$. The dashed lines correspond to the widths for the harmonic problem of frequency $\omega(0)$.

Throughout the foregoing analysis we have assumed that the friction constant Γ is temperature independent. Since the eigenvalues scale with Γ, it would not be difficult to extend our discussion to cases for which Γ is a function of T. This could occur if the nature of the main fluctuating force changes as the temperature is raised.

VII. CONCLUSION

We have used a Fokker-Planck approach to analyze the quasielastic peak in the neutron-scattering cross section for harmonic and anharmonic oscillators subject to weak frictional forces. By solving a diffusion equation in energy space, we have been able to investigate the effects of anharmonicity on quasielastic linewidth. The procedure used in this paper is particularly illuminating concerning the physics underlying the generation of the quasielastic peak by the addition of stochasticity. Our results may contribute to a better understanding of the phenomena investigated by quasielastic neutron-scattering experiments.

Although we have discussed our work in the context of local motions in glasses, our results could be applied to other systems for which local motions are relevant (e.g., zeolites and other porous materials[2]).

ACKNOWLEDGMENTS

Financial assistance by the Deutsche Forschungsgemeinschaft through the Sonderforschungbereich 306 is gratefully acknowledged. This research was also supported by the Research Corporation and by the National Science Foundation through Grant No. HRD-9450342. C.A.C. wishes to thank the Fakultät für Physik of the Universität Konstanz for its hospitality.

[1] *Dynamics of Disordered Materials,* Proceedings of the International Workshop, Grenoble, 1993, edited by A. J. Dianoux, W. Petry, and D. Richter (North-Holland, Amsterdam, 1993), reprinted from Physica A **201**, No. 1-3 (1993).

[2] M. Bée, *Quasielastic Neutron Scattering* (Hilger, Bristol, 1988).

[3] C. A. Condat and J. Jäckle, Phys. Rev. B **46**, 8154 (1992).

[4] U. Buchenau, M. Prager, N. Nücker, A. J. Dianoux, N. Ahmad, and W. A. Phillips, Phys. Rev. B **34**, 5665 (1986).

[5] M. I. Klinger, Phys. Rep. **165**, 275 (1988).

[6] U. Buchenau, Europhys. News **24**, 77 (1993).

[7] K. Bhattacharya, U. Buchenau, and K. W. Kehr, Phys. Rev. B **49**, 8696 (1994).

[8] M. I. Dykman, R. Mannella, P. V. E. McClintock, S. M. Soskin, and N. G. Stocks, Phys. Rev. A **43**, 1701 (1991), and references therein.

[9] S. M. Soskin, Physica A **155**, 401 (1989).

[10] W. Dieterich, I. Peschel, and W. R. Schneider, Z. Phys. B **27**, 177 (1977).

[11] W. Dieterich, T. Geisel, and I. Peschel, Z. Phys. B **29**, 5 (1978).

[12] F. Volino and A. Dianoux, Ann. Phys. **3**, 151 (1978).

[13] H. A. Kramers, Physica **VII**, 284 (1940).

[14] B. Carmeli and A. Nitzan, Phys. Rev. A **32**, 2439 (1985).

[15] H. Risken, *The Fokker-Planck Equation,* 2nd ed. (Springer-Verlag, Berlin, 1989).

[16] T. Matsubara, Prog. Theor. Phys. **48**, 351 (1972).

[17] C. A. Condat and J. Jäckle, J. Phys. A **24**, 985 (1991).

[18] E. C. Titchmarsh, *Eigenfunction Expansions,* 2nd ed. (Oxford University Press, Oxford, 1962).

[19] *Handbook of Mathematical Functions,* edited by M. Abramowitz and I. Stegun (Dover, New York, 1965).

[20] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series and Products* (Academic, San Diego, 1979).

[21] G. H. Vineyard, Phys. Rev. **110**, 999 (1958).

[22] L. D. Landau and E. M. Lifshitz, *Mechanics* (Pergamon, Oxford, 1960).