Introduction to Kramers Equation

Steven Jenks
Drexel University
Statistical Mechanics II

December 11, 2006

1 Introduction

Physicists have deserted the idea of determinism as a model for reality. Our most precise laws are quantum mechanical in nature, which limits our ability to predict (with precision) even the simplest systems of interest. Therefore probabilistic, stochastic, models are developed and refined in order to properly understand natural phenomena.

Kramers equation is a special form of the Fokker-Planck equation used to describe the Browian motion of a potential. The probability density is described in terms of $p(x,v,t)$ through a partial differential equation. In this short paper, Kramers equation is derived from the stochastic differential equations, general solutions to the partial differential equation are discussed and applied to a simple system that can be solved exactly (harmonically bound particle in a random force).

2 Derivation of Kramers equation

All continuous, Markov, stochastic normal processes have two alternative but mathematical equivalent descriptions. There is one that is a governed by random variables (stochastic differential equations) and another that is in terms of the probability density $p(x,v,t)$ and its partial differential equation. Remembering that each two variable process is governed by the two stochastic differential equations;

$$dV = a(X,V)dt + \sqrt{q(X,V)dt}N_t(0,1) \tag{1}$$

$$dX = V dt \tag{2}$$

with $a(X,V)$ and $q(X,V)$ being very general to accomadate many cases. Please note the notation used for the stochastic force, $\sqrt{q(X,V)dt}N_t(0,1)$, $N_t(0,1)$ being a normal distribution with a mean of 0 and variance of 1. This seems a bit odd but is very much equal to the normal notation of the stochastic force, $\Gamma(t)$. The reader is encouraged to investigate this notation from reference [1], as it is not explained in this paper. Now, the key to converting one description to another is equation (3) below.

$$\int\int f(x,v)\frac{\partial p}{\partial t}dxdv = \left\langle \frac{df(X,V)}{dt} \right\rangle, \tag{3}$$

$f(X,V)$ is a smooth function of X and V and

$$\begin{aligned} df &= \frac{\partial f}{\partial X}dX + \frac{\partial f}{\partial V}dV + \frac{\partial^2 f}{\partial V^2}\frac{(dV)^2}{2} \\ &= \frac{\partial f}{\partial X}V dt + \frac{\partial f}{\partial V}\left[adt + \sqrt{qdt}N_t(0,1)\right] + \frac{\partial^2 f}{\partial V^2}\frac{qdt}{2}, \end{aligned}$$

and the terms smaller then dt have been dropped. Substituting this result into equation (3) yields

$$\begin{aligned}\int\int f\frac{\partial p}{\partial t}dxdv &= \left\langle V\frac{\partial f}{\partial X}+a\frac{\partial f}{\partial V}+\frac{q}{2}\frac{\partial^2 f}{\partial V^2}\right\rangle \\ \int\int f\frac{\partial p}{\partial t}dxdv &= \int\int\left[v\frac{\partial f}{\partial x}+a\frac{\partial f}{\partial v}+\frac{q}{2}\frac{\partial^2 f}{\partial v^2}\right]pdxdv\end{aligned}$$

integrating by parts the right hand side and dropping the surface terms;

$$\int\int f(x,v)\frac{\partial p}{\partial t}dxdv = \int\int f(x,v)\left[-v\frac{\partial p}{\partial x}-\frac{\partial}{\partial v}(ap)+\frac{1}{2}\frac{\partial^2}{\partial v^2}(qp)\right]dxdv$$

Looking at both sides of the equation yield a result of

$$\frac{\partial p}{\partial t}+v\frac{\partial p}{\partial x} = -\frac{\partial}{\partial v}(ap)+\frac{1}{2}\frac{\partial^2}{\partial v^2}(qp) \tag{4}$$

With equation (4) being a general form of kramers equation. For example, the harmonically bound potential which is solved in this paper has $a=-\gamma V-\omega^2 x$ and $q=\frac{2kt\gamma}{m}$.

$$\frac{\partial p}{\partial t}+v\frac{\partial p}{\partial x} = \frac{\partial}{\partial v}\left[(\omega^2 x+\gamma v)p\right]+\frac{kt\gamma}{m}\frac{\partial^2 p}{\partial v^2} \tag{5}$$

3 General Solution of Kramers Equation

Some of the steps that are used here to develop a general solution of kramers equation require additional knowledge that go beyond the scope of this paper. It is not the purpose of this paper to go through all the rigorous mathematical steps that are needed to develop the general solution but just present the solution in a practical manner that can be applied to a simple application.

3.1 Preliminaries-Ornstein Uhlenbeck Process

A Langevin equation of this type;

$$\dot{\zeta}_i+\sum_{j=1}^{N}\gamma_{ij}\zeta_j=\Gamma_i(t); \qquad i=1,\ldots,N$$

with the δ-correlated Gaussian Langevin forces

$$\begin{aligned}\langle\Gamma_i(t)\rangle &= 0\\ \left\langle\Gamma_i(t)\Gamma_j(\acute{t})\right\rangle &= q_{ij}\delta(t-\acute{t})\\ q_{ij} &= q_{ji}\end{aligned}$$

describes the Ornstein-Uhlenbeck process, equations (1) and (2) are examples of this process. The main features are that the differential equations are linear and the strength of the noise doesn't depend on ζ. We now look for the homogeneous solution of the differential equations with the initial conditions satisfying $\zeta_i(0) = x_i$. Using the initial conditions, the solution can be expressed as

$$\zeta_i^h(t) = G_{ij}(t)x_j \tag{6}$$

where the Greens function $G_{ij}(t)$ must satisfy the initial condition $G_{ij}(0) = \delta_{ij}$. With this knowledge Greens function must also satisfy the differential equation

$$\dot{G_{ij}} + \gamma_{ik}G_{jk} = 0$$

and the general solution to being

$$\boldsymbol{G}(t) = exp(-\boldsymbol{\gamma} t) \tag{7}$$

For the purposes of this paper the inhomogeneous solution is just stated below

$$\zeta_i^{inh}(t) = \int_0^t G_{ij}(\acute{t})\Gamma_j(t-\acute{t})d\acute{t}$$

With the general solution of $\zeta_i(t)$

$$\zeta_i(t) = \zeta_i^h(t) + \zeta_i^{inh}(t) = G_{ij}(t)x_j + \int_0^t G_{ij}(\acute{t})\Gamma_j(t-\acute{t})d\acute{t} \tag{8}$$

3.1.1 Calculation of First Moment and Variance

From equation (8) and the properties of the Langevin force, it is easily seen that the first moment is

$$M_i(t) = \langle \zeta_i(t) \rangle = G_{ij}(t)x_j \tag{9}$$

and the variance is also easily obtained

$$\begin{aligned}
\sigma_{ij}(t) &= \sigma_{ji}(t) = \langle [\zeta_i(t) - \langle \zeta_i(t)\rangle]\,[\zeta_j(t) - \langle \zeta_j(t)\rangle] \rangle \\
&= \int_0^t \int_0^t G_{ik}(\acute{t_1})G_{js}(\acute{t_2})q_{ks}\delta(\acute{t_1} - \acute{t_2})d\acute{t_1}d\acute{t_2} \\
&= \int_0^t G_{ik}(\acute{t})G_{js}(\acute{t})q_{ks}d\acute{t} \qquad (10)
\end{aligned}$$

It can also be shown that

$$\dot{\sigma_{ij}} = -\gamma_{ik}\sigma_{kj} - \gamma_{jk}\sigma_{ki} + q_{ij} \tag{11}$$

by differentiating σ_{ij} and using the differential equation $\dot{G_{ij}} + \gamma_{ik}G_{jk} = 0$

3.2 Solution to Kramers Equation

We are now ready to solve the general Fokker-Planck equation for several variables, hence kramers equation. The transition probability, $P(\{x\}, \acute{t} \mid \{\acute{x}\}, \acute{t})$, is given in the partial differential equation

$$\frac{\partial P}{\partial t} = \gamma_{ij}\frac{\partial}{\partial x_i}(x_j P) + D_{ij}\frac{\partial^2 P}{\partial x_i \partial x_j} \tag{12}$$

where the matrices $\gamma_{ij}, D_{ij} = D_{ji}$ are constant and are the drift and diffusion coefficient respectively. One can see that equations (4) and (5) are of this form. Also, P must satisfy the initial condition $P(\{x\}, \acute{t} \mid \{\acute{x}\}, \acute{t}) = \delta(\{x\} - \{\acute{x}\})$. If P is expressed by its fourier transform with respect to the variables $\{x\}$ then the first order differential equation

$$\frac{\partial \tilde{P}}{\partial t} = -\gamma_{ij}k_i\frac{\partial \tilde{P}}{\partial k_j} - D_{ij}k_i k_j \tilde{P} \tag{13}$$

is obtained and the initial condition is now

$$\tilde{P}(\{x\}, \acute{t} \mid \{\acute{x}\}, \acute{t}) = exp(-ik_j \acute{x_j})$$

There is more then one way to solve this differential equation, however here the solution is acquired through the ansatz

$$\tilde{P}(\{x\}, \acute{t} \mid \{\acute{x}\}, \acute{t}) = exp\left[-ik_i M_i(t-\acute{t}) - \frac{1}{2}k_i k_j \sigma_i j(t-\acute{t})\right] \tag{14}$$

and inserting this solution back into equation (13) yields the following

$$(-ik_i\dot{M_i} - \frac{1}{2}k_i k_j \dot{\sigma_{ij}} - \gamma_{ij}k_i i M_j - \gamma_{ij}k_i\sigma_{jl}k_l + D_{ij}k_i k_j)\tilde{P} = 0 \tag{15}$$

and noting that the following two differential equations are a consequence of (15)

$$\dot{M_i} = -\gamma_{ij}M_j \tag{16}$$

$$\dot{\sigma_{ij}} = -\gamma_{il}\sigma_{lj} - \gamma_{jl}\sigma_{li} + 2D_{ij} \tag{17}$$

Using the initial condition of $\tilde{P}(\{x\}, \acute{t} \mid \{\acute{x}\}, \acute{t})$ gives the initial conditions to equations (16) and (17).

$$\begin{aligned} M_i(0) &= \acute{x_i} \\ \sigma_{ij}(0) &= 0 \end{aligned} \tag{18}$$

The solutions of (16) and (17) can be solved given the initial conditions above

$$M_i(t-\acute{t}) = G_{ij}(t-\acute{t})\acute{x_j} \tag{19}$$

$$\sigma_{ij}(t) = \int_0^t G_{ik}(\acute{t})G_{js}(\acute{t})2D_{ks}d\acute{t} \tag{20}$$

These two results should look familiar, as the Greens function G_{ij} is the same one as in section 3.1 satisfying the initial condition $G_{ij}(0) = \delta_{ij}$. Now Getting back to finding the solution of equation (12), to do this we then insert the solution $\tilde{P}$ back into its fourier transform and integrates to find,

$$\begin{aligned}\tilde{P}(\{x\}, \acute{t} \mid \{\acute{x}\}, \acute{t}) &= (2\pi)^{-\frac{N}{2}} \left[Det\,\sigma(t-\acute{t})\right]^{-\frac{1}{2}} \\ &\times exp\{-\frac{1}{2}\left[\sigma^{-1}(t-\acute{t})\right]_{ij}\left[x_i - G_{ik}(t-\acute{t})\acute{x_k}\right] \\ &\qquad \times \left[x_j - Gjl(t-\acute{t})\acute{x_l}\right]\}\end{aligned} \tag{21}$$

3.2.1 Expansion into a Biorthogonal Set

Now we are going to assume that a complete biorthogonal set of the matrix $\boldsymbol{\gamma}$ exists.

$$\gamma_{ij}u_j^{(\alpha)} = \lambda_\alpha u_i^{(\alpha)}; \quad v_i^{(\alpha)}\gamma_{ij} = \lambda_\alpha v_j^{(\alpha)} \tag{22}$$

with the orthonormality and completeness relation

$$\sum_\alpha v_i^{(\alpha)}u_j^{(\alpha)} = \delta_{ij}; \quad \sum_i u_i^{(\alpha)}v_i^{(\beta)} = \delta_{\alpha\beta} \tag{23}$$

Such a complete biorthogonal set exists if the N eigenvalues aren't degenerate. In order to avoid degenerate eigenvalues the matrix γ_{ij} may be changed to $\epsilon\hat{\gamma_{ij}}$. In the final result, the limit $\epsilon \to 0$. The decomposition of the matrix $\boldsymbol{\gamma}$ is

$$\gamma_{ij} = \sum_\alpha \lambda_\alpha u_i^{(\alpha)}v_j^{(\alpha)} \tag{24}$$

and we can find Greens function $G_{ij}(t)$

$$G_{ij}(t) = [exp(-\gamma t)]_{ij} = \sum_\alpha e^{-\lambda_\alpha t}u_i^{(\alpha)}v_j^{(\alpha)} \tag{25}$$

and $\sigma_{ij}(t)$ by inserting $G_{ij}(t)$ into equation (20), then perform the integration to find

$$\begin{aligned}\sigma_{ij}(t) &= 2\sum_{\alpha,\beta}\frac{1-e^{-(\lambda_\alpha+\lambda_\beta)t}}{\lambda_\alpha+\lambda_\beta}D^{(\alpha,\beta)}u_i^{(\alpha)}v_j^{(\alpha)} \\ D^{(\alpha,\beta)} &= v_k^{(\alpha)}D_{kl}v_l^{(\beta)}\end{aligned} \tag{26}$$

4 Application-Harmonically Bound Particle

Kramers equation for the harmonically bound particle is

$$\frac{\partial p}{\partial t} + v\frac{\partial p}{\partial x} = \frac{\partial}{\partial v}\left[(\omega^2 x + \gamma v)p\right] + \frac{kt\gamma}{m}\frac{\partial^2 p}{\partial v^2} \tag{27}$$

and the two matrices $\boldsymbol{\gamma}, \boldsymbol{D}$ can be found from equation 12

$$\gamma = \begin{pmatrix} 0 & -1 \\ \omega^2 & \gamma \end{pmatrix}; \qquad \mathbf{D} = \begin{pmatrix} 0 & 0 \\ 0 & \gamma v_{th}^2 \end{pmatrix} \tag{28}$$

with $v_{th} = \sqrt{\frac{kt}{m}}$. Now we can get the transition probability $P(x, v, t \mid \acute{x}, \acute{v}, 0)$ from equation (21);

$$\begin{aligned} P(x, v, t \mid \acute{x}, \acute{v}, 0) = (2\pi)^{-1}(Det\,\sigma)^{-\frac{1}{2}} exp\{-\frac{1}{2}\left[\sigma^{-1}(t)\right]_{xx}[x - x(t)]^2 \\ - \left[\sigma^{-1}(t)\right]_{xv}[x - x(t)][v - v(t)] - \frac{1}{2}\left[\sigma^{-1}(t)\right]_{vv}[v - v(t)]^2\} \end{aligned} \tag{29}$$

and the expectation values are found by using equation (19)

$$\begin{aligned} \langle x \rangle = x(t) = [exp(-\gamma t)]_{xx}\,\acute{x} + [exp(-\gamma t)]_{xv}\,\acute{v} \\ \langle v \rangle = v(t) = [exp(-\gamma t)]_{vx}\,\acute{x} + [exp(-\gamma t)]_{vv}\,\acute{v} \end{aligned} \tag{30}$$

The eigenvalues of the $\boldsymbol{\gamma}$ are now found to be

$$\lambda_{1,2} = \frac{1}{2}(\gamma \pm \sqrt{\gamma^2 - 4\omega^2}) \tag{31}$$

and noticing that;

$$\lambda_1 + \lambda_2 = \gamma, \qquad \lambda_1\lambda_2 = \omega^2 \tag{32}$$

By using equations (22-24) we find the column and row matrices,

$$\mathbf{u^{(1)}} = \begin{pmatrix} -1 \\ \lambda_1 \end{pmatrix}, \qquad \mathbf{u^{(2)}} = \begin{pmatrix} 1 \\ -\lambda_2 \end{pmatrix} \tag{33}$$

$$\mathbf{v^{(1)}} = \begin{pmatrix} \frac{\lambda_2}{\lambda_1 - \lambda_2} & \frac{1}{\lambda_1 - \lambda_2} \end{pmatrix}, \qquad \mathbf{v^{(2)}} = \begin{pmatrix} \frac{\lambda_1}{\lambda_1 - \lambda_2} & \frac{1}{\lambda_1 - \lambda_2} \end{pmatrix} \tag{34}$$

and using equation (25) we get

$$\begin{aligned} G_{xx}(t) = [exp(-\gamma t)]_{xx} &= \frac{\lambda_1 e^{-\lambda_2 t} - \lambda_2 e^{-\lambda_1 t}}{\lambda_1 - \lambda_2} \\ G_{xv}(t) = [exp(-\gamma t)]_{xv} &= \frac{e^{-\lambda_2 t} - e^{-\lambda_1 t}}{\lambda_1 - \lambda_2} \\ G_{vx}(t) = [exp(-\gamma t)]_{vx} &= \omega^2 \frac{e^{-\lambda_1 t} - e^{-\lambda_2 t}}{\lambda_1 - \lambda_2} \\ G_{vv}(t) = [exp(-\gamma t)]_{vv} &= \frac{\lambda_1 e^{-\lambda_1 t} - \lambda_2 e^{-\lambda_2 t}}{\lambda_1 - \lambda_2} \end{aligned} \tag{35}$$

the average values as one can see are

$$\begin{aligned} \langle x \rangle &= \frac{\lambda_1 e^{-\lambda_2 t} - \lambda_2 e^{-\lambda_1 t}}{\lambda_1 - \lambda_2}\acute{x} + \frac{e^{-\lambda_2 t} - e^{-\lambda_1 t}}{\lambda_1 - \lambda_2}\acute{v} \\ \langle v \rangle &= \omega^2 \frac{e^{-\lambda_1 t} - e^{-\lambda_2 t}}{\lambda_1 - \lambda_2}\acute{x} + \frac{\lambda_1 e^{-\lambda_1 t} - \lambda_2 e^{-\lambda_2 t}}{\lambda_1 - \lambda_2}\acute{v} \end{aligned}$$

Using equation (26) and finding that $\mathbf{D}^{(\alpha,\beta)} = \frac{\gamma v_{th}^2}{(\lambda_1-\lambda_2)^2}$, gives the $\boldsymbol{\sigma}$ matrix

$$\begin{aligned}
\sigma_{xx}(t) &= \frac{\gamma v_{th}^2}{(\lambda_1-\lambda_2)^2}\left[\frac{\lambda_1+\lambda 2}{\lambda_1\lambda_2} + \frac{4}{\lambda_1+\lambda 2}(e^{-(\lambda_1+\lambda_2)t}-1) - \frac{1}{\lambda_1}e^{-2\lambda_1 t} - \frac{1}{\lambda_2}e^{-2\lambda_2 t}\right] \\
\sigma_{xv}(t) &= \frac{\gamma v_{th}^2}{(\lambda_1-\lambda_2)^2}(e^{-\lambda_1 t}+e^{-\lambda_2 t})^2 \qquad (36) \\
\sigma_{vv}(t) &= \frac{\gamma v_{th}^2}{(\lambda_1-\lambda_2)^2}\left[\lambda_1+\lambda_2 + \frac{4\lambda_1\lambda_2}{\lambda_1+\lambda_2}(e^{-(\lambda_1+\lambda_2)t}-1) - \lambda_1 e^{-2\lambda_1 t} - \lambda_2 e^{-2\lambda_2 t}\right]
\end{aligned}$$

4.1 High Friction Limit

Let us now consider what happens in the high friction limit. First lets take a look at the eigenvalues and in this case they can be expanded as;

$$\lambda_{1,2} = \frac{1}{2}(\gamma \pm \sqrt{\gamma^2-4\omega^2} \approx \frac{1}{2}\gamma \pm \frac{1}{2}\gamma(1-\frac{2\omega^2}{\gamma^2}) \qquad (37)$$

$$\lambda_1 \approx \gamma, \qquad \lambda_2 \approx \frac{\omega^2}{\gamma} \qquad (38)$$

neglecting the terms $\frac{1}{\gamma^2}$. Consider now the average values for x and v, we see that both expressions contain exponentials with $-\lambda_1 t$ and $-\lambda_2 t$ in the exponent. For large γ this implies that one decreases exponentially with the other one decreasing slowly. Again removing the terms $\frac{1}{\lambda^2}$ and a little algebra gives you

$$\langle x(t)\rangle \approx \acute{x}e^{-\frac{\omega^2 t}{\gamma}} \qquad (39)$$

$$\langle v(t)\rangle \approx -\frac{\omega^2}{\gamma}\acute{x}e^{-\frac{\omega^2 t}{\gamma}} \qquad (40)$$

This is a very interesting result because the loss of an initial condition. This all points in the direction that in the high friction limit, the partial differential equation can be reduced to only include the position coordinate. This is exactly the case and although not derived in this paper, one will get the Smoluchowski differential equation.

4.2 Stationary Solution

For $\omega^2 > \gamma^2/4$ the real parts of the eigenvalues$\lambda_{1,2}$ are greater then zero and for $\gamma^2/4 \geq \omega^2$ the eigenvalues are greater then zero. Hence, equation (35) vanishes and for the σ matix;

$$\begin{aligned}
\sigma_{xx}(\infty) &= \frac{v_{th}^2}{\omega^2} \\
\sigma_{xv}(\infty) &= 0 \qquad (41) \\
\sigma_{vv}(\infty) &= v_{th}^2
\end{aligned}$$

and the probability distribution $P(x, v, \infty \mid \acute{x}, \acute{v}, 0)$ is derived from equation (21);

$$\begin{aligned} P(x, v, \infty \mid \acute{x}, \acute{v}, 0) &= \frac{\omega}{2\pi v_{th}^2} exp\left(-\frac{1}{2}\frac{v^2}{v_{th}^2} - \frac{\omega^2 x^2}{2v_{th}^2}\right) \\ &= \frac{m\omega}{2\pi kT} exp\left(-\frac{E}{kT}\right) \end{aligned} \tag{42}$$

4.3 Free Brownian Motion

For free Brownian motion without an external force,$\omega^2 \to 0$. The eigenvalues then go to $\lambda_1 \to \gamma, \lambda_2 \to 0$ and the expressions simplify to

$$\begin{aligned} \langle x(t) \rangle &= \acute{x} + \frac{(1 - e^{-\gamma t})\acute{v}}{\gamma} \\ \langle v(t) \rangle &= e^{-\gamma t}\acute{v} \\ \sigma_{xx}(t) &= v_{th}^2 \frac{(2\gamma t - 3 + 4e^{-\gamma t} - e^{-2\gamma t})}{\gamma^2} \\ \sigma_{xv}(t) &= v_{th}^2 \frac{(1 - e^{-\gamma t})^2}{\gamma} \\ \sigma_{vv}(t) &= v_{th}^2 (1 - e^{-2\gamma t}) \end{aligned}$$

References

[1] Lemons, Don. *An Introduction to Stochastic Processes in Physics*, Baltimore & London: Johns Hopkins, 2002.

[2] Risken, H. *The Fokker-Planck Equation*, Berlin: Springer, 1996.

[3] Oppenheim, Shuler, Weiss. *Stochastic Processes in Chemical Physics: The Master Equation*, Cambridge: MIT Press, 1977.

[4] Pathria, R.K. *Statistical Mechanics*, Oxford: Butterworth-Heinemann, 1996.