PHYSICAL REVIEW E VOLUME 61, NUMBER 6 JUNE 2000

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Nonlinearly coupled flows

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(Received 16 November 1999)

We study energy flows that are coupled at a higher than linear order. A number of examples are presented where a force brings about a flow in the perpendicular direction. In some cases the symmetry of the system is such that coupling can only take place at even orders. We apply the theory to recently proposed two-dimensional devices that separate colloidal particles by ratcheting the different particles in different directions.

PACS number(s): 05.40.−a, 02.50.Ey, 82.20−w

It is possible to drive a process energetically uphill with the energy coming from another process that is going energetically downhill. One can, for instance, drive a car up a hill with a battery and an electrical engine. The fluxes of mechanical and electrical energy are coupled. Going down the hill it is possible to recharge the battery again. When the coupling is linear at leading order the system can be approximated by [1]

$$\begin{pmatrix} J_1 \\ J_2 \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \end{pmatrix}. \tag{1}$$

So J_1 may be the electrical current and J_2 the speed at which the car ascends or descends; X_2 would be the electrical potential difference and X_1 the force due to gravity. Coupled flows such as these are particularly important in biophysics. An ion pump, for instance, is a protein that uses the energy it gets from the hydrolysis of adenosine triphosphate (ATP) to pump ions, such as Na^+ and K^+, across the membrane against the electrochemical gradient.

In this paper we will focus on situations where the leading order coupling is not linear, but quadratic. So $L_{21}=L_{12}=0$ and

$$J_1 = L_{11}X_1, \quad J_2 = \tilde{L}_{21}X_1^2. \tag{2}$$

The quadratic term makes it possible to drive a dc flow J_2 with an ac force in X_1.

Below we show some examples involving the flow of matter brought about by force or pressure in the perpendicular direction. The doubly periodic setup of Fig. 1 constitutes a macroscopic example. There are round vertical tubes the cross sectional area of which is A_1 for the wide half of the period and A_2 for the narrow half of the period. The tubes are positioned such that narrow segments neighbor wide segments to the left and right. Next little crosslinking tubes are added that connect wide segments on the left with narrow segments on the right. Fluid is pumped in the vertical direction. Continuity requires $J_y = v_1 A_1 = v_2 A_2$, where J_y is the vertical flow and v_1 and v_2 are the average velocities in the wide and narrow parts respectively. When fluid is forced through the narrower segment it moves faster and through Bernoulli's principle underpressure, i.e., suction, is created

$$P_1 - P_2 = \frac{1}{2}\rho(v_2^2 - v_1^2). \tag{3}$$

Here ρ represents the density of the fluid and P_1 and P_2 are the pressures in the wide and narrow part respectively. So in the case of Fig. 1 the vertical flow will also lead to a small horizontal flow.

To drive the flow an extra ΔP must be applied over every period. For simplicity we take the case that ΔP is negligible in comparison to P_1 and P_2. For sufficiently small pressures we have $J_y \propto \Delta P$, so $v_i \propto \Delta P / A_i$. If the crosslinking tube is sufficiently narrow the flow will be governed by Poiseuille's formula for viscous flow [1]

$$j_x = \frac{\pi r^4}{8 l \eta}(P_1 - P_2) = \frac{\pi r^4 \rho}{16 l \eta}(v_2^2 - v_1^2) \propto (\Delta P)^2, \tag{4}$$

where l is the length of a crosslink, r is the radius and η represents the coefficient of viscosity. Equation (4) shows that j_x is proportional to $(\Delta P)^2$.

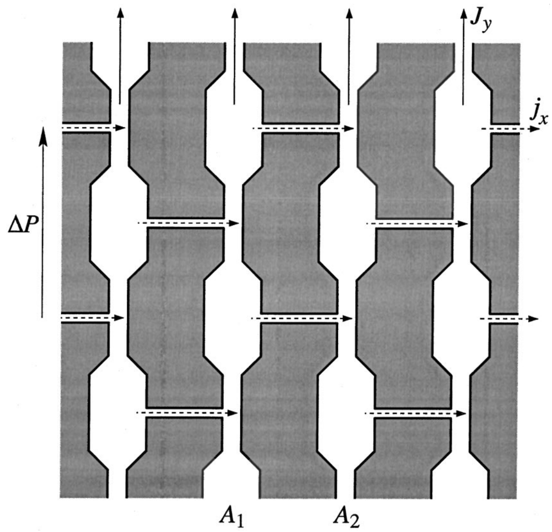

FIG. 1. A two-dimensional system of tubes. When fluid is pumped in the vertical direction a horizontal left to right flow is also brought about because of Bernoulli's principle [see Eq. (3)]. The horizontal flow is proportional to the square of the vertical force [see Eq. (2)].

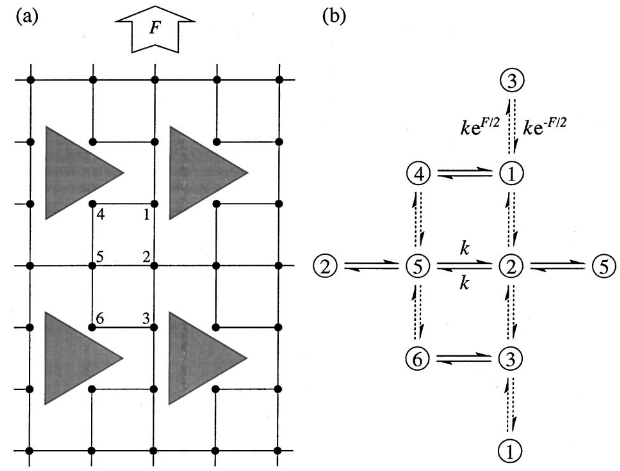

FIG. 2. (a) Obstacles are placed in a film of fluid in which Brownian particles are suspended. When the particles are moved in the vertical direction by an external force F the probability to deviate sufficiently to be pulled into the next right trench is larger than the probability to deviate sufficiently to be pulled into the next left trench. The particles thus exhibit net flow to the right. The superimposed Markov model (b) mimics the behavior of Brownian particles in this system.

Algebraically there is a quadratic relation between the applied vertical pressure and the horizontal flow because the Bernoulli equation is quadratic in the velocity. But there are symmetry arguments by which we can easily intuit how and why the system in Fig. 1 relates to Eq. (2). There is a reflection symmetry in the vertical direction, so upward and downward flow must induce identical horizontal flow. The horizontal flow must therefore be an even function of the vertical pressure. In the context of Eq. (1) this means that, with J_2 representing the horizontal flow, the term L_{21} must be zero. Onsager reciprocity [1] implies that the other cross term L_{12} must then also be zero. Coupling thus occurs at second or higher order. The necessary anisotropy in the horizontal direction derives from the cross link always connecting to a wide part on the left and to a narrow part on the right. In this system there is no longer anything like Onsager reciprocity: a pressure in the horizontal direction can never lead to a vertical flow; upward and downward flow are equivalent so there is no way for the system to ''decide.''

In 1998 a number of papers appeared [2,3] in which methods were proposed to separate small particles. The setup discussed in Ref. [3] has a symmetry similar to the system in Fig. 1 and follows the nonlinear coupling according to Eq. (2). Below we will present a system similar to the one discussed in Ref. [3]. Colloidal particles are suspended in a fluid that forms a film on a surface with obstacles [Fig. 2(a)]. The triangle shaped obstacles mark off an area that is inaccessible to the colloidal particles. The suspended particles are pulled in a fixed direction with, for instance, an electric field. Due to Brownian motion the particles deviate from their straight path and the smaller particles (higher diffusion constants) will on the average deviate more. Take the system in Fig. 2. Every time after the particles are pulled up vertically through a funnel between two triangles they spread out again. The obstacles are shaped such that when reaching the next row of triangles it is more likely to have sufficiently deviated to the right to go into the next column on the right than it is to have sufficiently deviated to the left to go into the next column on the left. We thus get a net flux to the right and that flux is larger for particles with larger diffusion constants. This makes it possible to use the device for the separation of particles. Such separation has recently been achieved experimentally [4].

Figure 2(b) depicts a 6 state 2D doubly periodic grid to simulate the dynamics of the setup of Fig. 2(a). The motion of a Brownian particle in the ''obstacle course'' can be modeled by Markovian transitions on this grid. We take all the horizontal transition rates to be equal to k. For reasons of symmetry we implement the effect of a vertical force F with equal apportionment over the upward and downward transition. So transition rates in the downward direction are $k\exp(\frac{1}{2}F)$ and rates in the upward direction are $k\exp(-\frac{1}{2}F)$. At stationarity each state i has a probability P_i. This probability remains unchanged and we thus get the time-independent master equation $\Sigma_j(k_{ji}P_j - k_{ij}P_i)=0$. Here k_{ji} are the rates of the transitions coming into state i and k_{ij} are the rates of the transitions going out of state i. The steady state equations for five states together with the normalization condition ($\Sigma_{i=1}^{6}P_i=1$, i.e., one particle per period) fully fix the system. The net flux in the horizontal direction is most easily expressed as $k(P_2-P_5)$. After some algebra one finds for this flux $J(F)=\frac{1}{7}k\tanh^2[F/4]$. This is an even function that is quadratic near $F=0$.

Next we will take a more fundamental approach and study the diffusion of particles on a potential surface [Fig. 3(a)] with a structure that resembles the ''obstacle course'' in Fig. 2. As with the obstacle course, the 2D potential is isotropic in the y direction and anisotropic in the x direction:

$$V(x,y)=U(x)\{1-\delta\sin(2\pi y)\}-Fy. \tag{5}$$

For $U(x)$ we take a piecewise linear potential as drawn in Fig. 3(b). In Fig. 3(a) $V(x,y)$ is drawn for $F=0$. When we

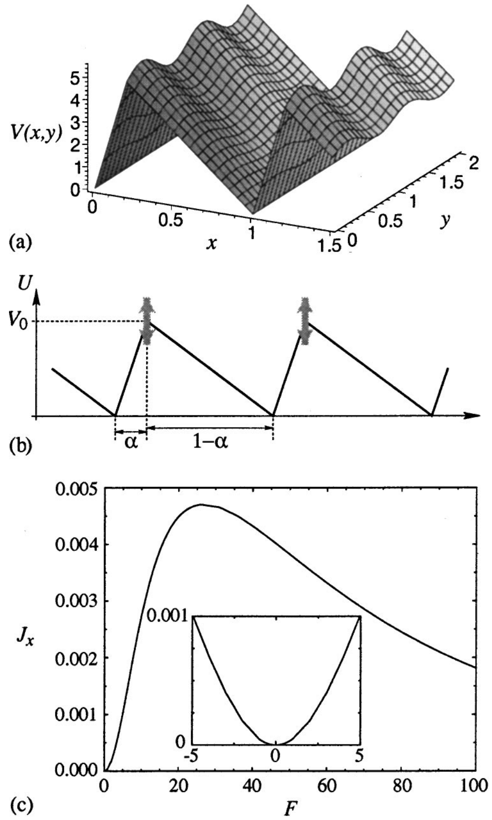

FIG. 3. (a) The 2D potential $V(x,y)$ of Eq. (5) with $F=0$ and (b) a cross section in the x direction. Traveling ''in the trench'' along the y direction a Brownian particle ''sees'' oscillating barriers. A Brownian particle subjected to an oscillating anisotropic potential like this will pass easier over the short slope than over the long slope and exhibit net motion to the left. (c) The flow J in the x direction as a function of the force F in the y direction for the potential of (a). The induced flow is an even function of F (see inset) and this flow is maximal for a finite, nonzero value of F.

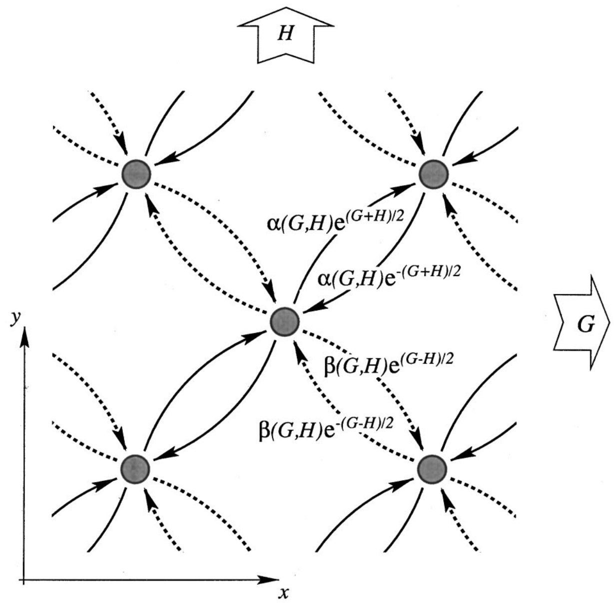

FIG. 4. A 2D one state Markov model. At $G=0$ the force H leads to flux in the horizontal direction.

apply the net macroscopic force F in the y direction particles are ''pushed through the trench.'' A particle that travels through a trench ''sees'' oscillating barriers on the left and right. This makes the situation very similar to that of a particle subjected to an oscillating periodic potential [5], but instead of a time coordinate we now have the y coordinate along which the particle moves at approximately constant speed. Oscillating and fluctuating one dimensional anisotropic potentials as in Fig. 3(b) have been studied extensively over the past half decade [5–9]. In an oscillating potential such as Fig. 3(b) a Brownian particle dwelling around the minimum will more easily move over the short oscillating slope on the right than over the long oscillating slope on the left. There is an optimum barrier height and an optimum period for the oscillation for which the difference of the rates, and thus the induced flow, is maximal.

The rigorous way to handle diffusive flow on the potential given by Eq. (5) is to solve the associated Fokker Planck equation for the overdamped case:

$$\frac{\partial P(x,y,t)}{\partial t} = -\nabla(f(x,y)P(x,y,t)) + \nabla^2 P(x,y,t). \quad (6)$$

Here $P(x,y,t)$ is the probability distribution of diffusing particles and $f(x,y) = -\boldsymbol{\nabla} V(x,y)$. We have taken the diffusion constant and the coefficient of friction to be equal to 1. The energy is in units of $k_B T$. Our interest is in stationary flow, i.e., the case where the time derivative is zero. This leads to a system of partial differential equations with independent variables x and y. We impose doubly periodic boundary conditions on $P(x,y)$, i.e., $P(0,y) = P(1,y)$ and $P(x,0) = P(x,1)$ and normalize the total probability on a unit square to 1, i.e., $\int_{x=0}^{1}\int_{y=0}^{1} P(x,y)\,dx\,dy = 1$. Given the solution $P(x,y)$ the total flux in the x direction in a strip of unit width is evaluated as $J_x = -\int_{y=0}^{1}\{\partial_x + [\partial_x V(x,y)]\}P(x,y)\,dy$. We solved Eq. (6) numerically with DIFFPACK 1.4 (SINTEF, Oslo, Norway). Figure 3(c) shows the flux J_x as a function of F for $\delta=0.1$, $\alpha=0.2$ and $V_0=5.0$ [see Eq. (5) and Fig. 3(a)]. At lowest order in F the flow J_x is expected to behave as Eq. (2) and near the origin of Fig. 3(c) we indeed see the expected parabolic shape (see inset).

We, furthermore, observe in Fig. 3(c) that the flow is maximal for a finite value of the force F and that the flow asymptotically goes to zero as $F \to \pm\infty$. For high values of $|F|$ the Brownian particle ''sees'' the slopes in the x direction change very fast and it will never be able to adjust its probability distribution in the x direction to either of the slopes. Instead it will form a Boltzmann distribution according to the average slope. So for high F it is similar to having a stationary periodic potential in the x direction with no net force. Hence no flow will occur. The time to relax to a Boltzmann distribution on a slope can be taken to be equal to the time to slide down that slope deterministically [10,11]. Maximal flow for the system in Fig. 3(a) occurs when F is fast enough such that no adjustment will occur on the long slope and slow enough for the particle's distribution to all the time be adjusted on the short slope. The harmonic $\sin(2\pi y)$ goes from one extremum to the other in the course of half a period. For the particle that is traveling in the y direction this change takes place in a time $1/(2F)$. It is easily derived that maximal flow should occur for $V_0/(2\alpha^2) < F < V_0/[2(1-\alpha)^2]$. For the parameter values in the system of Fig. 3 the lower and upper bound come out to be 4 and 63 and the actual maximum occurs for $F \approx 25$.

Finally we consider the doubly periodic 2D setup presented in Fig. 4. This is a 2D one state model and from each state four neighbors can be reached. The transition rates are indicated in the figure. By assigning nonzero values to G and H one basically imposes forces in the horizontal and vertical direction, respectively. The distance between the rows as well as the columns is taken to be unity and each state has a population of 1. The energy difference between two states on the 45° line (solid arrows) is $G+H$. So for two neighboring states along this line the ratio of the transition rates has to be $\exp(G+H)$ (energy is taken in units of k_BT). The energy difference between two states along the 135° line (dotted arrows) is $-G+H$. So for two neighboring states along this line the ratio of the transition rates has to be $\exp(-G+H)$. This leaves the prefactors $\alpha(G,H)$ and $\beta(G,H)$ as free parameters to vary the speed of the transitions. At steady state we find for the net flows in the horizontal and vertical direction, respectively,

$$J_x(G,H) = 2\alpha(G,H)\sinh\left[\frac{1}{2}(G+H)\right] + 2\beta(G,H)\sinh\left[\frac{1}{2}(G-H)\right],$$

$$J_y(G,H) = 2\alpha(G,H)\sinh\left[\frac{1}{2}(G+H)\right] - 2\beta(G,H)\sinh\left[\frac{1}{2}(G-H)\right]. \quad (7)$$

If we take $G=0$ and $H\neq 0$, then we get for the horizontal flow induced by the vertical force: $J_x(0,H) = 2\{\alpha(0,H) - \beta(0,H)\}[\sinh(H/2)]$. It is obvious that no couping occurs for $\alpha=\beta$. Expanding $J_x(0,H)$ to the first two orders around $H=0$ we obtain $J_x(0,H) \approx \{\alpha(0,0) - \beta(0,0)\}H + \partial_H\{\alpha(0,0) - \beta(0,0)\}H^2$. An obvious choice that leads to the a zero linear term and a nonzero quadratic term is $\alpha=1$ and $\beta = e^{(1/2)H}$. In that case $J_x(0,H) \approx -\frac{1}{2}H^2$. This system does not have the symmetry in the vertical direction of the first example and therefore $J_x(0,H)$ is not an even function of H.

A reflection symmetry (isotropy) in one direction and an anisotropy in the perpendicular direction is a setup that can easily arise and the nonlinear coupling of Eq. (2) may thus be encountered quite generally. But our last example shows that such symmetry constitutes a sufficient and not a necessary condition for quadratic coupling. It is finally worth noticing that the transverse flow in the systems of Figs. 2 and 3 only comes about because of the presence of thermal noise.

We are grateful to the NIH (Grant No. R29ES06620), the Komitet Badań Naukowych (Grant No. 2P03B 160 17), and the DAAD (Deutcher Akademischer Austauschdienst) for funding.

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