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AN EXACTLY SOLVABLE MODEL FOR BROWNIAN MOTION

III. MOTION OF A HEAVY MASS IN A LINEAR CHAIN

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Synopsis

The theory on Brownian motion, developed in previous papers[1] [2] is applied to a linear chain with harmonic coupling between nearest neighbours. All masses are equal except for one which is heavy compared to the others. This heavy particle behaves as a Brownian particle, which is not subject to an external field. The Langevin equation and the Fokker-Planck equation are derived for the classical and quantummechanical case, again without applying perturbation theory. It turns out that in addition to the transient times there exists a time τ_l, beyond which these equations loose their validity. This limit time is due to the fact that the frequency spectrum has a finite maximum.

1. *Introduction.* In the present paper the theory on Brownian motion, developed in recently published papers[1] [2] (hereafter quoted as I and II) will be applied to a special system, consisting of a linear chain with one heavy mass. This can be considered as a model for an impurity in a crystal. With respect to irreversibility this system has already been studied extensively in the classical case by Hemmer[3]), Rubin[4]), Takeno and Hori[5]), and Turner[6]). We will extend the treatment to quantummechanics and will show the existence of a quantumstatistical transient time (sects. 6 and 8).

Since the system is invariant for translations there exists a normal mode with zero frequency. Moreover, the strength function of the system is sharply cut off. Both these features make it necessary to modify the expressions for the evolution functions $A(t)$ and $A_n(t)$ from sect. I.5. The calculation of these functions (sect. 4) shows that they do not exhibit exponential behaviour for infinitely large times. This has been remarked by Hemmer[3]) and Takeno and Hori[5]). We shall find the same result and, moreover, the time region for which the process is Markoffian. In sect. 5 it will be shown that under similar conditions as given in sect. I.9 the heavy mass satisfies the Langevin equation of a free particle (free means: without external field) both in the classical and in the quantummechanical case. The joint distribution function of momentum and displacement is calculated in sect. 6. It satisfies the Fokker-Planck equation for a free particle. Furthermore, the familiar F.-P. equation for the distribution function of the momentum is derived. For times large compared to the relaxation time of the momentum it turns out that the diffusion equation holds, as was to be expected.

In the quantummechanical case we have derived a master equation for the distribution function of the momentum of the heavy mass under similar conditions as in sect. II.7 (sect. 7).

2. *Transformation of the Hamiltonian.* The Hamiltonian of the linear chain is given by

$$H = \sum_{-N}^{+N} \frac{p_i'^2}{2m_i} + \frac{\alpha}{2} \sum_{-N}^{N-1} (q_{i+1}' - q_i')^2, \tag{1}$$

where $m_i = m$ for $i \neq 0$, and $m_0 = M$. This Hamiltonian is semi-positive definite and invariant for translations. To transform eq. (1) to the form (I.1) the Hamiltonian is written as

$$H = H_- + H_0 + H_+, \tag{2}$$

where

$$\begin{aligned} H_\pm &= \sum_1^N \frac{p_{\pm i}'^2}{2m} + \frac{\alpha}{2} \sum_1^{N-1} (q_{\pm i\pm 1}' - q_{\pm i}')^2 + \frac{\alpha}{2} q_{\pm 1}'^2, \\ H_0 &= \frac{p_0'^2}{2M} + \alpha q_0'^2 - \alpha q_0'(q_1' + q_{-1}'). \end{aligned} \tag{3}$$

Now H_- and H_+ can be transformed to a diagonal form. As the momenta are already in diagonal form we have only to apply a linear transformation,

$$p_{\pm i}' = \sum t_{\pm i, \pm l} p_{\pm l}'', \quad q_{\pm i}' = \sum t_{\pm i, \pm l} q_{\pm l}'', \qquad 1 \leqslant l \leqslant N. \tag{4}$$

Solving the corresponding eigenvalue problem one obtains

$$t_{i,l} = t_{-i,-l} = \frac{2}{\sqrt{2N+1}} \sin\left(i \frac{2l-1}{2N+1} \pi\right), \qquad \begin{matrix} 1 \leqslant i \leqslant N, \\ 1 \leqslant l \leqslant N, \end{matrix} \tag{5}$$

and for the corresponding eigenvalues λ,

$$\lambda_l = \lambda_{-l} = 4 \sin^2 \frac{2l-1}{2(2N+1)} \pi, \qquad 1 \leqslant l \leqslant N. \tag{6}$$

After the subsequent transformation

$$\begin{aligned} m^{-\frac{1}{2}} p_i'' &= p_i, \quad m^{\frac{1}{2}} q_i'' = q_i, \\ M^{-\frac{1}{2}} p_0' &= P, \quad M^{\frac{1}{2}} q_0' = Q, \end{aligned} \tag{7}$$

we get the familiar Hamiltonian (I.1),

$$H = \tfrac{1}{2}(P^2 + \Omega^2 Q^2) + \sum_{i \neq 0} \tfrac{1}{2}(p_i^2 + \omega_i^2 q_i^2) + \sum_{i \neq 0} \varepsilon_i q_i Q, \tag{8}$$

where

$$\Omega^2 = \frac{2\alpha}{M}, \quad \omega_i^2 = \omega_0^2 \sin^2 \frac{2\,|i| - 1}{2(2N + 1)}\,\pi, \quad \omega_0^2 = \frac{4\alpha}{m}, \tag{9}$$

$$\varepsilon_i = -\alpha (mM)^{-\frac{1}{2}}\, t_{1,|i|}. \tag{10}$$

One verifies easily that

$$\sum_i \varepsilon_i^2 \omega_i^{-2} = \Omega^2, \tag{11}$$

which implies that eq. (I.16) has a root $z = 0$. This corresponds to the fact that the system is invariant for translations.

3. *Strength function* $\gamma(\omega)$. In the approximation of a continuous spectrum the density of the frequencies is

$$\rho(\omega) = \frac{\mathrm{d}i}{\mathrm{d}\omega} = \pi^{-1}(2N + 1)(\omega_0^2 - \omega^2)^{-\frac{1}{2}}. \tag{12}$$

Counting the frequencies ω_i for $i < 0$ negative we have

$$\int_{-\omega_0}^{+\omega_0} \mathrm{d}\omega\, \rho(\omega) = 2N + 1,$$

which gives the total number of oscillators. (Clearly in this limit the oscillator at $i = 0$ is also counted). Simple calculation yields

$$\varepsilon^2(\omega) = (2N + 1)^{-1}\, \mu\omega^2(\omega_0^2 - \omega^2), \qquad |\omega| \leqslant \omega_0, \tag{13}$$

where

$$\mu = m/M. \tag{14}$$

Now the strength function $\gamma(\omega)$ becomes (cf. eq. (I.24))

$$\begin{aligned} \gamma(\omega) = \varepsilon^2(\omega)\, \rho(\omega) &= \pi^{-1}\mu\omega^2(\omega_0^2 - \omega^2)^{\frac{1}{2}}, \qquad &|\omega| \leqslant \omega_0, \\ &= 0, &|\omega| > \omega_0. \end{aligned} \tag{15}$$

The condition (I.25) is fulfilled,

$$\int_{-\omega_0}^{+\omega_0} \omega^{-2} \gamma(\omega)\, \mathrm{d}\omega = \Omega^2. \tag{16}$$

Since the equality holds the equation (cf. eq. (I.16))

$$G(z) = 0 \tag{17}$$

has a root $z = 0$. This means that the summation formulae from app. II.A cannot be applied. Furthermore, the frequency spectrum is sharply cut off so that the contour around the poles of $G^{-1}(s^2)$ cannot be transformed into a contour enclosing the upper half s-plane, (cf. sect. I.5). Therefore $\dot{A}(t)$ and $\dot{A}_n(t)$ must be calculated separately.

The secular function $G(z)$ is here defined by

$$G(z) = z - \Omega^2 - \int_{-\omega_0}^{+\omega_0} \frac{\gamma(\omega)}{z - \omega^2}\, d\omega. \tag{18}$$

$G(z)$ has a cut on R_+ from zero to ω_0^2. One easily verifies that $\gamma(\omega)$ satisfies the Hölder condition so that $G(z)$ takes limiting values at the edges of the cut,

$$G_\pm(x) = (1 - \mu)\, x \pm i\mu\sqrt{x(\omega_0^2 - x)}. \tag{19}$$

4. *Calculation of $\dot{A}(t)$ and $\dot{A}_n(t)$*. As in eq. (I.21) one writes

$$\dot{A}(t) = \frac{1}{2\pi i} \oint_C \frac{\cos\sqrt{z}t}{G(z)}\, dz, \tag{20}$$

where the contour encircles the cut in the z-plane. In the limit of a continuous spectrum this can be rewritten,

$$\dot{A}(t) = \frac{1}{2\pi i} \int_0^{\omega_0^2} \cos\sqrt{x}t \left(\frac{1}{G_-(x)} - \frac{1}{G_+(x)}\right) dx. \tag{21}$$

Substituting eq. (19) and replacing x by s^2 one gets

$$\dot{A}(t) = \frac{\mu}{\pi} \int_{-\omega_0}^{+\omega_0} e^{ist} \frac{\sqrt{\omega_0^2 - s^2}}{(1 - 2\mu)\, s^2 + \mu^2\omega_0^2}\, ds. \tag{22}$$

This integral can be calculated by extending the integration path to the contour C' in fig. 1.

One then has

$$\dot{A}(t) = \frac{\mu}{\pi} \oint_{C'} \frac{\sqrt{\omega_0^2 - s^2}}{(1 - 2\mu)\, s^2 + \mu^2\omega_0^2}\, e^{ist}\, ds - R(t), \tag{23}$$

where $R(t)$ denotes the correction due to the contribution of the added vertical paths. If $\mu < \frac{1}{2}$, contour integration yields for the integral

$$\frac{1 - \mu}{1 - 2\mu} \exp\left(-\frac{\mu}{\sqrt{1 - 2\mu}}\, \omega_0 t\right). \tag{24}$$

Now $\dot{A}(t)$ is in good approximation given by

$$\dot{A}(t) = \exp(-\mu\omega_0 t), \tag{25}$$

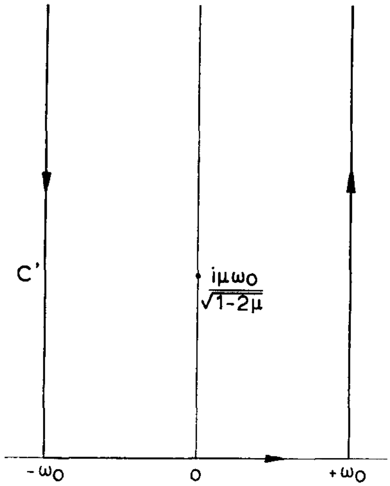

Fig. 1. Integration path C'. See eq. (23).

if both $R(t)$ and higher order terms in μ are neglected. We shall estimate the time region for which eq. (25) is valid. Therefore we must investigate the time behaviour of $R(t)$. For $\omega_0 t \gg 1$ $R(t)$ is well approximated by

$$R(t) \simeq -\mu \sqrt{\frac{2}{\pi}} \, \frac{\sin(\omega_0 t - \pi/4)}{(\omega_0 t)^{\frac{3}{2}}}, \tag{26}$$

where higher order terms in μ are again neglected. Thus $R(t)$ is for $t \gg \omega_0^{-1}$ an oscillating function and tends to zero. As the exponential tends more rapidly to zero than $(\omega_0 t)^{-\frac{3}{2}}$ there exists a time τ_l' such that ($\mu \ll 1$)

$$\dot{A}(t) \simeq -R(t) \simeq \mu \sqrt{\frac{2}{\pi}} \, \frac{\sin(\omega_0 t - \pi/4)}{(\omega_0 t)^{\frac{3}{2}}}, \qquad \begin{array}{l} \omega_0 t \gg 1, \\ t \gg \tau_l'. \end{array} \tag{27}$$

This time is defined by

$$\exp(-\mu\omega_0 \tau_l') = \frac{\mu}{(\omega_0 \tau_l')^{\frac{3}{2}}}, \tag{28}$$

which yields roughly

$$\tau_l' = \frac{5}{2\mu\omega_0} \ln \frac{1}{\mu}. \tag{29}$$

We must remark that in contradiction to the model of the electron in an electromagnetic field (cf. sect. I.6) here the time region for the validity of the exponential behaviour is restricted for large times, owing to the fact that the strength function is sharply cut off. Summarizing we conclude

$$\ddot{A} + \mu\omega_0 \dot{A} = 0, \qquad \frac{1}{\omega_0} \ll t \ll \tau_l'. \tag{30}$$

From eq. (25) one easily finds the expressions for $\ddot{A}(t)$ and $\dddot{A}(t)$ by differentiating. One convinces oneself readily that

$$A(t) = \sum_{\nu} X_{0\nu}^2 s_\nu^{-1} \sin s_\nu t \tag{31}$$

exists, and can be calculated by integrating $\dot{A}(t)$ under the condition that $A(0) = 0$. One gets

$$A(t) = (\mu\omega_0)^{-1} (1 - \exp(-\mu\omega_0 t)). \tag{32}$$

The existence of a zero frequency has the effect that

$$\mathring{A}(t) = \sum X_{0\nu}^2 s_\nu^{-2} \cos s_\nu t \tag{33}$$

does not exist. In calculations, however, one encounters the expression

$$\sum' X_{0\nu}^2 s_\nu^{-2} \cos s_\nu t, \tag{34}$$

where the prime indicates that the zero frequency is excluded. In app. A the sum (34) is calculated,

$$\sum' X_{0\nu}^2 s_\nu^{-2} \cos s_\nu t = -(\mu\omega_0)^{-1}\{t - (\mu\omega_0)^{-1}(1 - \exp(-\mu\omega_0 t))\} + \\ + \tfrac{1}{2} X_{00}^2 t^2 + \sum' X_{0\nu}^2 s_\nu^{-2}. \tag{35}$$

Clearly the eqs. (32) and (35) are approximations in lowest order of μ and valid for

$$\tau_t \ll t \ll \tau_l'. \tag{36}$$

The calculation of

$$\mathring{A}_n(t) = \frac{1}{2\pi i} \oint_C \frac{\cos\sqrt{z}t}{(z - \omega_n^2)\, G(z)}\, \mathrm{d}z, \tag{37}$$

is similar to that of $\mathring{A}(t)$. In an analogous way one finds (cf. also sect. I.5).

$$\mathring{A}_n(t) = \frac{\mu}{\pi} \varepsilon_n \oint_{C'}^{+} \frac{\sqrt{\omega_0^2 - s^2}}{\{(1 - 2\mu)\, s^2 + \mu^2\omega_0^2\}(s^2 - \omega_n^2)}\, \mathrm{e}^{ist}\, \mathrm{d}s + \\ + \frac{\varepsilon_n}{2}\left(\frac{\mathrm{e}^{i\omega_n t}}{G_-(\omega_n^2)} + \frac{\mathrm{e}^{-i\omega_n t}}{G_+(\omega_n^2)}\right) - R_n(t). \tag{38}$$

The $+$-sign means that the contour passes the poles $s = \pm\omega_n$ in the upper half plane. The integral in eq. (38) satisfies, as $\mathring{A}(t)$, eq. (30). The second term represents undamped oscillations. Furthermore, investigation of the time behaviour of $R_n(t)$ shows that this term can be neglected for times t which satisfy the inequality

$$\frac{1}{\omega_0} \ll t \ll \tau_l, \tag{39}$$

with

$$\tau_l = \tfrac{3}{2}(\mu\omega_0)^{-1} \ln \mu^{-1}. \tag{40}$$

Thus we may conclude that in the case of the linear chain the time region for which the decay terms and oscillating terms are good approximations of $A(t)$ and $A_n(t)$ and their derivatives, is restricted by the condition (39).

Summarizing we conclude that there exist three time scales

1. transient time, $\tau_t = \omega_0^{-1}$,
2. relaxation time, $\tau_r = \gamma^{-1} = (\mu\omega_0)^{-1}$,
3. limit time, $\tau_l = \tfrac{3}{2}(\mu\omega_0)^{-1} \ln \mu^{-1}$.

These times satisfy the relation

$$\frac{\tau_l}{\tau_r} = \tfrac{3}{2} \ln \frac{\tau_r}{\tau_t}, \tag{41}$$

which shows that with the ratio of the relaxation time and transient time also the ratio of the limit time and relaxation time increases.

5. *The Langevin equation.* Applying the results and methods from the previous section and the sects. I.9 and I.10 one may write the Langevin equation for the heavy particle of the linear chain as

$$\ddot{Q} + \gamma\dot{Q} = F(t), \quad \tau_t \ll t \ll \tau_l, \tag{42}$$

with

$$F(t) = \sum_i \{(\dddot{A}_i + \gamma\ddot{A}_i)\, q_i(0) + (\ddot{A}_i + \gamma\dot{A}_i)\, p_i(0)\}. \tag{43}$$

$F(t)$ satisfies the equations

$$\langle F(t)\rangle = 0, \tag{44}$$

and

$$\Phi_F(\tau) = \langle F(t)\, F(t+\tau)\rangle =$$

$$= \frac{2\mu}{1-2\mu}\,\frac{1}{\pi}\int_0^{\omega_0} \mathrm{d}\omega\, \sqrt{\omega_0^2 - \omega^2}\,E(\omega, T)\cos\omega\tau, \qquad \tau_t \ll t \ll \tau_l. \tag{45}$$

The average is taken over the bath of small oscillators, represented by the frequencies ω_i. The bath, i.e. the linear chain without the heavy particle, is supposed to be in thermal equilibrium at $t = 0$.

Let us first consider the classical case, $E(\omega, T) = kT$. Then eq. (45) is reduced to

$$\Phi_F(\tau) = \frac{\gamma\omega_0}{1-2\mu}\,\frac{kT}{2}\,[J_0(\omega_0\tau) + J_2(\omega_0\tau)], \qquad \tau_t \ll t \ll \tau_l, \tag{46}$$

where J_n represent the ordinary Bessel functions. Obviously, $\Phi_F(\tau)$ is not a narrow peaked and damped function as we found in eq. (I.85). For

$\tau \gg \omega_0^{-1}$ it behaves as

$$\frac{\gamma\omega_0}{1-2\mu}\,kT\,\frac{2}{\pi}\,\frac{\sin(\omega_0\tau-\pi/4)}{(\omega_0\tau)^{\frac{3}{2}}}\,. \tag{47}$$

Due to these oscillations the main contribution to the integral $\int_{-\infty}^{+\infty}\Phi_F(\tau)\,d\tau$ comes from the region $(-\omega_0^{-1}, +\omega_0^{-1})$, so that the assumption in conventional theories that $\Phi_F(\tau)$ can be replaced by a δ-function,

$$\Phi_F(\tau) = 2\gamma kT\delta(\tau), \tag{48}$$

is reasonable only with respect to functions which vary slowly over regions with a length ω_0^{-1}.

Solving eq. (42) exactly one obtains for the mean kinetic energy

$$\frac{\langle P^2(t)\rangle}{2} = \frac{P^2(0)}{2}\,e^{-2\gamma t} + \frac{e^{-2\gamma t}}{2}\int_0^t d\zeta\int_0^t d\zeta'\,\Phi_F(\zeta-\zeta')\,e^{\gamma(\zeta+\zeta')}, \qquad \tau_t \ll t \ll \tau_l. \tag{49}$$

Substituting eq. (45) into this equation one obtains after a simple calculation for the second term

$$\frac{\mu}{2(1-2\mu)}\,\frac{kT}{\pi}\,e^{-2\gamma t}\int_{-\omega_0}^{+\omega_0} d\omega\,\frac{\sqrt{\omega_0^2-\omega^2}}{\omega^2+\gamma^2}\cdot (e^{(\gamma+i\omega)t}-1)(e^{(\gamma-i\omega)t}-1), \qquad \tau_t \ll t \ll \tau_l. \tag{50}$$

Since we already consider times $t \ll \tau_l$, we apply the same method of contour integration as used for the calculation of $\dot{A}(t)$ (cf. sect. 4). We get for the mean kinetic energy to lowest order in μ

$$\frac{\langle P^2(t)\rangle}{2} = \frac{P^2(0)}{2}\,e^{-2\gamma t} + \frac{kT}{2}\,[1-e^{-2\gamma t}], \qquad \tau_t \ll t \ll \tau_l, \tag{51}$$

which represents the ordinary expression for the kinetic energy of a free particle, subject to Brownian motion. Thus, in spite of the fact that the autocorrelation function of the statistical part of the external forces (exerted by the small oscillators) is not a peaked and a rapidly damped function of time the heavy particle in the linear chain undergoes Brownian motion if

1. only approximations to first order in μ are considered; hence, the condition $\mu \ll 1$ must be satisfied.

2. times are considered which are restricted by the condition (39).

It has to be remarked that a new time scale is introduced. In our general model (cf. sect. I.11) the central oscillator undergoes Brownian motion within a very long time, which is comparable to the Poincaré period. Here the allowed time region is much smaller than the Poincaré period. This is due to the fact that the frequency spectrum of the bath is cut off sharply at its highest frequency ω_0.

In the quantummechanical case eq. (42) has to be considered as an operator equation. If now $\langle P^2(0)\rangle$ represents the quantummechanical expectation value of the kinetic energy at time zero one finds for the mean kinetic energy

$$\tfrac{1}{2}\langle P^2(t)\rangle = \tfrac{1}{2}\langle P^2(0)\rangle\, e^{-2\gamma t} +$$

$$+\frac{\mu}{2(1-2\mu)}\,\frac{e^{-2\gamma t}}{\pi}\int_{-\omega_0}^{+\omega_0} d\omega\,\frac{\sqrt{\omega_0^2-\omega^2}}{\omega^2+\gamma^2}\,\cdot$$

$$\cdot\, E(\omega, T)(e^{(\gamma+i\omega)t}-1)(e^{(\gamma-i\omega)t}-1), \qquad \tau_t \ll t \ll \tau_l. \tag{52}$$

For $\omega_0 t \gg 1$ $E(\omega, T)$ may be replaced by $E(\omega_0, T)$ in the integrals along the extended vertical paths of C' (cf. the estimation of $R(t)$ in sect. 4). This implies that we may apply the same reasoning as in the classical case because the factor $E(\omega, T)$ does not change in an appreciable way the terms one neglects. Now one gets contributions of the poles $\pm i\mu\omega_0$ and of those of $E(\omega, T)$. The latter poles generate decay terms with the factors $\exp(-l\cdot 2\pi kTt/\hbar)$, $(l = 1, 2, \ldots)$. As already argued in sect. I.11 these terms must rapidly die out, to get Brownian motion. This leads to the conditions

$$\hbar\mu\omega_0 \ll kT \quad \text{or} \quad \frac{\hbar\omega_0}{kT} \ll \frac{1}{\mu}, \tag{53}$$

and

$$t \gg \hbar/kT. \tag{54}$$

In the contribution of the poles, $\omega = \pm i\gamma = \pm i\mu\omega_0$, the terms $E(\pm i\mu\omega_0, T)$ appear, but because of the condition (53) these factors become kT. This was to be expected for a free Brownian particle. Here again it is demonstrated that in the quantummechanical case Brownian motion can exist because the relation

$$\mu\hbar\omega_0 \ll kT \ll \sqrt{\frac{\mu}{2}}\,\hbar\omega_0 = \hbar\Omega \tag{55}$$

can be fulfilled. Moreover, the condition (54) is a fundamental one. It is independent of the interaction.

6. *Distribution function, Fokker-Planck equation and diffusion equation.* In a previous paper[2]) a distribution function of the displacement and momentum of the central oscillator was calculated, the bath of small

oscillators being chosen in thermal equilibrium at the initial time. The same procedure can be applied here. If the initial values of displacement and momentum of the heavy particle are Q_0 and P_0 the distribution function f at time t is given by

$$f(P, Q, t; P_0, Q_0) = \\ = \frac{1}{2\pi kT(\sigma_1\sigma_2 - \sigma_3^2)^{\frac{1}{2}}} \exp\left[-\frac{(\sigma_1\tilde{P}^2 + 2\sigma_3\tilde{P}\tilde{Q} + \sigma_2\tilde{Q}^2)}{2kT(\sigma_1\sigma_2 - \sigma_3^2)}\right]. \tag{56}$$

Here (cf. sect. II.2)

$$\sigma_1 = \sum_n (A_n^2 + \omega_n^{-2}\dot{A}_n^2), \quad \sigma_2 = \sum_n (\dot{A}_n^2 + \omega_n^{-2}\ddot{A}_n^2), \quad \sigma_3 = \tfrac{1}{2}\dot{\sigma}_1, \tag{57}$$

$$\tilde{P} = P - \langle P(t)\rangle, \quad \tilde{Q} = Q - \langle Q(t)\rangle. \tag{58}$$

By means of the expressions from app. B one obtains, neglecting higher order terms in μ, for $\tau_t \ll t \ll \tau_l$,

$$\sigma_1 = \gamma^{-2} + 2\gamma^{-1}t - \gamma^{-2}(2 - e^{-\gamma t})^2, \tag{59}$$

$$\sigma_2 = 1 - e^{-2\gamma t}. \tag{60}$$

Using these formulae we can derive in the same way as in sect. II.4 a Fokker-Planck equation for $f(P, Q, t; P_0, Q_0)$. We obtain

$$\frac{\partial f}{\partial t} = \gamma \frac{\partial}{\partial P} Pf - P\frac{\partial f}{\partial Q} + \gamma kT \frac{\partial^2 f}{\partial P^2}, \qquad \tau_t \ll t \ll \tau_l. \tag{61}$$

Clearly, no term corresponding to an external force appears because in this model the Brownian motion of a particle without binding is described.

Integration of eq. (61) over Q yields the familiar F.P.-equation for the distribution function of the momentum of a Brownian particle without an external force

$$\frac{\partial f_p}{\partial t} = \gamma \frac{\partial}{\partial P}\left(Pf_p + kT\frac{\partial f_p}{\partial P}\right), \qquad \tau_t \ll t \ll \tau_l, \tag{62}$$

where

$$f_p(P, t; P_0, Q_0) = \int f(P, Q, t; P_0, Q_0)\, dQ. \tag{63}$$

As is well known, from eq. (62) it follows immediately that f_P tends to the Maxwell distribution with the relaxation time γ^{-1}.

As the heavy mass behaves as a free Brownian particle one cannot expect the same behaviour in time for P and Q. To get a distribution function for the displacement we integrate f over P,

$$f_Q(Q, t; P_0, Q_0) = \int f(P, Q, t; P_0, Q_0)\, dP. \tag{64}$$

This yields

$$f_Q = (2\pi kT\sigma_1)^{-\frac{1}{2}} \exp - \frac{\tilde{Q}^2}{2kT\sigma_1}. \tag{65}$$

Inserting the eqs. (25) and (32) for $\dot{A}(t)$ and $A(t)$ and eq. (59) for $\sigma_1(t)$ one obtains ($\tau_t \ll t \ll \tau_l$)

$$f_Q(Q, t; P_0, Q_0) = \frac{\gamma(2\pi kT)^{-\frac{1}{2}}}{[1 + 2\gamma t - \{2 - \mathrm{e}^{-\gamma t}\}^2]^{\frac{1}{2}}} \times$$
$$\times \exp - \frac{\{Q - \mathrm{e}^{-\gamma t}\, Q_0 - \gamma^{-1}(1 - \mathrm{e}^{-\gamma t})\, P_0\}^2}{2kT[1 + 2\gamma t - \{2 - \mathrm{e}^{-\gamma t}\}^2]}. \tag{66}$$

If we consider times t large compared to γ^{-1} we may neglect the exponentials. Consequently, the dependence on the initial values P_0 and Q_0 vanishes. One obtains, putting $D = \gamma^{-1}kT$,

$$f_Q(Q, t) = (4\pi Dt)^{-\frac{1}{2}} \exp[-(4Dt)^{-1}\, Q^2], \qquad \gamma^{-1} \ll t \ll \tau_l, \tag{67}$$

which satisfies the well known diffusion equation

$$\frac{\partial f_Q}{\partial t} = D\, \frac{\partial^2 f_Q}{\partial Q^2}, \qquad \gamma^{-1} \ll t \ll \tau_l. \tag{68}$$

Obviously, from eq. (67) follows the well known Einstein relation for the fluctuation of the displacement,

$$\Delta Q^2 = 2Dt, \qquad \gamma^{-1} \ll t \ll \tau_l. \tag{69}$$

Here it should be noted that in contrast to the familiar diffusion equation in the present model the diffusion equation only holds for a small time interval,

$$\frac{1}{\mu\omega_0} \ll t \ll - \frac{3}{2}\, \frac{\ln \mu}{\mu\omega_0}, \tag{70}$$

so that the model is not very appropriate for the description of the diffusion process.

7. *Quantummechanical master equation.* In sect. II.7 we derived a master equation for the probability to find the central oscillator at time t in an eigenstate of the Hamiltonian, $H_0 = \frac{1}{2}(P^2 + \Omega_0^2 Q^2)$. Since the heavy mass in the present model behaves as a free particle, only undergoing the stochastic forces exerted by the chain, we cannot apply exactly the same method. Now it is more natural to deduce a master equation for the probability that the heavy mass has a given momentum at time t.

For convenience we choose the particle in an one-dimensional box with length l and require periodical boundary conditions. At the end we take the limit $l \to \infty$. The eigenstates of the particle are given by

$$\frac{1}{\sqrt{l}}\, \mathrm{e}^{ik_L Q}, \quad k_L = L \cdot \frac{2\pi}{l}, \qquad L = 0, \pm 1, \pm 2, \ldots . \tag{71}$$

At the initial time the linear chain, except the heavy mass, is again chosen in thermal equilibrium with temperature T ($\beta = 1/kT$). The probability distribution of the momentum k_L at time t, conditional on the initial momentum k_M, is given by

$$\begin{aligned} P_L^M(t) = \prod_n (\mathrm{e}^{\beta\hbar\omega_n/2} - \mathrm{e}^{-\beta\hbar\omega_n/2}) \times \\ \times \sum_{\substack{m_1,\ldots,m_N \\ l_1,\ldots,l_N}} |\langle L, l_1, \ldots, l_N|\, \mathrm{e}^{-i(Ht/\hbar)}\, |M, m_1, \ldots, m_N\rangle|^2 \times \\ \times \exp -\beta\{(m_1 + \tfrac{1}{2})\, \hbar\omega_1 + \ldots + (m_N + \tfrac{1}{2})\, \hbar\omega_N\}. \end{aligned} \tag{72}$$

As in sect. II.6 a double characteristic function is introduced,

$$G(\xi', \xi'', t) = \sum_{L,M} \mathrm{e}^{i\xi' k_M}\, \mathrm{e}^{i\xi'' k_L}\, P_L^M(t). \tag{73}$$

Substituting eq. (73) into this expression one obtains after some rearrangements

$$\begin{aligned} G(\xi', \xi'', t) = \prod_n (\mathrm{e}^{\beta\hbar\omega_n/2} - \mathrm{e}^{-\beta\hbar\omega_n/2}) \times \\ \times \operatorname{Tr}(\mathrm{e}^{(i/\hbar)\xi' P}\, \mathrm{e}^{-\beta H_1} \ldots \mathrm{e}^{-\beta H_N}\, \mathrm{e}^{(i/\hbar)\xi'' P(t)}), \end{aligned} \tag{74}$$

where

$$P(t) = \mathrm{e}^{(i/\hbar)Ht}\, P\, \mathrm{e}^{-(i/\hbar)Ht}, \tag{75}$$

$$H_n = \tfrac{1}{2}(p_n^2 + \omega_n^2 q_n^2). \tag{76}$$

Substituting for $P(t)$ its solution, given by eq. (I.7) one can write $G(\xi', \xi'', t)$ as a product of traces,

$$\begin{aligned} G(\xi', \xi'', t) = \prod_n (\mathrm{e}^{\beta\hbar\omega_n/2} - \mathrm{e}^{-\beta\hbar\omega_n/2}) \times \\ \times \operatorname{Tr}(\mathrm{e}^{(i/\hbar)\xi' P}\, \mathrm{e}^{(i/\hbar)\xi''(\dot{A}P + \ddot{A}Q)}) \times \prod_n \operatorname{Tr}(\mathrm{e}^{-\beta H_n}\, \mathrm{e}^{(i/\hbar)\xi''(\dot{A}_n p_n + \ddot{A}_n q_n)}). \end{aligned} \tag{77}$$

Applying the eqs. (II.36) and (II.37) for the calculation of the product of traces one obtains

$$\begin{aligned} G(\xi', \xi'', t) = \mathrm{e}^{i\xi''^2 \dot{A}\ddot{A}/2\hbar}\, \mathrm{e}^{i\xi'\xi''\ddot{A}/\hbar}\, \frac{(\mathrm{e}^{-i\xi''\ddot{A}l/\hbar} - 1)}{\dfrac{i\xi''\ddot{A}l}{\hbar}} \times \\ \times \mathrm{e}^{-(\xi''^2/2\hbar^2)\sum_n (\dot{A}_n^2 + \omega_n^{-2}\ddot{A}_n^2)E(\omega_n, T)} \times \sum_L \mathrm{e}^{ik_L(\xi' + A\xi'')}. \end{aligned} \tag{78}$$

Eq. (78) is still exact. Now the following assumptions and approximations are made.

1. We consider again the spectrum of the oscillators with frequencies ω_n dense, so that we may apply the calculations from the sects. 4 and 5.

2. We consider only times t so that

$$\tau_t \ll t \ll \tau_l. \tag{79}$$

This implies that $\dot{A}(t)$ and $\ddot{A}(t)$ are approximated by

$$\dot{A} = e^{-\gamma t}, \quad \ddot{A} = -\gamma\, e^{-\gamma t}. \tag{80}$$

3. Because of the first assumption we have

$$\sum_n (\dot{A}_n^2 + \omega_n^{-2}\ddot{A}_n^2)\, E(\omega_n, T) \simeq \int_{-\omega_0}^{+\omega_0} \rho(\omega)(\dot{A}^2(\omega) + \omega^{-2}\ddot{A}^2(\omega))\, E(\omega, T)\, d\omega, \tag{81}$$

where $\rho(\omega)$ represents the density of the spectrum. As the several terms of $\dot{A}_n(t)$, given by eq. (38) contain the factors $s \pm i\gamma$ in their denominators the main contribution to the integral (81) comes from the region $\omega \approx 0$. Therefore we make the approximation

$$\int_{-\omega_0}^{+\omega_0} \rho(\omega)\{\dot{A}^2(\omega) + \omega^{-2}\ddot{A}^2(\omega)\}\, E(\omega, T)\, d\omega =$$

$$= kT \int_{-\omega_0}^{+\omega_0} \rho(\omega)\{\dot{A}^2(\omega) + \omega^{-2}\ddot{A}(\omega)\}\, d\omega \simeq kT \sum (\dot{A}_n^2 + \omega_n^{-2}\ddot{A}_n^2). \tag{82}$$

By means of the relations (57), (60) and (25) one obtains in the same approximation

$$\sum (\dot{A}_n^2 + \omega_n^{-2}\ddot{A}_n^2)\, E(\omega_n, T) = kT(1 - \dot{A}^2), \qquad \tau_t \ll t \ll \tau_l. \tag{83}$$

In the same way as in app. II.B we obtain for the validity of eq. (83) the additional conditions

1. $$\hbar\gamma \ll kT. \tag{84}$$

2. only times t are considered which are large compared to the quantum-statistical transient time,

$$t \gg \hbar/kT. \tag{85}$$

Putting these approximations into the expression for $G(\xi', \xi'', t)$ one obtains

$$G(\xi', \xi'', t) = e^{-i\gamma\xi''^2\dot{A}^2/2\hbar}\, e^{-i\gamma\xi'\xi''\dot{A}/\hbar}\, \frac{(e^{-i\gamma\xi''\dot{A}l/\hbar} - 1)}{\dfrac{-i\gamma\xi''\dot{A}l}{\hbar}} \times$$

$$\times\, e^{-(\xi''^2/2\hbar^2)kT(1-\dot{A}^2)} \times \sum_L e^{ik_L(\xi' + \dot{A}\xi'')}. \tag{86}$$

One verifies readily that $G(\xi', \xi'', t)$ satisfies the equation

$$\frac{\partial G}{\partial t} = -\gamma\xi''\left(\frac{\partial G}{\partial \xi''} + \frac{kT}{\hbar^2}\,\xi''\,\frac{\partial G}{\partial \xi''}\right). \tag{87}$$

As was to be expected this equation does not depend on ξ', and hence, not on the initial state of the particle. This means that

$$P_L^M(t) \quad \text{and} \quad P_L(t) = \sum_M \mathrm{e}^{ik_M\xi'} P_L^M(t)$$

satisfy the same equation, so that it is sufficient to derive an equation for $P_L(t)$. From the definition of $G(\xi', \xi'', t)$ follows

$$P_L(t) = \frac{1}{l} \int_{-l/2}^{+l/2} \mathrm{e}^{-ik_L\xi'}\, G(\xi', \xi'', t)\, \mathrm{d}\xi''. \tag{88}$$

Taking the limit $l \to \infty$ one obtains

$$P(k, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{e}^{-ik\xi''}\, G(\xi', \xi'', t)\, \mathrm{d}\xi''. \tag{89}$$

Multiplying eq. (87) by $\mathrm{e}^{-ik\xi''}$ and integrating from zero to infinity one obtains the equation

$$\frac{\partial P(k, t)}{\partial t} = \gamma \frac{\partial}{\partial k}\left[kP(k, t) + \frac{kT}{\hbar^2} \frac{\partial P(k, t)}{\partial k}\right]. \tag{90}$$

As argued in sect. II.7 the same equation holds for $\mathsf{P}(k, t)$ which is defined as the probability to find the heavy mass at time t with momentum k. The initial state may be an arbitrary superposition of eigenstates provided one assumes that the phases of the expansion coefficients of the initial state of the heavy particle are randomly distributed.

8. *Conclusions*. In the preceding sections it was shown that the heavy mass behaves as a free Brownian particle. For the validity of the Langevin equation, the Fokker-Planck equation and the master equation one has in addition to the familiar assumptions and restrictions (cf. sect. II.8) to impose the conditions:

1. only lowest order approximations in the mass ratio μ are considered;
2. times are considered which lie between the transient time $\tau_t = \omega_0^{-1}$ and the limit time $\tau_l = \frac{3}{2}(\mu\omega_0)^{-1} \ln 1/\mu$,

$$\tau_t \ll t \ll \tau_l.$$

This limit time is due to the sharp cutoff of the frequency spectrum.

In addition to this conclusion we have the following remark. If one applies perturbation theory one verifies easily that the probability to find the heavy mass in an eigenstate of the unperturbed Hamiltonian, $H_0 = \frac{1}{2}(P^2 + \Omega^2 Q^2)$, satisfies the master equation (II.29). However, this equation cannot be derived from the exact expression for the probability, given in the sects. II.6 and II.7, because the time dependence of $\sigma_1(t)$ is not only exponential but also linear. This demonstrates that perturbation theory does not always lead to the correct master equation.

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APPENDIX

A. *Calculation of* $\sum' X_{0\nu}^2 s_\nu^{-2} \cos s_\nu t$. By means of the eqs. (31) and (32) one may write

$$\sum' X_{0\nu}^2 s_\nu^{-2} \cos s_\nu t = -\sum' X_{0\nu}^2 \int_0^t s_\nu^{-1} \sin s_\nu t' \,\mathrm{d}t' + \sum' X_{0\nu}^2 s_\nu^{-2} =$$

$$= -\int_0^t A(t')\,\mathrm{d}t' + \tfrac{1}{2} X_{00}^2 t^2 + \sum' X_{0\nu}^2 s_\nu^{-2} =$$

$$= -(\mu\omega_0)^{-1}\{t - (\mu\omega)^{-1}(1 - \exp(-\mu\omega_0 t))\} + \tfrac{1}{2} X_{00}^2 t^2 + \sum' X_{0\nu}^2 s_\nu^{-2}. \quad \text{(A.1)}$$

B. *Calculation of* $\sigma_1(t)$ *and* $\sigma_2(t)$. If the system is invariant for translations the calculation of $\sigma_1(t)$ is different from that in sect. II.A.*e* because of the existence of a zero eigenfrequency. In fact the calculation is reduced to the evaluation of $\sum_n \omega_n^{-2} X_{n\nu} X_{n\mu}$, for

$$\sigma_1(t) = \sum_{\nu,\mu} X_{0\nu} X_{0\mu} \cos s_\nu t \cos s_\mu t \sum_n \omega_n^{-2} X_{n\nu} X_{n\mu} +$$

$$+ \sum_{\nu,\mu} X_{0\nu} X_{0\mu} s_\nu^{-1} s_\mu^{-1} \sin s_\nu t \sin s_\mu t \sum_n X_{n\nu} X_{n\mu}. \quad \text{(A.2)}$$

By means of the eqs. (I.14), (II.A.3) and (11) one verifies easily,

$$\sum X_{n\nu} X_{n\mu} \omega_n^{-2} = s_\nu^{-2} \delta_{\nu,\mu}, \qquad \nu \neq 0, \quad \mu \neq 0, \quad \text{(A.3)}$$

$$\sum X_{n0} X_{n\mu} \omega_n^{-2} = -s_\mu^{-2} X_{00} X_{0\mu} (1 + \sum \varepsilon_n^2 \omega_n^{-4}), \qquad \mu \neq 0, \quad \text{(A.4)}$$

$$\sum X_{n0}^2 \omega_n^{-2} = X_{00}^2 \sum \varepsilon_n^2 \omega_n^{-6}. \quad \text{(A.5)}$$

From eq. (I.18) follows

$$1 + \sum \varepsilon_n^2 \omega_n^{-4} = X_{00}^{-2}. \quad \text{(A.6)}$$

Multiplying eq. (I.12) by $X_{0\nu} s_\nu^{-4}$ and using the relations (II.A.1) and (11) one obtains

$$\sum \varepsilon_n^2 \omega_n^{-6} = X_{00}^{-4} \sum' X_{0\nu}^2 s_\nu^{-2} \quad \text{(A.7)}$$

(The prime means that the term with $s_\nu = 0$ is excluded).

Subsequently for $\sigma_1(t)$ one obtains

$$\sigma_1(t) = [2 \sum' X_{0\nu}^2 s_\nu^{-2} + X_{00}^2 t^2 - 2 \sum' X_{0\nu}^2 s_\nu^{-2} \cos s_\nu t - A^2(t)], \quad \text{(A.8)}$$

and with (A.1),

$$\sigma_1(t) = 2 \int_0^t A(t')\, \mathrm{d}t' - A^2(t). \quad \text{(A.9)}$$

Furthermore, one verifies easily

$$\sigma_2(t) = 1 - \dot{A}^2(t). \quad \text{(A.10)}$$

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