Network representation yielding the evolution of Brownian motion with multiple particle interactions

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A network representation is used to derive nonlinear evolution equations for Brownian motion.

The classical analysis of diffusion[1] neglected inertial effects, exchange of momentum between diffusing particles, and cross diffusional effects. These approximations are appropriate for the range of visible Brownian motions considered and for infinite dilution. Extensions of the diffusion equation in the Smoluchowski's form[2]

$$\frac{\partial n_i}{\partial t} = D\nabla\cdot\left[\nabla\left[-\frac{F}{k_BT}\right]\right]n_i \ , \tag{1}$$

have been given by Murphy and Aguirre[3] and by Wilemski,[4] in which the diffusion constant D is (rigorously) replaced by a second-rank tensor which reflects the frictional interactions between diffusing particles. If the internal force on the particles, $\mathbf{E}$, is found from the gradient of the internal energy U and the particle distribution is denoted by P, the resultant equation of motion is

$$\frac{\partial P}{\partial t} = \nabla\cdot\vec{D}\cdot\left[\vec{\nabla}P + P\frac{\nabla U}{k_BT}\right] \ . \tag{2}$$

This equation has been utilized by Berkowitz *et al.*[5] to obtain a variational formula for the steady-state coordinates of a diffusion controlled process in which there are internal reaction coordinates of the form described by Kramers.[6] These systems are homologous to the Brownian motion problems and have been described for reaction, diffusion convection, and diffusion convection reaction by the author[7–11] in terms of resistive networks which serve to formally connect the manifold by means of an equivalent potential. This basic analogy between the Brownian motion problem[12] and the further homology with other network properties is used here to extend the analysis of process evolution to the nonstationary case with interacting particles and path dependent momentum transfer between the n diffusing species.

The network formalism is not used here as a modeling technique, but as a convenient and powerful approach to obtain and summarize covariant equations[13] utilizing Kirchoff's laws[14,15] and the connectivity of the potential energy manifold.[16] The following results are stated without proof, because they are simple exercises in network representation[16–18] and do not add anything substantial in themselves: (1) Einsteinian diffusion of n species is isomorphic to a disconnected n-resistance network in which the "voltage" across the resistance is the driving diffusional force for the given species; the resistance is the frictional diffusion coefficient, and the conjugate through "current" is the flow of solute [(Fig. 1(a)]; (2) the introduction of inertial delays, with no particle interaction[19] adds an inductor (Newton's second law) in the path of each previous resistance, as shown in Fig. 1(b); (3) the further inclusion of Onsager-type cross diffusional terms—i.e., the introduction of a symmetric diffusion tensor—leads to a connected resistive network with input inductors denoting inertial effects [Fig. 1(c)]; and (4) the transfer of momentum among the various diffusing species is naturally included by allowing mutual inductances (the conserved "magnetic field" flux is analogous to the conserved momentum).

The last network, given in Fig. 1(d) is the one of interest, because it includes inertia, dissipation, and momentum transfer. The manifold coordinates $\dot{x}_i$, which describe the

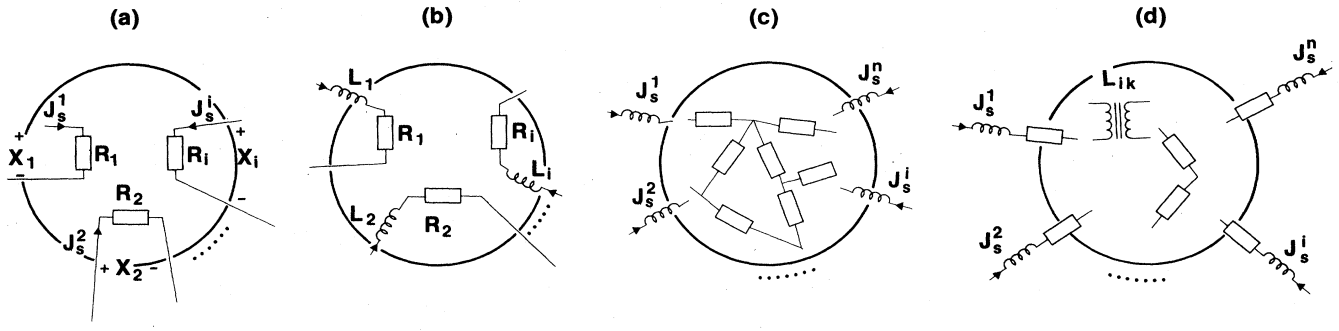

FIG. 1. (a) Einsteinian diffusion is represented by disconnected resistances (friction coefficients). (b) Inertial effects are added by means of serious inductors; in the range of Brownian motion observable under the light microscope, the inductors dissapear and the network reduces to (a). (c) A diffusional tensor is introduced by means of a connected resistive network whose measurable frictional tensor, f, is related to the (diagonal) resistance matrix by $f = T^{\dagger}RT$, in which T is the tie set matrix for the network graph. Input inductances account for inertial effects. (d) The introduction of time varying mutual inductances whose fluxes are identified with the momentum exchanged between different species completes the representation of the n-species diffusional system with inertia, dissipation, momentum exchange, and Onsager-type cross frictional effects.

path, s, followed by the evolving Brownian motion are the input "charges" in the network, while their time variations (we assume the path has been time calibrated) are given by the input currents $\dot{x}_i$. Tellegen's theorem[14] readily yields expressions for the dissipated energy, $\frac{1}{2}R_{ij}\dot{x}_i\dot{x}_j$—in which R_{ij} is the inverse diffusional, or friction tensor—and the internal kinetic energy, $\frac{1}{2}L_{ij}\dot{x}_i\dot{x}_j$—in which L_{ii} are masses and L_{ij} are interaction coefficients reflecting average effective cross-sectional areas for momentum transfer between two species at a given time—once the constitutive equations for the diffusional (resistive or frictional) steps ($f_i = R_{ik}\dot{x}_k$) and the inertial and momentum exchange steps ($p_i = L_{ik}\dot{x}_k$) are given.

Tellegen's theorem, with some rearrangement of variables[16] finally leads to Lagrange's equation for the system containing dissipation and kinetic energy (inertia and momentum exchange):[13]

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{x}^k}\right) - \frac{\partial T}{\partial x^k} + \frac{\partial D}{\partial \dot{x}^k} = F_k \ .$$

In the absence of external forces this yields the geodesic equation (with dissipation)

$$R_{\alpha\beta}\dot{x}^\beta + L_{\alpha\beta}\ddot{x}^\beta + \Gamma_{\beta\gamma,\alpha}\dot{x}^\beta\dot{x}^\alpha = 0 \ , \qquad (3)$$

in which the Christoffel symbol can be *physically* defined by

$$\Gamma_{mn,k} = \frac{\partial L_{mk}}{\partial x^n} - \frac{1}{2}\frac{\partial L_{mn}}{\partial x^k} \ ,$$

rather than in its more familiar differential form. Equation (3) underlies the evolution of the Brownian motion with dissipation when there are no external forces acting on it; otherwise, the right hand side becomes equal to the force acting on component α. If the mass of a diffusing species remains constant in the motion and the average cross-sectional areas for momentum exchange remain constant, the connection coefficients and, clearly, the curvature vanishes and the equations reduce to their linear form.

Although this approach to obtaining evolution equations is extremely simple minded, the resultant equations are free from the restrictions of stationarity previously imposed. A more elegant derivation would completely ignore the network as an intermediary step, but the advantage of including the network view is the clear separation of the various forms of energy and clear identification of which are dissipative steps and which are energy storing steps. The conceptual economy should also be clear by comparing this analysis to the typical statistical mechanical approaches.[20]

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