GIBBS-METHOD CALCULATION OF TRAJECTORY PROBABILITIES FOR A BROWNIAN PARTICLE

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*A method is derived for calculating trajectory probabilities for a Brownian particle in configuration space and phase space on the basis of general principles of Gibb's statistical mechanics. The method is freed of the usual theoretical limitations (i.e., a special form of the random process, a lack of correlation in the impulsive forces, etc.) and is applicable to various types of physical systems, including systems displaying an aftereffect. The method is illustrated for various examples of linear systems.

All available theoretical methods for describing Brownian motion are characterized by special limitations on the physical system (a δ-correlation of the impulsive forces, smallness of the fluctuations, the assumption of a stochastic Markovian process, etc.).

Below we derive a trajectory distribution for a Brownian particle without resorting to the usual theoretical limitations, using instead the basic principles of statistical mechanics. We will use the Gibbs method, derived by Terletskii, Vladimirskii, and Magalinskii [2, 4-7], which permits problems to be solved with minimal restrictions on the physical system.

§1. BROWNIAN PARTICLE IN CONFIGURATION SPACE

We consider a system whose microstates are described by the set X of all its canonical variables: $X=(X_1,\ldots, X_{6N})$, where N is the number of particles in the system. Let $F_1(X),\ldots, F_s(X)$ denote certain functions of the canonical variables of the system. If the system is held at a constant temperature (as is assumed everywhere below), the probability for a transition from the state $F = F_0$ (i.e., $F_1(X)=F_{10},\ldots, F_s(X)=F_{s0}$) at time t_0 to the state in which $F(X) = (F_1(X)=F_1,\ldots, F_s(X)=F_s)$ at some other time $t>t_0$ is, according to the general principles of Gibbs statistical mechanics,*

$$W(Ft, F_0t_0)=\int\limits_{(X^0)} \delta[F-F(X^t)]\,\frac{e^{\frac{\psi-H(X^0)}{\theta}}}{W_0(F_0)}\,\delta[F_0-F(X^0)]\,dX^0, \tag{1}$$

where $\delta[F]$ is the Dirac δ-function, $W_0(F_0)$ is the equilibrium probability density for a given F_0, and the canonical variables X^t and X^0 of the system are related by $X^t=\varkappa(X^0t_0;\, t)$. This is the solution of the dynamic equations of a system with a Hamiltonian H(X).

We divide the time interval (t_0, t) of interest here into n equal[1] parts by intermediate points $t_1, t_2,\ldots, t_{n-1}$; then the probability that the system, in the state $F = F_0$ at initial time t_0, will be in state $F = F_1$ at time $t_1>t_0$, in state $F = F_2$ at time $t_2>t_1$, etc., i.e., the probability that the system will have fixed F values at fixed times, is

$$W(Ft, F_{n-1}t_{n-1},\ldots, F_0t_0)=\int\limits_{(X^0)} \delta[F-F(X^t)]\,\delta[F_{n-1}-F(X^{t_{n-1}})]\ldots$$
$$\ldots\frac{e^{\frac{\psi-H(X^0)}{\theta}}}{W_0(F_0)}\,\delta[F_0-F(X^0)]\,dX^0, \tag{2}$$

where $X^{(t_i)}=\varkappa(X^0t_0;\, t_i)$ is the solution of the Hamiltonian equations. In the limit as $n\to\infty$, $t-t_0=\mathrm{const}$ and $\Delta t_i = t_i-t_{i-1}\to 0$, there is a transition to a continuous W{F(t)} dependence, and equation (2) is replaced by

$$W\{F(t)\}=\int\limits_{(X^0)} \delta\{F(t)-F(X^t)\}\,\frac{e^{\frac{\psi-H(X^0)}{\theta}}}{W_0(F_0)}\,dX^0,$$

*See /1-3/: Equation 1 was first derived by Ya. P. Terletskii.

where we have introduced the concept of δ-functional,* defined by

$$\delta\{F(t)\} = \lim_{\substack{n\to\infty \\ n\Delta t = t - t_0}} \prod_{k=1}^{n} \delta(F_k),$$

where $F_k \equiv F(t_k)$, $\Delta t = t_i - t_{i-1}$.

In the case in which we have F = x, i.e., F is the coordinate of the Brownian particle, x(t) becomes a trajectory in the Wiener sense, i.e., a continuous, nondifferentiable function of the time.

We must therefore derive from equation (2) the probability density for a trajectory for particular systems. Substituting into equation (2) the integral representation of the δ-function, introducing for W a characteristic function ϕ defined such that we have

$$W(Ft, \ldots, F_0 t_0) = \frac{1}{(2\pi)^n} \int_{-\infty}^{+\infty} \ldots \int \exp\left\{ i \sum_{j=1}^{n} \xi_j F_j \right\} \varphi(a_n t_n, \ldots, a_1 t_1) \prod_{j=1}^{n} d\xi_j, \tag{3}$$

and using the notation

$$Z(a_n t_n, \ldots, a_1 t_1) = e^{-\psi/\theta} \varphi(a_n t_n, \ldots, a_1 t_1), \tag{4}$$

we find

$$Z(a_n t_n, \ldots, a_1 t_1) = \int_{(X^0)} R\{F(X^0)\} \exp\left\{ -\frac{H(X^0) + \Sigma a_j F_{t_j}}{\theta} \right\} dX^0,$$

where

$$F_{t_j} \equiv F(X^{t_j}),\ a_j = i\xi_j\theta,\ R\{F(X^0)\} = \frac{\delta[F_0 - F(X^0)]}{W_0(F_0)}. \tag{5}$$

Using the Liouville theorem regarding conservation of phase volume, and using energy conservation, we rewrite (5) as

$$Z(a_n t_n, \ldots, a_1 t_1) = \int_{(X^\tau)} R\{F(X^0)\} \exp\left\{ -\frac{H(X^\tau) + \Sigma a_j F_{t_j}}{\theta} \right\} d(X)^\tau,$$

where

$$X^{t_j} = \varkappa(X^\tau \tau;,\ t;),\ F_{t_j} \equiv F(X^{t_j}).$$

Let us consider the probability density for some nonequilibrium process

$$w(X^\tau, \tau) = \frac{1}{Z} R\{F(X^0)\} \exp\left\{ -\frac{H(X^\tau) + \Sigma a_j F_{t_j}}{\theta} \right\}, \tag{6}$$

which obeys the equation of motion of a phase ensemble. Equation (6) can be treated as a nonequilibrium probability density for a phase ensemble formed from an equilibrium ensemble with a Hamiltonian $H' = H + \sum_{j=1}^{n} a_j F_{t_j}$ by a particular prescription** for fixing the canonical variables X^{t_0} at time t_0 by means of the function $R\{F(X^0)\} = \frac{\delta[F_0 - F(X^0)]}{W_0(F_0)}$. A system with a Hamiltonian $H + \Sigma a_j F_{t_j}$ can be treated as an equilibrium system [9] under the influence of additional external forces $-a_j$ which are turned on instantaneously at times t_{j-1} and which operate for time intervals (t_{j-1}, t_j) in the directions of the generalized coordinates F_{t_j} $(j = 1, 2, \ldots, n)$. All the moments of the distribution function are expressed in terms of the characteristic function: differentiating equation (5) and using equation (6) we find

$$a_j \overline{F_{t_j}^k}^a = \frac{-\theta}{Z} \frac{\partial Z}{\partial t_j}, \tag{7}$$

$$\overline{F_{t_j}^k}^a = \frac{(-\theta)^k}{Z} \frac{\partial^k Z}{\partial a_j^k}, \tag{8}$$

where the bar and the superscript a denote an averaging over ensemble (6), which we will below refer to as ensemble a.

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*Only for convenience; this is not a necessary condition.

**According to a theorem proved by A. Ya. Khinchin, any nonequilibrium ensemble can be extracted from an equilibrium ensemble by specifying certain mechanical quantities or their initial distribution.

Knowing the moments of the quantities F calculated for ensemble (6), we can thus find $Z(a_n t_n, \ldots, a_1 t_1)$ and, consequently $W(F_n t_n, \ldots, F_0 t_0)$. These times can be found: first, if we know the behavior of the averages $\bar{F}^a$ whereof the corresponding average velocities $\dot{\bar{F}}^a$ in the nonequilibrium process under the influence of additional external constant "forces," second, if we have a relation among the various moments $\bar{F}^a$. This relation is usually found by averaging the known phenomenological (Langevin) equations over ensemble (6).

In the former case W was found by an immediate integration of equations (7) and (8); in the latter case, a differential equation is found for W.

We defined the function $\Delta\psi_n$ by

$$\Delta\psi_n(a_n t_n, \ldots, a_1 t_1) = -\theta \ln Z(a_n t_n, \ldots, a_1 t_1). \tag{9}$$

Using (3)-(5) and (9), we find

$$W(F_n t_n, \ldots, F_0 t_0) = \frac{1}{(2\pi)^n} \int_{-\infty}^{\infty} \cdots \int \exp\left\{ i \sum_{j=1}^{n} \xi_j F_j - \frac{\Delta\psi_n(a_n t_n, \ldots, a_1 t_1)}{\theta} \right\} \prod_{j=1}^{n} d\xi_j. \tag{10}$$

We can use this equation to find the probability for a trajectory from the known $\Delta\psi_n$.

Let us assume that F = x is the coordinate of the Brownian particle (for simplicity, we restrict the analysis to a single dimension; the generalization to three dimensions is trivial). Equations (7) and (8) can be rewritten as

$$a_j \dot{\bar{x}}^a_{t_j} = \frac{\partial \Delta\psi_n}{\partial t_j}, \tag{7'}$$

$$\bar{x}^a_{t_j} = \frac{\partial \Delta\psi_n}{\partial a_j}, \qquad \overline{x^k_{t_j}}^a = \frac{(-\theta)^k}{Z} \frac{\partial^k Z}{\partial a_j^k}. \tag{8'}$$

We supplement equations (7') and (8') with initial conditions. Since

$$W(xt, \ldots, x_0 t_0)|_{t_{i-1}=t_i} = \delta(x_i - x_{i-1}) W(xt, \ldots, x_i t_i, x_{i-2} t_{i-2}, \ldots, x_0 t_0),$$

we find from (10) that

$$\Delta\psi_n(a_n t_n, \ldots, a_1 t_1)|_{t_i = t_{i-1}} = a_i x_{i-1} + \Delta\psi_{n-1}(a_n t_n, \ldots, a_i t_i, a_{i-2} t_{i-2}, \ldots, a_1 t_1). \tag{11}$$

If, instead of (n−1) intermediate points, we use a single intermediate point, we find

$$\Delta\psi_2(a_2 t_2, a_1 t_1)|_{t_2=t_1} = a_2 x_1 + \Delta\psi(a_1 t_1), \tag{11'}$$

where [7]

$$\Delta\psi(at) = a \int_{t_0}^{t} \dot{\bar{x}}^a(\tau)\, d\tau + a x_0. \tag{12}$$

The solution of system (7) with auxiliary conditions (11), (11'), and (12) is thus

$$\Delta\psi_n(a_n t_n, \ldots, a_1 t_1) = \sum_{j=1}^{n} a_j \int_{t_{j-1}}^{t_j} \dot{\bar{x}}^a(\tau_j)\, d\tau_j + \sum_{j=1}^{n} a_j x_{j-1}, \tag{13}$$

where $-a$ denotes an averaging over the ensemble which is influenced by a constant external force $-a_1$ during the time interval (t_0, t_1), by $-a_2$ in the interval (t_1, t_2), etc., we note that $\int_{t_{j-1}}^{t_j} \dot{\bar{x}}^a(\tau)\, d\tau = \bar{x}^a_{t_j} - \bar{x}^a_{t_{j-1}}$ can be treated as the average displacement of the Brownian particule during the time $(t_j - t_{j-1})$ caused by the additional constant $-a_j$.

Knowing the behavior of the average rate of change of the coordinate of a Brownian particle caused by additional external force (directly from experiment or by averaging the well-known phenomenological equations), we can thus calculate $\Delta\psi_n(a_n t_n, \ldots, a_1 t_1)$ from equation (13) and then find the trajectory probability from equation (10).

We will illustrate this method with some simple examples.

FREE BROWNIAN MOTION. Neglecting the particles inertia, we write the Langevin equation $\gamma\dot{x} = \zeta(t)$. Averaging this equation over ensemble $\hat{a}$, and using $\bar{\zeta}^a(t) = 0$, we find $\gamma \dot{\bar{x}}^a_{t_j} = -a_j$. According to equation (13), we have

$$\Delta\psi_n = -\sum_{j=1}^{n} \frac{a_j^2}{\gamma}(t_j - t_{j-1}) + \sum_{j=1}^{n} a_j x_{j-1}. \tag{14}$$

Substituting (14) into (10) and replacing a_j by $i\xi_j\theta$ and integrating over all a_j, we find (in the system of units in which we have $\gamma/4\theta = 1$)

$$W(x_n t_n, \ldots, x_0 t_0) = \frac{1}{\sqrt{\pi^n (\Delta t)^n}} \exp\left\{-\sum_{j=1}^{n} \frac{(x_j - x_{j-1})^2}{\Delta t}\right\}, \tag{15}$$

i.e., the familiar Wiener measure (see e.g. [10]). Using the arguments above about the nature of the trajectory of a Brownian particle, we can write this measure symbolically as

$$W\{x(t)\} = \frac{1}{N} \exp\left\{-\int_{t_0}^{t} \left[\frac{dx(\tau)}{d\tau}\right]^2 d\tau\right\},$$

where N is a normalization factor. We note that equation (15) could be derived (as in fact is usually done) as the product (if, of course, the process is assumed to be Markovian) of independent or nonintersecting time intervals of Gaussian distributions or, equivalently, as the product of solutions of diffusion differential equation $\frac{\partial W}{\partial t} = D \frac{\partial^2 W}{\partial x^2}$ with the appropriate initial conditions. However, we have nowhere restricted the analysis to Markovian processes; instead we have proceeded from a specific form of the Langevin equation*.

OSCILLATOR IN A VISCOUS MEDIUM. The Langevin equation averaged over ensemble a is

$$\gamma \dot{\bar{x}}_{t_j}^{a} + k \bar{x}_{t_j}^{a} = -a_j. \tag{16}$$

Using equations (7') and (8') we can replace (16) by

$$\gamma \frac{\partial \Delta\psi_n}{\partial t_j} + a_j k \frac{\partial \Delta\psi_n}{\partial a_j} + a_j^2 = 0. \tag{17}$$

Solving equation (17) by the method of characteristics with the initial conditions which follow from (11), we find

$$\Delta\psi_n = \sum_{j=1}^{n} \Delta\psi(a_j t_j) = -\sum_{j=1}^{n} \frac{a_j^2}{2k}\left(1 - e^{-2\frac{k}{\gamma}\Delta t}\right) + \sum_{j=1}^{n} a_j x_{j-1} e^{-\frac{k}{\gamma}\Delta t}.$$

For W we find

$$W(x_n t_n, \ldots, x_0 t_0) = \sqrt{\frac{k^n}{(2\pi\theta)^n \left(1 - e^{-2\frac{k}{\gamma}\Delta t}\right)^n}} \times$$

$$\times \exp\left\{-\sum_{j=1}^{n} \frac{k\left(x_j - x_{j-1} e^{-\frac{k}{\gamma}\Delta t}\right)^2}{2\theta\left(1 - e^{-2\frac{k}{\gamma}\Delta t}\right)}\right\},$$

or, letting $\Delta t \to 0$, we find (in symbolic form

$$W\{x(t)\} = \frac{1}{N} \exp\left\{-\int_{t_0}^{t} \left[\left(\dot{x}(\tau) + \frac{k}{\gamma} x(\tau)\right)^2 - \frac{1}{2}\frac{k}{\gamma}\right] d\tau\right\},$$

which is the same result as that found by Beilinson [11] through a replacement of variables in the functional integral.

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*It was recently shown by Stratonovich [12] that the very use of phenomenological macroscopic first-order equations is equivalent to adopting the hypothesis that the process is a Markovian process. The use of first-order Langevin equations in these examples is not, however, a fundamental part of the method. Higher-order equations could be used as phenomenological equations (i.e., those describing a non-Markovian process in a phase space of the given dimensionality), but this procedure would involve mathematical difficulty.

§2. CALCULATION OF THE TRAJECTORY PROBABILITY IN PHASE SPACE

We can also use this method to calculate the trajectory probability $W\{x(t)v(t)\}$ in phase space. We assume that the functions F(X) of the canonical variables are $F_1(X^t) = x(X^t)$, the coordinate of the Brownian particle, and $F_2(X^t) = p(X^t)$, the corresponding momentum. Omitting the arguments analogous to those in section §1 we write down the equations corresponding to equations (7), (8), (7'), (8'), (11), (12) and (10):

$$a_k\overline{x_{t_k}}^{ab} + b_k\overline{p_{t_k}}^{ab} = \frac{-\theta}{Z}\frac{\partial Z}{\partial t_k}, \tag{18}$$

$$\overline{x^{\nu}_{t_k}}^{ab} = \frac{(-\theta)^{\nu}}{Z}\frac{\partial^{\nu} Z}{\partial a_k^{\nu}}, \quad \overline{p^{\nu}_{t_k}}^{ab} = \frac{(-\theta)^{\nu}}{Z}\frac{\partial^{\nu} Z}{\partial b_k^{\nu}}, \tag{19}$$

$$\frac{\partial \Delta\psi_n}{\partial t_k} = a_k\overline{x_{t_k}}^{ab} + b_k\overline{p_{t_k}}^{ab}, \tag{20}$$

$$\frac{\partial \Delta\psi_n}{\partial a_k} = \overline{x_{t_k}}^{ab}, \quad \frac{\partial \Delta\psi_n}{\partial b_k} = \overline{p_{t_k}}^{ab}, \tag{21}$$

$$W(x_n p_n t_n, \ldots, x_0 p_0 t_0) = \frac{1}{(2\pi)^{2n}} \int_{-\infty}^{+\infty} \cdots \int \prod_{k=1}^{n} d\xi_k d\eta_k \times$$

$$\times \exp\left\{ i\sum_{k=1}^{n} (\xi_k x_k + \eta_k p_k) - \frac{\Delta\psi_n}{\theta}\right\}, \tag{22}$$

$$\Delta\psi_n(a_n b_n t_n, \ldots, a_1 b_1 t_1)|_{t_i = t_{i-1}} = a_i x_{i-1} + b_i p_{i-1} + \Delta\psi_{n-1}, \tag{23}$$

where $\Delta\psi_1$ is found from the condition

$$\Delta\psi_1|_{t=t_0} = ax_0 + bp_0;$$

if

$$W(xpt, x_0 p_0 t_0)|_{t=t_0} = \delta(x - x_0)\,\delta(p - p_0). \tag{24}$$

The probability for a trajectory in phase space can be calculated in the following manner.

From the averages calculated over ensemble ab known directly from experiment or from the phenomenological Langevin equations, we find $\Delta\psi_n$ or Z from equations (20), (21) or (18), (19) with an account of equations (23) and (24); the physical nature of the quantities a and b depends in each particular case on the quantities x and p.

Substituting $i\xi_k\theta$ and $i\eta_k\theta$, into $\Delta\psi_n$ (or into Z) for a_k and b_k, respectively, and integrating over all ξ and all η, we find the final trajectory probability $W(x_n p_n t_n, \ldots, x_0 p_0 t_0)$. To find the continuous* trajectory, we must evidently go to the limit $\Delta t \to 0$, $n \to \infty$, and $\Delta t n = t - t_0$.

To illustrate the calculation, we show the trajectory probability calculated for a free Brownian particle. We write the Langevin equations $\dot{x} = \frac{p}{m}$, $\dot{p} = -\gamma\dot{x} + \xi(t)$. In this case the probability W for a trajectory in phase (coordinate and velocity) space is

$$W(x_n v_n t_n, \ldots, x_0 v_0 t_0) = \sqrt{\frac{\gamma^n}{2^n (2\pi\theta)^{2n} \left(1 - e^{-2\frac{\gamma}{m}\Delta t}\right)^n f^n(t)}} \times$$

$$\times \exp\left\{ -\frac{m}{2\theta}\sum_{k=1}^{n} \frac{\left(v_k - v_{k-1}e^{-\frac{\gamma}{m}\Delta t}\right)^2}{1 - e^{-2\frac{\gamma}{m}\Delta t}} \right\} \exp\left\{ -\sum_{k=1}^{n} \frac{\gamma^2 A_k^2}{4m\theta f(t)} \right\},$$

where

$$A_k = x_k - x_{k-1} - \frac{m}{\gamma} v_{k-1}\left(1 - e^{-\frac{\gamma}{m}\Delta t}\right) - \frac{m\left(v_k - v_{k-1}e^{-\frac{\gamma}{m}\Delta t}\right)\left(1 - e^{-\frac{\gamma}{m}\Delta t}\right)}{\gamma\left(1 + e^{-\frac{\gamma}{m}\Delta t}\right)}.$$

As $\Delta t \to 0$ $\left(\Delta t \ll \frac{m}{\gamma}\right.$ in any case$\left.\right)$,

$$f(t) \to \frac{1}{12}\frac{\gamma^3}{m^3}(\Delta t)^3 + o(\Delta t^3), \quad A_k \to x_k - x_{k-1} - \frac{v_k + o(\Delta t^3)}{2}\Delta t,$$

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*In the above indicated case.

and the trajectory probability can be written symbolically as

$$W\{x(t)v(t)\} = \frac{1}{N}\exp\left\{-\int_{t_0}^{t}\left[\left(\dot{v}(\tau)+\frac{\gamma}{m}v(\tau)\right)^2-\frac{1}{2}\frac{\gamma}{m}\right]\dot{v}\tau\right\}\times$$

$$\times\,\delta\left\{x(t)-x(t_0)-\int_{t_0}^{t}v(\tau)\,d\tau\right\}.$$

The δ-functional appears in the latter equation for an obvious reason: it established the integral relation between x(t) and ν(t).

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