Kramers' Equation

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1 Fokker–Planck equation, Smoluchowski equation and Kramers' equation.

As the title of his paper indicates, Kramers [1] was interested in using the concept of Brownian motion to describe motion of particles over a barrier as a model for chemical reactions in solution. The equation he uses is an example of a Fokker–Planck (FP) equation. The first part of his paper is a rather general description of the motion of a Brownian particle in an external potential, after which he considers a variety of cases. We will first describe his starting equation and derive in great detail several of the equations used in subcases.
Starting point of the whole analysis is an equation for the transition probability $P(x_0, p_0|x, p, t) \equiv P(x, p, t)$, *i.e.* the probability of finding a particle at time t on position x with momentum p, *given* that at time 0 its position was x_0 and its momentum was p_0. This equation is the well–known FP equation which we write as:

$$\frac{\partial P(x,p,t)}{\partial t} = -\left[K(x)\frac{\partial}{\partial p} + \frac{p}{m}\frac{\partial}{\partial x}\right] P(x,p,t) + \zeta\frac{\partial}{\partial p}\left[k_B T\frac{\partial}{\partial p} + \frac{p}{m}\right] P(x,p,t) \tag{1.1}$$

with initial condition

$$P(x,p,0) = \delta(x - x_0)\delta(p - p_0) \tag{1.2}$$

In this equation m is the mass of the particle, ζ is a friction constant, T is the temperature and k_B Boltzmann's contant and $K(x)$ is an external field of force to which the particle is subjected.
Several remarks on this equation are in order.
The first part of this equation describes a purely mechanistic proces and is therfore nothing but the classical Liouville equation for a particle with Hamiltonian

$$\mathcal{H} = \frac{p^2}{2m} + V(x) \tag{1.3}$$

where $V(x)$ is an external potential, such that

$$K(x) = -\frac{\partial V(x)}{\partial x} \tag{1.4}$$

A simple derivation shows that the Liouville equation can indeed be written

$$\frac{\partial P(x,p,t)}{\partial t} = \{\mathcal{H}, P\} = \left[\frac{\partial \mathcal{H}}{\partial x}\frac{\partial}{\partial p} - \frac{\partial \mathcal{H}}{\partial p}\frac{\partial}{\partial x}\right] P(x,p,t) = -\left[K(x)\frac{\partial}{\partial p} + \frac{p}{m}\frac{\partial}{\partial x}\right] P(x,p,t) \tag{1.5}$$

where $\{\mathcal{H}, P\}$ is the so–called Poisson bracket of $\mathcal{H}$ and P.
The equilibrium distribution $P_{eq}(x,p)$ is given by

$$P_{eq}(x,p) = \frac{e^{-\beta\mathcal{H}}}{\int dxdp\, e^{-\beta\mathcal{H}}} \tag{1.6}$$

where β is equal to $(k_B T)^{-1}$. This is obviously a solution of eq. (1.5) and also of eq. (1.1). However, the solutions of eq. (1.5) do not converge to the equilibrium solution for long times, but the solutions of eq. (1.1) do. It is clear that whatever extension of the Liouville equation one considers, the equilibrium probability has to be a solution. The equilibrium probability can after all be derived using only equilibrium statistical mechanics, and knows nothing of the dynamics of the system. This is the case for eq. (1.1) since

$$\left[k_B T \frac{\partial}{\partial p} + \frac{p}{m}\right] e^{-\beta \mathcal{H}} = 0 \tag{1.7}$$

Eq. (1.1) appears to be the simplest extension of the Liouville equation which exhibits approach to equilibrium, leaves the equilibrium solution unaltered and furthermore gives the old equations for the average position and momentum.

The average equations are, as can be easily derived by performing the appropriate integrations:

$$\frac{d\langle x\rangle}{dt} = \langle v\rangle \tag{1.8}$$

and

$$m\frac{d\langle v\rangle}{dt} = -\zeta\langle v\rangle + \langle K(x)\rangle \tag{1.9}$$

We note that this is not a closed system of equations. Only when the force is linear, *i.e.* for a harmonic restoring force is this system closed. In all other cases certain approximations have to be made in order to obtain solutions.

It is probably of interest to remark here that the potential $V(x)$ is a potential of mean force, that is, a potential derived from the average force the particle experiences. The averaging is over all possible configurations of the surrounding fluid molecules.

Kramers derives the FP equation from a Langevin equation through the well–known procedure of calculating moments. He does give a number of other more complicated equations, which to his knowledge have no applications. As far as I know that situation is unaltered.

Since he is apparently unable to solve eq. (1.1) in general, he then proceeds to consider various limiting cases for which the equation reduces to a simpler one which he either can solve directly, or give limiting solutions for. He first considers two limits: that of low and of high friction. Since his derivation of this limits is upon first, but also on repeated reading rather unclear, I would like to give a derivation based on the Langevin equation. This description is equivalent to the FP equation, as Kramers himself showed, and it gives a nice introduction to later sections where I will look at Kramers equation from a more general perspective.

1.1 The high friction limit.

To illustrate the method Kramers uses to reduce his FP equation to a Smoluchowski equation, we consider the case of a harmonically bound particle in a random force field. We use a Langevin description, *i.e.* the equations that the particle satisfies are:

$$m\frac{dv}{dt} = -\zeta v - m\omega^2 + F_R(t) \tag{1.10}$$

and

$$\frac{dx}{dt} = v \tag{1.11}$$

In this equations $F_R(t)$ is a Gaussian random force, the "strength" of which is related to the friction ζ by a fluctuation–dissipation theorem. We solve this equation with initial conditions x_0 and v_0 in appendix A. The solution can be written as:

$$x(t) - \langle x(t)\rangle = \frac{1}{m(s_1 - s_2)} \int_0^t d\tau\, F_R(\tau) \left[e^{s_1(t-\tau)} - e^{s_2(t-\tau)}\right] \tag{1.12}$$

where the average $\langle x(t)\rangle$ is given by

$$\langle x(t)\rangle = \frac{1}{s_1 - s_2}\left[x_0\left(s_1 e^{s_1 t} - s_2 e^{s_2 t}\right) + \left(v_0 + \frac{\zeta}{m}x_0\right)\left(e^{s_1 t} - e^{s_2 t}\right)\right] \tag{1.13}$$

and where the roots of the propagator are

$$s_{1,2} = -\frac{\zeta}{2m} \pm \frac{1}{2}\sqrt{\frac{\zeta^2}{m^2} - 4\omega^2} \tag{1.14}$$

In addition we give the average velocity of the particle:

$$\langle v(t)\rangle = \frac{1}{s_1 - s_2}\left[x_0\left(s_1^2 e^{s_1 t} - s_2^2 e^{s_2 t}\right) + \left(v_0 + \frac{\zeta}{m}x_0\right)\left(s_1 e^{s_1 t} - s_2 e^{s_2 t}\right)\right] \tag{1.15}$$

Let us now consider what happens if we let the friction increase. In that case the roots $s_{1,2}$ can be expanded as:

$$s_{1,2} = -\frac{\zeta}{2m} \pm \frac{\zeta}{2m}\sqrt{1 - \frac{4m^2\omega^2}{\zeta^2}} \approx -\frac{\zeta}{2m} \pm \frac{\zeta}{2m}\left(1 - \frac{2m^2\omega^2}{\zeta^2}\right) \tag{1.16}$$

That means that for large values of the friction we get for the roots

$$s_1 \approx -\frac{m\omega^2}{\zeta} \qquad and \qquad s_2 \approx -\frac{\zeta}{m} \tag{1.17}$$

Now consider eqs. (1.13) and (1.15). Both expressions contain exponentials with $s_1 t$ and $s_2 t$ in the exponent. For large ζ that implies that one of the exponents decreases rapidly, namely the one with $s_2 t$ whereas the other becomes slower and slower. To lowest order in $1/\zeta$ we get after a short calculation:

$$\langle x(t)\rangle \approx x_0 e^{-m\omega^2 t/\zeta} \tag{1.18}$$

and

$$\langle v(t)\rangle = -\frac{m\omega^2}{\zeta} x_0 e^{-m\omega^2 t/\zeta} = -\frac{m\omega^2}{\zeta}\langle x(t)\rangle \tag{1.19}$$

So we notice two things here: after a short intitial time, necessary for the other exponent to vanish, *i.e.* for times such that $t >> m/\zeta$, motion in phase space is along the line

$$\langle v(t)\rangle + \frac{m\omega^2}{\zeta}\langle x(t)\rangle \tag{1.20}$$

Secondly we notice loss of an initial condition: only x_0 occurs in the solution. This all points to the proper way of making the general reduction of the FP equation in the high friction limit: we have to use a from of singular perturbation theory, since scaling time and dividing the equation by ζ and subsequently letting $1/\zeta$ go to zero leads to loss of higher derivatives. The procedure followed is outlined in appendix B. The result is that for large friction we can write down an equation for the position coordinate only (strickly speaking this position coordinate has a small momentum component, but in the high friction limit this component is again negligible) which is the Smoluchowski equation:

$$\frac{\partial}{\partial t}P(x,t) = D\frac{\partial}{\partial x}\left(\frac{\partial}{\partial x} + \frac{m\omega^2}{k_B T}x\right)P(x,t) \tag{1.21}$$

where $D = k_B T/\zeta$. This equation can be solved exactly for the harmonic force.
Kramers then proceeds to calculate the stationary current between two points A and B on the position coordinate. For the stationary current j we can neglect the time–derivative and write the equation in the form

$$j_{st} = \frac{D}{k_B T}K(x)P_{st}(x) - D\frac{\partial P_{st}(x)}{\partial x} = \text{constant} \tag{1.22}$$

Here we used a slightly more general expression involving a slowly varying force $K(x)$. Since the force can be derived fom a potential $V(x)$ *cf.* eq. (1.4), this can also be written in the form

$$j_{st} == -De^{-V(x)/k_B T}\frac{\partial}{\partial x}\left(e^{V(x)/k_B T}P_{st}(x)\right) \tag{1.23}$$

A simple integration then yields one of Kramers essential results:

$$j_{st} = -D \frac{\left[e^{V(x)/k_BT} P_{st}(x)\right]_A^B}{\int_A^B dx\, e^{V(x)/k_BT}} \tag{1.24}$$

This result is used to discuss escape over a barrier.

1.2 The low friction limit.

The low friction limit is simpler than the high friction limit since we do not need singular perturbation theory, at least at first sight, actually I think you do, since by letting ζ go to zero one does loose the highest derivative with respect to p. We'll come back to that later, let us first give Kramers arguments in this case. We will first base ourselves on the Langevin equation again.
If we multiply eq. (1.10) by v and eq. (1.11) by $m\omega^2 x$ and subsequently add the equations, we get

$$\frac{d}{dt}\left(\frac{1}{2}mv^2 + \frac{1}{2}m\omega^2 x^2\right) = \frac{d}{dt}E = -\zeta v^2 + vF_R(t) \tag{1.25}$$

Assuming that the friction is small, we can expand with respect to ζ. That means we can calculate v^2 as if friction were absent. Averaging over one period of the motion, we get for the average loss in energy during one period:

$$\frac{d}{dt}\overline{E} = -\frac{\zeta}{m}\left(\overline{E} - k_BT\right) \tag{1.26}$$

To derive this we also used that in absence of the friction

$$\frac{1}{2}m\overline{v}^2 = \frac{1}{2}\overline{E} \tag{1.27}$$

and

$$\langle v(t)F_R(t)\rangle = \frac{\zeta k_BT}{m} \tag{1.28}$$

cf. eq. (A.9).
We are dealing with a slow relaxation of the energy here. I think Kramers implicitly assumes that the phase relaxes very rapidly, at least much faster than the energy, which is indeed found to be true, but could he have known that? He is rather confusing on this point, since he states that the averaging is over one period of the motion. In appendix C we go into more detail of his derivation. Also, as we will see when we calculate rates in this case, does the low friction limit give incorrect results when taking $\zeta \to 0$. Finally the derivation is only given for periodic motion so that strictly speaking motion during barrier crossing cannot be described by the equation derived below. Kramers solves this problem by stating that if the top of the barrier is reached, the reaction occurs in all cases, since the friction is so low.
We will now first give a formal derivation of Kramers energy diffusion equation from the FP equation. To that end we do not consider the probability as a function of x and p, but as a function of the energy E and the phase angle θ.
Using the scaled coordinates of appendix B, the FP equation can be written:

$$\frac{\partial}{\partial t}P(t) = \left[\omega\left(\xi\frac{\partial}{\partial \pi} - \pi\frac{\partial}{\partial \xi}\right) + \frac{\zeta}{m}\left(\frac{\partial}{\partial \pi}\pi + \frac{k_BT}{\hbar\omega}\frac{\partial^2}{\partial \pi^2}\right)\right]P(t) \tag{1.29}$$

Next we introduce the quantities E and θ defined as:

$$E = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 = \frac{1}{2}\hbar\omega\left(\pi^2 + \xi^2\right), \qquad \text{with} \qquad \epsilon = \frac{2E}{\hbar\omega} \tag{1.30}$$

and

$$\theta = \arctan\left(\frac{\pi}{\xi}\right) = \arctan\left(\frac{p}{m\omega x}\right) \tag{1.31}$$

In terms of these quantities the FP equation becomes:

$$\frac{\partial}{\partial t}P(E,\theta,t) = \omega\frac{\partial}{\partial\theta}P(E,\theta,t) + \frac{\zeta}{m}\left(2\sqrt{\epsilon}\sin\theta\frac{\partial}{\partial\epsilon}+\frac{1}{\sqrt{\epsilon}}\cos\theta\frac{\partial}{\partial\theta}\right)\left[\sqrt{\epsilon}\sin\theta+\frac{k_BT}{\hbar\omega}\left(2\sqrt{\epsilon}\sin\theta\frac{\partial}{\partial\epsilon}+\frac{1}{\sqrt{\epsilon}}\cos\theta\frac{\partial}{\partial\theta}\right)\right]P(E,\theta,t) \tag{1.32}$$

We note that the non–dissipative part, the Liouville equation, does not contain the variable E. That means that to lowest order in the friction we can write $P(E,\theta,t) = P(E,t)P(\theta,t)$. We now do two things: in the first place we are only interested in the lowest order correction to the Liouville equation, *i.e.* in the second term of eq. (1.29) we use this decomposition, and in addition we integrate over one period of the motion. We are thus left an equation for the average probability distribution:

$$\frac{\partial}{\partial t}\overline{P}(E,t) = \frac{\zeta}{m}\left(\frac{\partial}{\partial E}E + k_BT\frac{\partial}{\partial E}E\frac{\partial}{\partial E}\right)\overline{P}(E,t) \tag{1.33}$$

This equation looks like a Smoluchowski equation but now for the energy, and therefore Kramers considers this a case of energy diffusion. In fact it is a somewhat more general form of the Smoluchowski equation.
As in the previous subsection we can derive an expression for the stationary current. In appendix C. we derive a morgeneral equation for periodic motion using action–angle variables. It should be noted that the θ introduced above is not the angle variable conjugate to the action. The formal Hamiltonian formalism must be used to dervie the canonical transformation neccesary.

2 Chemical reaction and the stationary current over a barrier.

On of the main aspects of Kramers' papers is the realization that the reaction rate can be related to the stationary current over a barrier. To put this into a somewhat more general perspective, and to get more insight into the limitations of kramers' theory, we will first discuss a general expression for the rate of a reaction.
Chemical reaction can be viewed as a process by which reactants are changed into products, and in general some sort of energy barrier has to be crossed in order for this process to take place The generic picture is as follows:
R and P stand for reactant and product region respectively, and I is the intermediate, barrier, region. In general there is something we can call a reaction coordinate. This can be a true coordinate but there are many other possibilities: in isomerization reactions it could represent an angle, but in Kramers case of energy diffusion, *i.e.* the low friction case, it can also stand for the energy, or more properly the action. The separation between these three areas is more or less arbitrary, by a so–called reactant and product surface.
Kramers' idea was that, at least in a number of cases, and in fact only those case where it is proper to speak of a reaction rate (rather than a rate kernel)

3 Remarks.

Hynes in [2] states that Kramers stresses there are three regimes: high friction, low friction and intermediate friction, and that in the intermediate friction regime transition state theory applies. However, Janssen [3] has devoted a paper on what he calls "Kramers problem", and which is just the study of the intermediate regime, to which apparently a host of other papers, having to do with first passage time approaches have also been devoted. In the same paper the remark is made that Kramers equation is unlikely to be valid since molecular frequencies are almost never small compared to decay times of the friction.
In his derivation of the high friction limit, *i.e.* the Smoluchowski limit, Kramers assumes that the force does not vary much over the short distance the particle travels during momentum relaxation. This assumption is certainly correct for the harmonic potential (although for very high values of ω there could be a problem), but it seems to me that in the cusped barrier case there is a problem, since the force has a jump in the barrier region, which is an extremely rapid change over a very short distance. It seems that there should

be an argument relating the derivative of the force and the friction constant to a range of validity of the Smoluchowski equation.

In the case of a harmonic well, and a harmonic barrier it is possible to solve the FP equation itself. So several questions remain concerning Kramers paper: why didn't he use the general solution in the harmonic well/barrier case, how do the various limits get connected in those cases. Another question is why he did not use the Langevin approach which turns out to be simpler, and which he starts from, deriving a FP equation first. See also appendix C.

In his derivation of the low friction limit Kramers appears to assume without stating explicitly that $\overline{p^2\rho} = \overline{p^2}\,\overline{\rho}$. Is this assumption consistent? It probably is to lowest order, but it would be nicer if he had explained why he suddenly uses two overbars.

In the thesis "Elimination of fast variables" the energy diffusion is also treated, as far as I remember. However, Kramers does not say anything about fast or slow here, although maybe the implicit assumption is that the phase does not relax very fast, since averaging over a period would the constantly change. In real systems phase relaxation is much faster that energy relaxation, so maybe there is something more to say about this.

A Harmonic damped oscillator solution.

In this appendix we solve eqs. (1.8) and (1.9). Combination of both equations yields a second order differential equation which can be written as:

$$m\frac{d^2x}{dt^2} + \zeta\frac{dx}{dt} + m\omega^2 x = F_R(t) \tag{A.1}$$

The Laplace tranform of a function $f(t)$ is defined as:

$$\mathcal{L}[f] = \int_0^\infty dt\, f(t)e^{-st} = \hat{f}(s) \tag{A.2}$$

with inverse

$$f(t) = \frac{1}{2\pi i}\int_{-i\infty}^{i\infty} ds\, \hat{f}(s)e^{st} \tag{A.3}$$

Transforming eq. (A.1) the yields:

$$\left[s^2 + s\frac{\zeta}{m} + \omega^2\right]\hat{x}(s) = v_0 + \left(s + \frac{\zeta}{m}\right)x_0 + \frac{\hat{F}_R(s)}{m} \tag{A.4}$$

This is now just an algebraic equation wich can be solved trivially for $\hat{x}(s)$:

$$\hat{x}(s) = \frac{v_0 + \left(s + \frac{\zeta}{m}\right)x_0 + \frac{1}{m}\hat{F}_R(s)}{s^2 + s\frac{\zeta}{m} + \omega^2} \tag{A.5}$$

The propagator has two simple poles $s_{1,2}$ given by:

$$s_{1,2} = -\frac{\zeta}{2m} \pm \frac{1}{2}\sqrt{\frac{\zeta^2}{m^2} - 4\omega^2} \tag{A.6}$$

Both poles are in the left half–plane, either on the negative real axis or symmetrically opposed with respect to this axis. In both cases we can close the contour for the inverse transformation in the left half–plane for positive times, such that both poles are inside the contour. For negative times we have to close in the right half–plane where there are no poles, and the integral yields 0, as it should for causality reasons. We find for $x(t)$, performing the inverse transformation:

$$x(t) = \frac{1}{2\pi i}\int_{-i\infty}^{i\infty} ds\, e^{st}\frac{v_0 + \left(s + \frac{\zeta}{m}\right)x_0}{(s-s_1)(s-s_2)} + \frac{1}{2\pi i m}\int_{-i\infty}^{i\infty} ds\, e^{st}\frac{\hat{F}_R(s)}{(s-s_1)(s-s_2)} \tag{A.7}$$

Performing the integrations, and using caausality then gives for $x(t)$:

$$x(t) = x_0\frac{s_1e^{s_1t} - s_2e^{s_2t}}{s_1 - s_2} + \left(v_0 + \frac{\zeta}{m}x_0\right)\frac{e^{s_1t} - e^{s_2t}}{s_1 - s_2} + \frac{1}{m(s_1 - s_2)}\int_0^t d\tau\, F_R(\tau)\left(e^{s_1(t-\tau)} - e^{s_2(t-\tau)}\right) \tag{A.8}$$

and for the velocity $v(t)$

$$v(t) = x_0\frac{s_1^2e^{s_1t} - s_2^2e^{s_2t}}{s_1 - s_2} + \left(v_0 + \frac{\zeta}{m}x_0\right)\frac{s_1e^{s_1t} - s_2e^{s_2t}}{s_1 - s_2} + \frac{1}{m(s_1 - s_2)}\int_0^t d\tau\, F_R(\tau)\left(s_1e^{s_1(t-\tau)} - s_2e^{s_2(t-\tau)}\right) \tag{A.9}$$

It is usually assumed that the random force has zero average and is uncorrelated at different times, which can be written

$$\langle F_R(t)\rangle = 0, \qquad \text{and} \qquad \langle F_R(t)F_R(t')\rangle = c\delta(t-t') \tag{A.10}$$

We now find the constant c by calculating the fluctuations in velocity. These can be written

$$\begin{aligned}\left\langle (v(t) - \langle v(t)\rangle)^2\right\rangle &= \frac{c}{m^2(s_1 - s_2)^2}\int_0^t d\tau\, \left[s_1e^{s_1(t-\tau)} - s_2e^{s_2(t-\tau)}\right]^2 \\ &= \frac{c}{m^2(s_1 - s_2)^2}\left[-\frac{1}{2}s_1\left(1 - e^{2s_1t}\right) + \frac{2s_1s_2}{s_1 + s_2}\left(1 - e^{(s_1+s_2)t}\right) - \frac{1}{2}s_2\left(1 - e^{2s_2t}\right)\right]\end{aligned} \tag{A.11}$$

Both poles $s_{1,2}$ have a negative real part, so for $t \to \infty$ all exponents vanish and we get:

$$\lim_{t\to\infty} \left\langle (v(t) - \langle v(t)\rangle)^2 \right\rangle = \frac{c}{m^2(s_1 - s_2)^2} \left[-\frac{1}{2}s_1 + \frac{2s_1 s_2}{s_1 + s_2} - \frac{1}{2}s_2 \right] = \frac{c}{2m\zeta} \tag{A.12}$$

In addition the average velocity vanishes for long times as can be seen by taking the average of eq. (A.9) and subsequently the limit $t \to \infty$. On the other hand we require that for long times the Brownian particle is thermalized, in other words satisfies the thermal equilibrium distribution for which holds that

$$\frac{1}{2}m \left\langle v^2 \right\rangle_{eq} = \frac{1}{2}k_B T \tag{A.13}$$

From these last two equations we then get the constant c which yields the fluctuation–dissipation theorem:

$$\langle F_R(t) F_R(t') \rangle = 2k_B T \zeta \delta(t - t') \tag{A.14}$$

B From Fokker–Planck to Smoluchowski.

We introduce new coordinates ξ and new momenta π according to the scaling transformation:

$$\xi = x\sqrt{\frac{m\omega}{\hbar}} \qquad \text{and} \qquad \pi = \frac{p}{\sqrt{m\hbar\omega}} \tag{B.1}$$

The use of Planck's constant here is purely to make dimensionless units, and serves no futher purpose. This is not a canonical transformation. In terms of these new variables we get for the FP equation:

$$\frac{\partial P(\xi,\pi,t)}{\partial t} = \left[\omega \left(\xi \frac{\partial}{\partial \pi} - \pi \frac{\partial}{\partial \xi} \right) + \frac{\zeta}{m} \left(\frac{\partial}{\partial \pi}\pi + \frac{k_B T}{\hbar\omega} \frac{\partial^2}{\partial \pi^2} \right) \right] P(\xi,\pi,t) \tag{B.2}$$

We divide the resulting equation by ζ/m and introduce the dimensionless timescale $\tau = \zeta t/m$ to get

$$\frac{\partial P(\xi,\pi,\tau)}{\partial \tau} = \left[\frac{m\omega}{\zeta} \left(\xi \frac{\partial}{\partial \pi} - \pi \frac{\partial}{\partial \xi} \right) + \left(\frac{\partial}{\partial \pi}\pi + \frac{k_B T}{\hbar\omega} \frac{\partial^2}{\partial \pi^2} \right) \right] P(\xi,\pi,\tau) \tag{B.3}$$

We note here that the expansion paprameter is now obvious: it must be $m\omega/\zeta$. It is clear that we cannot just leave out the first (Liouville) term from the equation in the high friction limit. The derivative with respect to ξ would then disappear and we get a different equation altogether. Also, what is often stated, integration with respect to π does not give the Smoluchowski equation. Such a procedure would lead to the vanishing of all π derivatives (assuming the probability goes to zero for large values of π), and we are left with a very simple equation containing a derivative with respect to ξ but with an unknown quantity, something related to $\langle \pi \rangle$. In addition we know that after a short time π and ξ do not move independently but rather in concert. On the other hand we do know that motion along the "slow" coordinate is, after a short initial time, independent of the motion along the "fast" coordinate, so it makes sense to perform a transformation to a new coordinate frame in which these motions are nicely separated.
The coordinate along which the average motion takes place after a short initial period is given by eq. (1.20), and can be written in terms of the new variables as

$$\langle \pi \rangle + \frac{m\omega}{\zeta} \langle \xi \rangle = 0 \tag{B.4}$$

which is along the line

$$\pi = \xi \tan\theta \tag{B.5}$$

in phase space, with

$$\tan\theta = -\frac{m\omega}{\zeta} \tag{B.6}$$

We note that for large ζ the angle θ approaches 0, so that eventually motion is along the coordinate ξ only.

This suggests a rotation to a new coordinate frame, defined by

$$\overline{\pi} = \pi\cos\theta + \xi\sin\theta \qquad \text{and} \qquad \overline{\xi} = -\pi\sin\theta + \xi\cos\theta \tag{B.7}$$

To lowest order in the expansion parameter this becomes:

$$\overline{\pi} = \pi - \frac{m\omega}{\zeta}\xi \qquad \text{and} \qquad \overline{\xi} = \xi + \frac{m\omega}{\zeta}\pi \tag{B.8}$$

Inversion yields:

$$\pi = \overline{\pi} + \frac{m\omega}{\zeta}\overline{\xi} \qquad \text{and} \qquad \xi = \overline{\xi} - \frac{m\omega}{\zeta}\pi \tag{B.9}$$

The derivatives are given by:

$$\frac{\partial}{\partial\pi} = \frac{\partial}{\partial\overline{\pi}} + \frac{m\omega}{\zeta}\frac{\partial}{\partial\overline{\xi}} \qquad \text{and} \qquad \frac{\partial}{\partial\xi} = \frac{\partial}{\partial\overline{\xi}} - \frac{m\omega}{\zeta}\frac{\partial}{\partial\overline{\pi}} \tag{B.10}$$

Introducing these relations into the FP equation then gives after a short calculation:

$$\begin{aligned}\frac{\partial}{\partial\tau}P(\overline{\xi},\overline{\pi},\tau) = \frac{m\omega}{\zeta}&\left[\left(1+\frac{m^2\omega^2}{\zeta^2}\right)\left(\overline{\xi}\frac{\partial}{\partial\overline{\pi}} - \overline{\pi}\frac{\partial}{\partial\overline{\xi}}\right)\right]P(\overline{\xi},\overline{\pi},\tau) + \\ &\frac{\partial}{\partial\overline{\pi}}\left[\overline{\pi} + \frac{m\omega}{\zeta}\overline{\xi} + \frac{k_BT}{\hbar\omega}\left(\frac{\partial}{\partial\overline{\pi}} + \frac{m\omega}{\zeta}\frac{\partial}{\partial\overline{\xi}}\right)\right]P(\overline{\xi},\overline{\pi},\tau) + \\ &\frac{m\omega}{\zeta}\frac{\partial}{\partial\overline{\xi}}\left[\overline{\pi} + \frac{m\omega}{\zeta}\overline{\xi} + \frac{k_BT}{\hbar\omega}\left(\frac{\partial}{\partial\overline{\pi}} + \frac{m\omega}{\zeta}\frac{\partial}{\partial\overline{\xi}}\right)\right]P(\overline{\xi},\overline{\pi},\tau)\end{aligned} \tag{B.11}$$

Now we can delete without any problem terms quadratic in the expansion parameter in the first term, they are negligible compared to 1. Also integration over the new momentum variable can be performed, since it is independent of the other variable. This makes the second term vanish entirely, and in addition part of the first term. We are left with:

$$\frac{\partial}{\partial\tau}P(\overline{\xi},\tau) = -\frac{m\omega}{\zeta}\frac{\partial}{\partial\overline{\xi}}\int d\overline{\pi}\,\overline{\pi}P(\overline{\xi},\overline{\pi},\tau) + \frac{m\omega}{\zeta}\frac{\partial}{\partial\overline{\xi}}\int d\overline{\pi}\left[\overline{\pi} + \frac{m\omega}{\zeta}\overline{\xi} + \frac{k_BT}{\hbar\omega}\left(\frac{\partial}{\partial\overline{\pi}} + \frac{m\omega}{\zeta}\frac{\partial}{\partial\overline{\xi}}\right)\right]P(\overline{\xi},\overline{\pi},\tau) \tag{B.12}$$

We note that the terms which contain an unknown integral now cancel, and in addition the integral with the derivative with respect to $\overline{\pi}$ vanishes when we assume the probability to vanish for large values of $\overline{\pi}$. This leaves us with:

$$\frac{\partial}{\partial\tau}P(\overline{\xi},\tau) = \frac{m^2\omega^2}{\zeta^2}\frac{\partial}{\partial\overline{\xi}}\left(\overline{\xi} + \frac{k_BT}{\hbar\omega}\frac{\partial}{\partial\overline{\xi}}\right)P(\overline{\xi},\tau) \tag{B.13}$$

Backtransformation to the old time (*i.e.* multiplication by ζ/m and to the unnormalized coordinate $\overline{x} = \sqrt{\hbar/m\omega\overline{\xi}}$) yields:

$$\frac{\partial}{\partial\tau}P(\overline{x},t) = \frac{k_BT}{\zeta}\frac{\partial}{\partial\overline{x}}\left(\frac{\partial}{\partial\overline{x}} + \frac{m\omega^2}{k_BT}\overline{x}\right)P(\overline{x},t) \tag{B.14}$$

This is exactly the Smoluchowski equation for the spatial diffusion of a particle in a harmonic well if we introduce the diffusion constant D as

$$D = \frac{k_BT}{\zeta} \tag{B.15}$$

All the above manipulations were necessary to correctly make the transformation to new coordinates and momenta. The essential assumption made in the derivation was that we could integrate over the new momenta without influencing the new coordinate. As we showed in the main body of the text this only holds after a short initial time m/ζ. The Smoluchowski equation is therefore only valid after this initial interval.

The derivation was given for a particle in a harmonic well. This is not an essential restriction. First we will mainly consider particles moving either in a harmonic potential well, of over a harmonic barrier. But even if that is not the case, to use the Smoluchowski equation we must assume the friction to be so large that during the equilibration of the momentum coordinate there is hardly any motion along the position coordinate. Kramers even makes the assumption that during that part of the motion the force on the particle is constant.

C Energy diffusion for general periodic motion.

In this appendix we derive eq. (1.34) for general periodic motion. To that end we use action–angle variables, *cf. e.g.* k Goldstein [4]. The action J is defined for a periodic system with coordinate x and conjugate momentum p as:

$$J(E) = \oint p\,dx = \oint \sqrt{2m(E - V(x))}\,dx \tag{C.1}$$

On the other hand we can formally solve the equation of motion in the following way: the equation of motion can be written

$$m\frac{dv}{dt} = F(x) = -\frac{dV(x)}{dx} \tag{C.2}$$

Multiplying both sides by $v = dx/dt$ this is equal to

$$\frac{d}{dt}\left(\frac{1}{2}mv^2 + V(x)\right) = 0 \tag{C.3}$$

which can be integrated to

$$\left(\frac{dx}{dt}\right)^2 = \frac{2}{m}(E - V(x)) \tag{C.4}$$

Taking the square root, and separating variables we then get

$$\frac{dx}{\sqrt{\frac{2}{m}(E - V(x)}} = dt \tag{C.5}$$

which, upon integration becomes:

$$\int \frac{dx}{\sqrt{\frac{2}{m}(E - V(x)}} = \int dt = t \tag{C.6}$$

This is therefore the implicit solution of x as a function of t. For periodic motion we can choose the final time equal to one period, which is $2\pi/\omega$, where ω is the frequency of the motion, so that we get:

$$\frac{2\pi}{\omega} = \oint \frac{dx}{\sqrt{\frac{2}{m}(E - V(x)}} \tag{C.7}$$

Differentiating eq. (C.1) with respect to E we get after a straightforward derivation:

$$\frac{\partial J}{\partial E} = \oint \frac{dx}{\sqrt{\frac{2}{m}(E - V(x)}} \tag{C.8}$$

which, on comparison to eq. (C.7) yields the relation:

$$\frac{\partial J}{\partial E} = \frac{2\pi}{\omega} \tag{C.9}$$

In general we want to express the hamiltonian of the system in terms of the so–called action–angle variables. This means we have to find a generating function $W(x, J)$ of the old coordinate x and new momentum for which we take J which makes the hamiltonian a constant. According to the general theory of canonical transformations the new coordinate which is the so–called angle variable θ and the old momentum can be found from:

$$\theta = \frac{\partial W}{\partial J}, \qquad \text{and} \qquad p = \frac{\partial W}{\partial x} \tag{C.10}$$

If we want the new hamiltonian to be a constant, we have to find the generating function by solving the Hamilton–Jacobi equation

$$\mathcal{H}\left(x, \frac{\partial W}{\partial x}\right) = E \tag{C.11}$$

From this we get immediately

$$W(x,J) = \int dx\, \sqrt{2m(E(J) - V(x))} \tag{C.12}$$

where $E(J)$ can be found from inverting (C.1). The Hamilton equations then become

$$\frac{\partial \mathcal{H}}{\partial J} = \dot{\theta} = \frac{\omega}{2\pi} = \nu \tag{C.13}$$

and

$$\frac{\partial \mathcal{H}}{\partial \theta} = -\dot{J} = 0 \tag{C.14}$$

The solution is trivial: J is a constant of motion (that was after all the way it was set up) and

$$\theta(t) = \nu t + \theta_0 \tag{C.15}$$

Next we come to the FP equation. As Kramers states, the Liouville part is trivial. The density ρ is now a function of J and θ, and we can use the Poisson bracket to get

$$\frac{\partial}{\partial t}\rho(J,\theta,t) = \{\mathcal{H},\rho\} = \frac{\partial \mathcal{H}}{\partial \theta}\frac{\partial \rho}{\partial J} - \frac{\partial \mathcal{H}}{\partial J}\frac{\partial \rho}{\partial \theta} = -\nu\frac{\partial \rho}{\partial \theta} \tag{C.16}$$

If we average this over a full period:

$$\overline{\rho}(J,t) = \frac{1}{2\pi}\int_0^{2\pi} d\theta\, \rho(J,\theta,t) \tag{C.17}$$

we find of course:

$$\frac{\partial}{\partial t}\overline{\rho}(J,t) = 0 \tag{C.18}$$

which shows that this part of Kramers statement is correct. The second, dissipative part of the FP equation is less trivial. The direct way would be to transform the derivative with respect to p to derivatives with respect to J and θ. Obviously the old coordinate and momentum must be functions of the new. Another guiding principle is that the equilibrium solution:

$$\rho_{eq}(J) = e^{-E(J)/k_BT} \tag{C.19}$$

still has to be a solution of the general equation, which would lead directly to the following expression, which has to occur:

$$\left(\nu(J) + k_BT\frac{\partial}{\partial J}\right) e^{-E(J)/k_BT} = 0 \tag{C.20}$$

But even using this the possibilities are still endless. A proper starting point would of course be a Langevin equation for energy diffusion, calculating moments, making assumtptions about the higher moments, and in that way derive FP.

C.1 Application to the harmonic oscillator.

For the harmonic oscillator, the action is given by:

$$J = \frac{2\pi}{\omega}E \tag{C.21}$$

so that $E(J)$ is equal to:

$$E(J) = \frac{\omega J}{2\pi} = \nu J \tag{C.22}$$

The angle variable is given by

$$\theta = \frac{\partial W}{\partial J} = m\nu \int dx\, \frac{1}{\sqrt{2m\nu J - m^2\omega^2 x^2}} = \frac{1}{2\pi}\arcsin x\sqrt{\frac{\pi m\omega}{J}} = \frac{1}{2\pi}\arcsin x\sqrt{\frac{m\omega^2}{2E}} \tag{C.23}$$

In this case it is easy to express p and x in J and θ; after a short calculation we find:

$$x = \sqrt{\frac{J}{\pi m\omega}} \sin 2\pi\theta \qquad \text{and} \qquad p = \sqrt{\frac{m\omega J}{\pi}} \cos 2\pi\theta \tag{C.24}$$

The inverse transformation is also straightforward, we get

$$J = \frac{\pi}{m\omega} p^2 + \pi m\omega x^2 \tag{C.25}$$

and

$$\theta = \frac{1}{2\pi} \arctan\left(\frac{m\omega x}{p}\right) \tag{C.26}$$

Note that this definition of θ differs slightly from the one used in eq. (1.31). To get the connection, one can use $\arctan(1/x) = \pi/2 - \arctan x$. From these expressions it follows immediately that

$$\frac{\partial}{\partial p} = \frac{\partial J}{\partial p}\frac{\partial}{\partial J} + \frac{\partial \theta}{\partial p}\frac{\partial}{\partial \theta} = \sqrt{\frac{4\pi J}{m\omega}} \cos 2\pi\theta \frac{\partial}{\partial J} - \frac{\sin 2\pi\theta}{\sqrt{4\pi m\omega J}}\frac{\partial}{\partial \theta} \tag{C.27}$$

So now we can calculate the second term in the FP equation, of which the operator part can be written:

$$\zeta k_B T \left(\frac{\partial^2}{\partial p^2} + \frac{1}{m k_B T}\frac{\partial}{\partial p} p\right) \tag{C.28}$$

The resulting expression is of course similar to eq. (1.31), and we will not go into the details here.

D General solution of the FP equation for the damped oscillator.

The general solution of the FP equation for the damped oscillator can be found in [5]. We rewrite it here in our notation and give various limiting cases. First we introduce the functions ξ and η as:

$$\xi = (s_1 x - v)e^{-s_2 t} \qquad \text{and} \qquad \eta = (s_2 x - v)e^{-s_1 t} \tag{D.1}$$

with initial values

$$\xi_0 = (s_1 x_0 - v_0) \qquad \text{and} \qquad \eta_0 = (s_2 x_0 - v_0) \tag{D.2}$$

We note here that x and v are stochastic variables, whereas x_0 and v_0 are given quantities.
Furthermore we define three functions a, b and h as respectively

$$a = \frac{\zeta k_B T}{m^2 s_1}\left(1 - e^{-2s_1 t}\right) \tag{D.3}$$

$$b = \frac{\zeta k_B T}{m^2 s_2}\left(1 - e^{-2s_2 t}\right) \tag{D.4}$$

and

$$h = -2\frac{\zeta k_B T}{m^2(s_1+s_2)}\left(1 - e^{-(s_1+s_2)t}\right) = 2\frac{k_B T}{m}\left(1 - e^{\zeta t/m}\right) \tag{D.5}$$

and a function Δ as:

$$\Delta = ab - h^2 \tag{D.6}$$

The solution of the FP equation for P can then be written as

$$P(t) = \frac{e^{\zeta t/m}}{2\pi\sqrt{\Delta}} \exp\left(-\frac{a(\xi-\xi_0)^2 + 2h(\xi-\xi_0)(\eta-\eta_0) + b(\eta-\eta_0)^2}{2\Delta}\right) \tag{D.7}$$

This is the general solution of the FP equation for a harmonically bound particle. We now consider a number of limiting cases.

The limit $t \to 0$.

If we let $t \to 0$, we should get back the initial distribution, which is a product of delta functions. Expanding all quantities as functions of t we get:

$$a \to 2\frac{\zeta k_B T}{m^2}(t - s_1 t^2 \cdots), \quad b \to 2\frac{\zeta k_B T}{m^2}(t - s_2 t^2 \cdots), \quad h \to -2\frac{\zeta k_B T}{m^2}\left(t + \frac{\zeta}{2m}t^2 \cdots\right) \tag{D.8}$$

The limit $t \to \infty$.

If we let $t \to \infty$ we should get the equilibrium distribution. In this limit all exponents occuring in the above expressions go to ∞, which means we can neglect constant terms like ξ_0 and η_0 compared to resp. ξ and η. We get for the various quantities:

$$a \sim -\frac{\zeta k_B T}{m^2 s_1} e^{-2s_1 t}, \quad b \sim -\frac{\zeta k_B T}{m^2 s_2} e^{-2s_2 t}, \quad \text{and} \quad h \sim 2\frac{k_B T}{m} e^{\zeta t/m} \tag{D.9}$$

In view of the above remarks, it is easy to see that

$$a(\xi - \xi_0)^2 \sim -\frac{\zeta k_B T}{m^2 s_1} e^{-2s_1 t}(s_1 x - v)^2 e^{-2s_2 t} = -\frac{\zeta k_B T}{m^2 s_1}(s_1 x - v)^2 e^{2\zeta t/m} \tag{D.10}$$

Similarly

$$b(\eta - \eta_0)^2 \sim -\frac{\zeta k_B T}{m^2 s_2} e^{-2s_2 t}(s_2 x - v)^2 e^{-2s_1 t} = -\frac{\zeta k_B T}{m^2 s_2}(s_2 x - v)^2 e^{2\zeta t/m} \tag{D.11}$$

and

$$2h(\xi - \xi_0)(\eta - \eta_0) \sim 4\frac{k_B T}{m}(s_1 x - v)(s_2 x - v) e^{2\zeta t/m} \tag{D.12}$$

In addition we get for Δ:

$$\Delta \sim \left(\frac{k_B T}{m}\right)^2 \left(\frac{\zeta^2}{m^2 \omega^2} - 4\right) e^{2\zeta t/m} \tag{D.13}$$

and for the sum of (D.10)–(D.12) we get:

$$a(\xi-\xi_0)^2 + 2h(\xi-\xi_0)(\eta-\eta_0) + b(\eta-\eta_0)^2 \sim \frac{k_B T}{m}\left(-\frac{\zeta}{m s_1}(s_1 x - v)^2 + 4(s_1 x - v)(s_2 x - v) - \frac{\zeta}{m s_2}(s_2 x - v)^2\right) e^{2\zeta t/m} \tag{D.14}$$

The limit $\zeta \to 0$.

In this limit we expect to get the solution to the Liouville equation which is just a product of delta functions, reflecting the fact that motion is deterministic in this case. In this limit $s_{1,2}$ approach $\pm i\omega$ and consequently $s_1 + s_2 \to 0$. Up to order ζ we get for the various quantities:

$$a \to -i\zeta\frac{k_B T}{m^2 \omega}, \quad b \to i\zeta\frac{k_B T}{m^2 \omega}, \quad \text{and} \quad h \to -2\zeta t\frac{k_B T}{m^2} \tag{D.15}$$

$$\xi \to (i\omega x - v)e^{i\omega t}, \quad \eta \to (-i\omega x - v)e^{-i\omega t}, \quad \xi_0 \to (i\omega x_0 - v_0), \quad \text{and} \quad \eta_0 \to (-i\omega x_0 - v_0) \tag{D.16}$$

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