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ABSTRACT

An alternative to Langevin description of Brownian motion is presented. The equations of motion *are deterministic* **and time-reversal** *invariant. The* **friction and random forces appearing in the Langevin equation are replaced by** *pseudo-friction terms,* **which** *emulate the energy and momentum exchange between the Brownian particle and the medium.*

The starting point in the study of Brownian motion is almost always the celebrated Langevin equation

$$\dot{v}(t) = -\gamma v(t) + f(t), \tag{1}$$

where $v(t)$ is the velocity of the Brownian particle, $\gamma > 0$ the friction coefficient and $f(t)$ is an ideal random force. This random force is described by a stationary Gaussian process

$$\langle f(t) \rangle = 0, \quad \langle f(t) f(t') \rangle = \xi \delta(t - t'), \tag{2}$$

where the brackets stand for an ensemble average. The friction coefficient and the magnitude of the correlations of the random forces satisfy the Einstein relation (or fluctuation-dissipation theorem)

$$\xi = 2T\gamma, \tag{3}$$

where T is the temperature (in energetic units). From the above relations, one can derive the Fokker-Plank equation (or vice-versa), which describes statistically the diffusion process. Langevin description is purely phenomenological. The form of the terms on the right hand side of Eq. (1) are by no means unique. For example, friction at relatively high velocities depends on higher powers of the velocity and one can assume that the random force can have properties other than that of a simple stationary Gaussian process. However, the spirit of economy of thought and simplicity makes the Langevin equation one of the most beloved objects of theoretical study. To a certain extent, the fact that one needs two different types of forces in order to describe Brownian motion is unsatisfactory.

The random force describes the resultant force arising from the collision between the Brownian particle and the surrounding molecules. One might think that such a term would be sufficient, since it can lead to both acceleration and deceleration of the Brownian particle, and the introduction of the additional friction term would serve at least part of the same purpose as the random force. But with only one of these terms, one cannot obtain a satisfactory description of Brownian motion.

The irreversible character of the Langevin description is due to the presence of both dissipative and random forces. On the other side, the "true" equations of motion for the Brownian particle and the medium are time-reversible. In the literature one can find an almost equal number of arguments in favor and against such a description, however we shall not rally ourselves with one or the other of the contending factions. Instead we shall introduce an alternative phenomenological approach to Brownian motion, which is both deterministic and time-reversal invariant. At least from the very narrow point of view of an individual who wants to produce a real numerical simulation of a diffusion process, the present approach seems to have definite practical advantages; it is far more stable numerically and the equations of motion can be integrated with higher precision and likely faster. If one intends to apply the present approach to different physical phenomena, the assumption that the motion is overdamped could be dropped. Further, there is much more freedom in choosing the form of coupling between the Brownian particle and the medium. The assumption that the motion is overdamped physically corresponds to restricting the description to time scales which are significantly larger than the characteristic collision times. There are many situations however,

where one would like to have a phenomenological approach valid at time intervals comparable with the collision times (e.g. heavy-ion reactions in nuclear physics).

We will follow the ideology of the molecular dynamics simulations [1-4] , which we briefly review. For a classical system, described by the canonical variables $(q_1,...,q_N,p_1,...,p_N)$ and a Hamiltonian $H(q,p)$ in contact with a thermal bath at a temperature T, we are interested in computing the ensemble average of an arbitrary observable $A(q,p) = A(q_1,...,q_N,p_1,...,p_N)$

$$\langle A \rangle = \frac{1}{Z} \int dqdpA(q,p) \exp\left(-\frac{H(q,p)}{T}\right). \tag{4}$$

Here Z is a normalization constant and $\int dqdp$ stands for the integration over the entire phase space. This formula is strictly valid if one can neglect the terms responsible for the interaction between the system and the thermal bath in the total Hamiltonian. In order to develop a feasible computational method for such averages, one can introduce an extended classical space, described by the variables $(q_1,...,q_N,p_1,...,p_N,\xi,\zeta)$, and a distribution function $f(q,p,\xi,\zeta,t)$ and require that this distribution satisfies the following generalized Liouville equation

$$\frac{\partial f}{\partial t} + \sum_{i=1}^{N}\left[\frac{\partial(f\dot{q}_i)}{\partial q_i} + \frac{\partial(f\dot{p}_i)}{\partial p_i}\right] + \frac{\partial(f\dot{\xi})}{\partial \xi} + \frac{\partial(f\dot{\zeta})}{\partial \zeta} = 0, \tag{5}$$

where the dot represents the partial time derivative. We shall assume that the time evolution of the canonical variables (q,p) are governed by the following equations of motion

$$\dot{q}_i = \frac{\partial H(q,p)}{\partial p_i} - h_2(\xi)F_i(q,p), \qquad \dot{p}_i = -\frac{\partial H(q,p)}{\partial q_i} - h_1(\zeta)G_i(q,p), \tag{6}$$

where $F_i(q,p)$ and $G_i(q,p)$ are some yet undetermined functions. Imposing the

constraint that $\partial\dot{\zeta}/\partial\zeta = \partial\dot{\xi}/\partial\xi = 0$ and requiring that the canonical distribution

$$f(q,p,\xi,\zeta) = \exp\left(-\frac{1}{T}\left[H(q,p) + \frac{g_2(\xi)}{\beta} + \frac{g_1(\zeta)}{\alpha}\right]\right), \tag{7}$$

is a stationary solution of Eq.(5) one can show that the time dependence of the pseudo-friction coefficients ζ and ξ is governed by [1-4]

$$\dot{\zeta} = \alpha\left[\frac{\partial H}{\partial p_i}G_i - T\frac{\partial G_i}{\partial p_i}\right], \qquad \dot{\xi} = \beta\left[\frac{\partial H}{\partial q_i}F_i - T\frac{\partial F_i}{\partial q_i}\right]. \tag{8}$$

Here α and β are arbitrary constants (sum over repeated indices implied) and the constraint imposed above implies that [4]

$$h_1(\zeta) = \frac{dg_1(\zeta)}{d\zeta}, \qquad h_2(\xi) = \frac{dg_2(\xi)}{d\xi}. \tag{9}$$

The number of pseudo-friction coefficients one can consider is arbitrary. It can be shown that Eqs. (6) and (8) conserve the pseudo-energy

$$\mathcal{E} = H(q,p) + \frac{g_1(\zeta)}{\alpha} + \frac{g_2(\xi)}{\beta} + T\int_0^t dt'\left[\frac{\partial G_i}{\partial p_i}h_1(\zeta) + \frac{\partial F_i}{\partial q_i}h_2(\xi)\right]. \tag{10}$$

In the case when the equations of motion (6) and (8) describe ergodic motion, one can replace the ensemble average (4) by a much simpler to compute time average

$$\langle A\rangle = \frac{1}{t}\int_0^t dt' A(q(t'),p(t')), \qquad (t \to \infty). \tag{11}$$

The net result of this exercise is a very simple method for modeling the coupling of a classical system to a thermal bath, which is mocked by some pseudo-friction

coefficients. The emerging equations of motion are both deterministic and even time-reversible (the time-reversible properties of the pseudo-friction coefficients, which purportedly describe the thermostat, depend on the explicit form of the couplings) and at the same time the trajectories are ergodic [4]. Both the time and ensemble average of the friction terms in Eqs. (6) are vanishing (as one would expect on physical grounds). The pseudo-friction terms induce fluctuations around the mean trajectory in such a way as to imitate the (supposedly weak) coupling to the thermostat at the given temperature.

One might hope to describe pure Brownian motion as well, using this kind of approach, if $H(q,p) \equiv p^2/2m$. However, as one will readily observe, neither the original proposed scheme [1,2] (which relied on only one pseudo-friction coefficient), nor our improved method [3,4] (which included at least two pseudo-friction coefficients ζ, ξ), is able to produce an ergodic trajectory for the case of a free particle in contact with a thermal bath, i.e. the case of a Brownian particle in particular. In our opinion, the case of a Brownian particle should receive a satisfactory solution in the framework of molecular dynamics simulations, if one is going to compute transport/nonequilibrium properties. We have found that a relatively minor modification of the above described scheme can lead to such a result. We shall describe a Brownian particle (for the sake of simplicity in one-dimension only, higher dimensions can be treated in a similar way) by the following set of equations (unit mass $m = 1$)

$$\dot{q} = p, \tag{12}$$

$$\dot{p} = -\alpha\zeta^3 p - \beta\xi(p^2 - a) - \gamma\epsilon p^3, \tag{13}$$

$$\dot{\zeta} = p^2 - T, \tag{14a}$$

$$\dot{\xi} = p(p^2 - a) - 2Tp, \tag{14b}$$

$$\dot{\epsilon} = p^4 - 3Tp^2, \tag{14c}$$

where, as before T is the absolute temperature in energetic units and a, α, β, γ are some arbitrary constants, to be specified later. These equations display a time-reversal invariance if the phase space coordinates change as

$$q, p, \zeta, \xi, \epsilon \rightarrow q, -p, -\zeta, \xi, -\epsilon, \tag{15}$$

when $t \rightarrow -t$.

The physical meaning of Eq. (12) is obvious, whereas Eqs. (13)-(14) deserve some discussion. Since we are dealing with a free particle in a medium, there is no conservative force. The influence of the medium is described in the present case by three pseudo-friction terms. The reason why we introduce three such terms, and not one or two as before, is simple: for one or two pseudo-friction terms we were not able to produce an ergodic trajectory. We suspect that a (relatively simple) counterexample to this assertion is probably hard to find. For the person who closely followed our derivation of the Eqs. (5)-(10) it will be obvious that Eqs. (13)-(14) will generate the following stationary distribution for the momentum and the pseudo-friction coefficients (ergodicity implied)

$$f(p, \zeta, \xi, \epsilon) = \exp\left(-\frac{p^2}{2T} - \frac{\zeta^4}{4T} - \frac{\xi^2}{2T} - \frac{\epsilon^2}{2T}\right). \tag{16}$$

Consequently, the distribution for the momentum is exactly the one expected. The distribution for the pseudo-friction coefficients and the particular types of

coupling used by us in Eq. (13) are rather arbitrary, as was the case with Eqs. (5)-(10), and were generated (by our educated guess) in such a manner as to produce ergodic trajectories and obtain thermalization. One can introduce a distribution function $f(q,p,\zeta,\xi,\varepsilon,t)$, which satisfies the generalized Liouville equation

$$\frac{\partial f}{\partial t}+\frac{\partial(f\dot{q})}{\partial q}+\frac{\partial(f\dot{p})}{\partial p}+\frac{\partial(f\dot{\xi})}{\partial \xi}+\frac{\partial(f\dot{\zeta})}{\partial \zeta}+\frac{\partial(f\dot{\varepsilon})}{\partial \varepsilon}=0, \tag{17}$$

and show that a pseudo-energy similar to the one introduced in relation (10) can be defined and is conserved. Since the distribution (16) is stationary, the coordinate distribution alone satisfies, in a certain sense, a much simpler equation (if the phase space variable $q,p,\zeta,\xi,\varepsilon$ are statistically independent)

$$\frac{\partial f(q,t)}{\partial t}+\frac{\partial f(q,t)}{\partial q}p(t)=0, \tag{18}$$

where the time evolution of the momentum is determined by Eqs. (13)-(14). This reduced form of the Liouville equation implies an ensemble average of $f(q,t)$ over momentum distribution. (We hope that our use of the same notation for total and different partial distribution functions is not confusing the reader.)

In Fig. 1 the distributions for p,ζ,ξ,ε obtained by evolving in time Eqs. (13)-(14) are shown. The fact that these equations can accurately describe the thermalization process is evident. The characteristic time evolution of a trajectory, $q(t)$, $p(t)$, $\zeta(t)$, $\xi(t)$, $\varepsilon(t)$, as well as the time evolution of the three pseudo-friction terms present in Eq. (13) are shown in Fig. 2. As one can see, the trajectory is rather irregular. Namely, due to this feature of the motion (ergodicity), the system is able to explore the whole phase space and eventually to

reproduce the canonical distribution. In Fig. 3 we present the coordinate distributions obtained by evolving in time Eqs. (12)-(14) with $q(0) = 0$ and a set of 10^4 random initial conditions (10^5 for small times) for p, ζ, ξ and ϵ, generated according to the thermal distribution (16). Even though we have chosen not to show the distributions for these variables at different times, we would like to mention that they are time-independent (within inherent statistical errors, arising from finite number of points per bin). The reason why we show ensemble averages for the coordinate distribution is because this distribution is not stationary (as it was the case of canonical distributions mentioned earlier) and the expected diffusion is going to manifest itself in a predictable way only at the statistical level. For relatively small times, the spatial distribution is well reproduced by a Gaussian shape, but with a "wrong" time dependence. The mean spreading velocity is proportional to time. The explanation is trivial. For small times the momenta practically do not change and the space distribution is simply linked to the momentum distribution (since for each particular momentum $q(t) \simeq p(0)t$ for sufficiently small t). For intermediate times the spatial distribution no longer has a Gaussian shape. These times should be associated with collision times, i.e. the time it takes to change significantly the momentum of the Brownian particle. For times much longer than the collision times however, the spatial distribution acquires an expected Gaussian shape again and the explanation is quite simple. For any given trajectory, the particle suffered a significant number of "collisions" and the corresponding momentum is practically thermalized. At this stage the mean spreading velocity reached the asymptotic behaviour $\sim \sqrt{t}$. The actual value of the diffusion coefficient is determined by the particular type of coupling

with the thermal bath chosen and especially its strength. For such time scales one can substitute the exact equation (18) with an approximate Fokker-Plank equation, after a suitable ensemble average over p, ζ, ξ and ϵ is performed.

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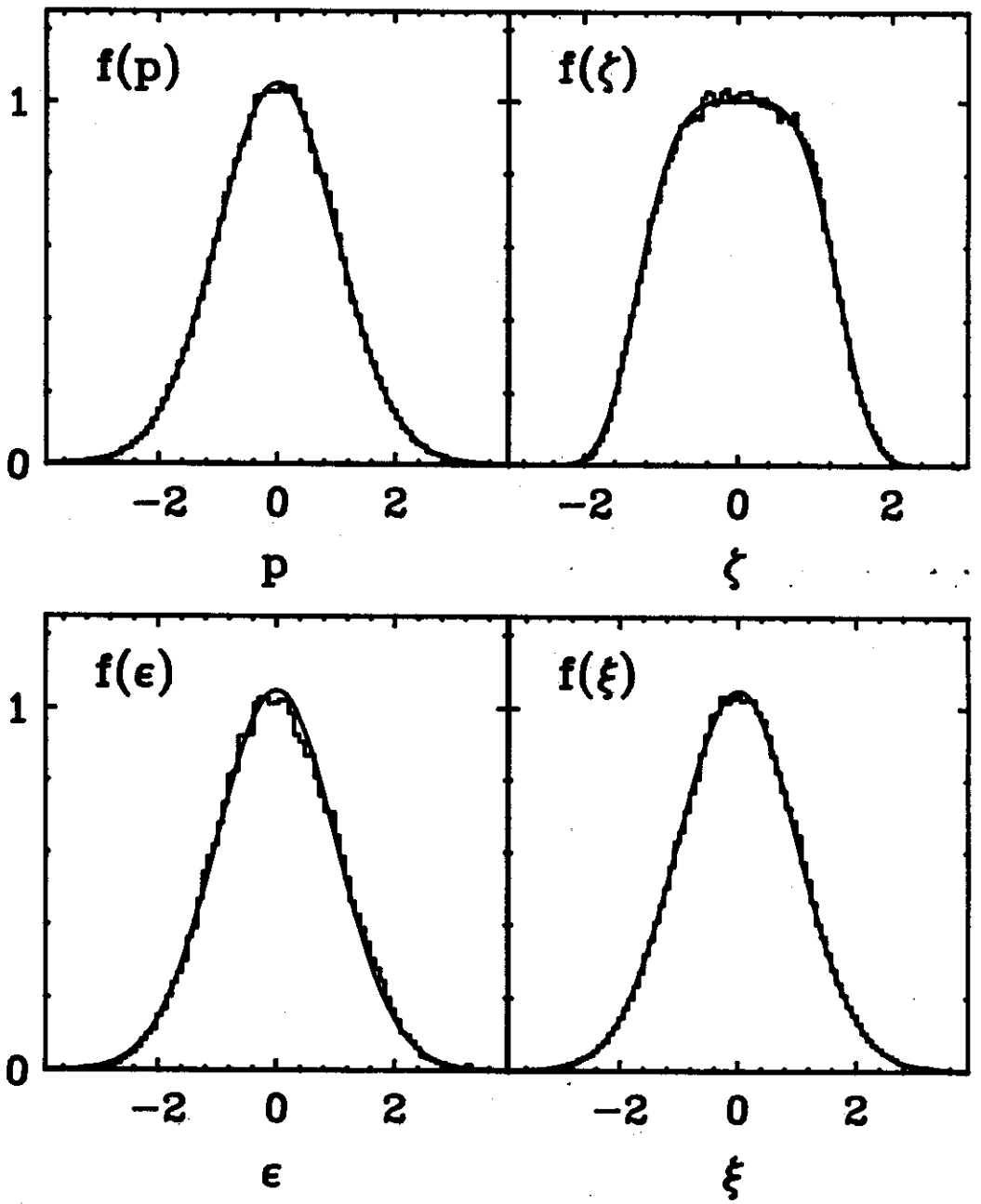
FIGURE CAPTIONS

1) Exact thermal distributions (solid) compared to computed distributions (histogram) obtained by integrating Eqs. (13)-(14) up to time $t = 7500$ and sampling the trajectory every $\Delta t = 0.025$. The values $T = 1$, $a = 2.713$, and $\alpha = \beta = \gamma = 1$ were used in all numerical results presented in this paper.

2) Characteristic time evolution: (a) $p(t)$ (solid) and $q(t)$ (dashed, multiplied by 5), (b) $\zeta(t)$ (solid) and its corresponding pseudo-friction force in Eq. (13) $-\zeta^3(t)p(t)$ (dashed, multiplied by 0.333), (c) $\xi(t)$ (solid) and $-\xi(t)(p^2(t) - a)$ (dashed, multiplied by 0.3), (d) $\epsilon(t)$ (solid) and $-\epsilon(t)p^3(t)$ (dashed, multiplied by 0.2).

3) Spatial (unnormalized) distributions $f(q,t)$, obtained by integrating Eqs. (12)-(14) with random initial conditions for the momentum and pseudo-friction coefficients, generated according to relation (16) and $q(0) = 0$. There are 10^5 initial conditions for $t = 0.1$ and $t = 1$, and 10^4 for $t = 4$ and $t = 20$.

4) The time dependence of the inverse of the width of the Gaussian distribution $f(q,t) = \sqrt{\Gamma(t)/\pi}\exp(-\Gamma(t)q^2)$, obtained by fitting the spatial distribution at different times.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f(ζ)
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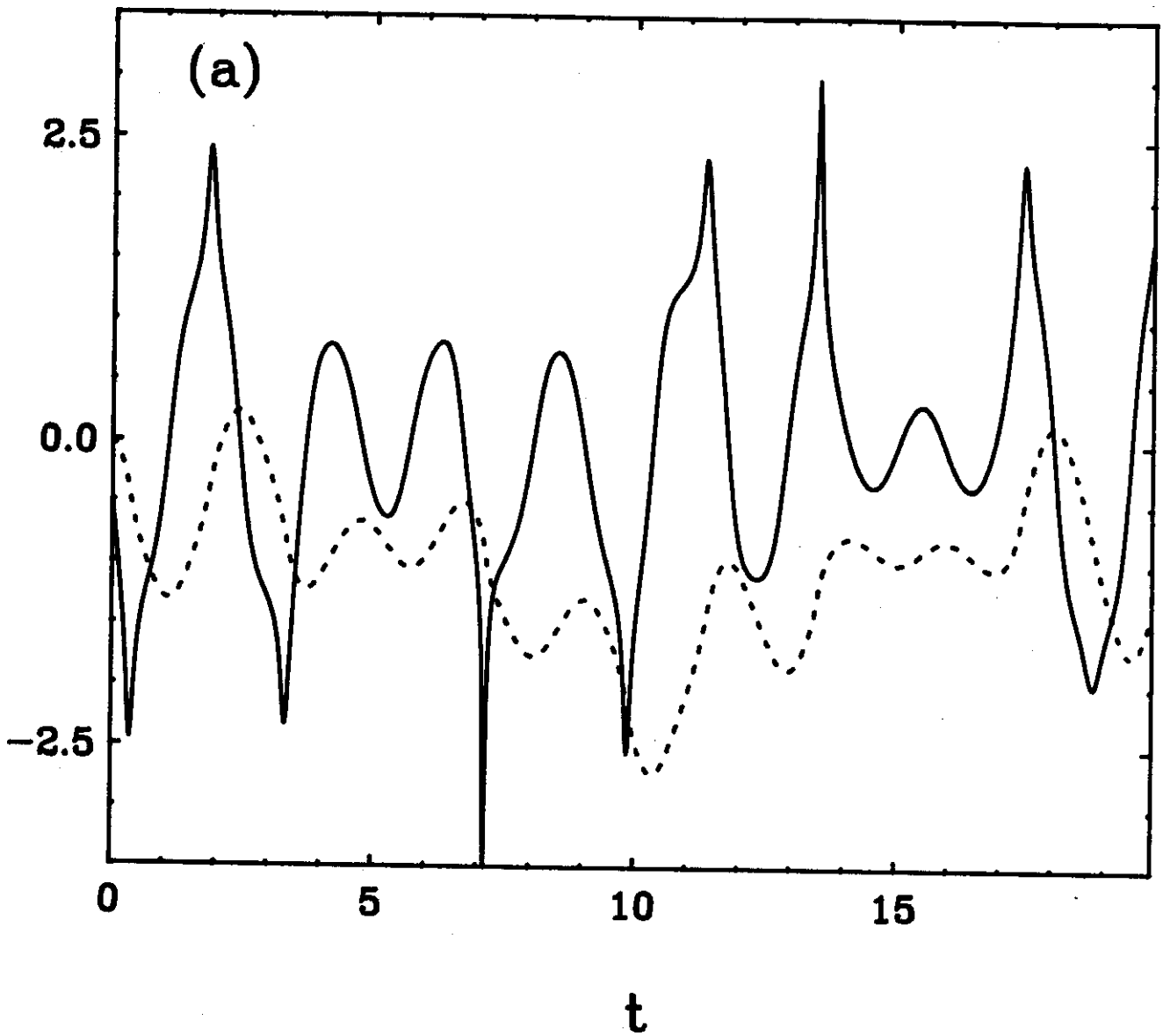
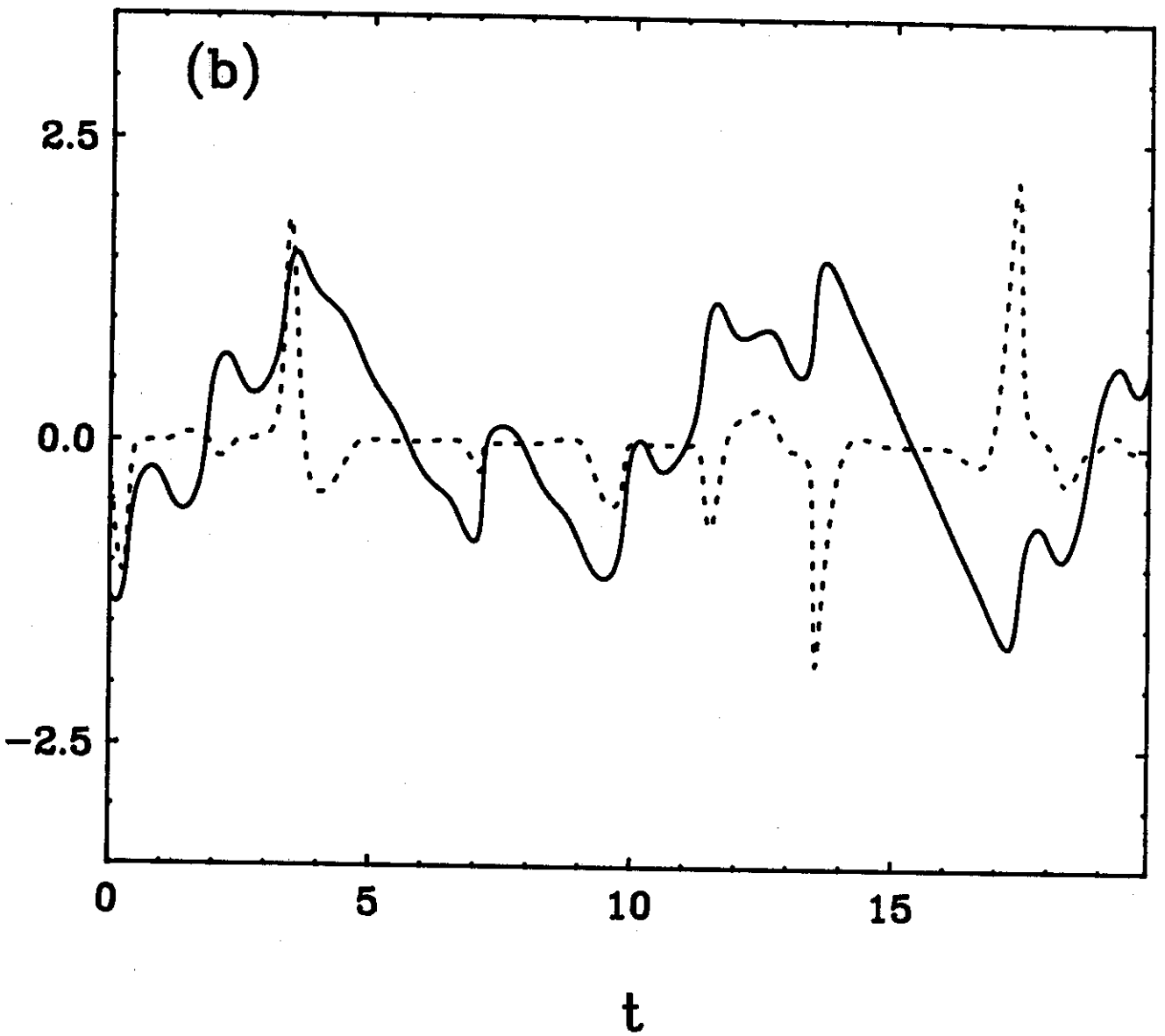
0
−2
0
2
p
ζ
f(ϵ)
f(ξ)
ϵ
ξ


(a)
2.5
0.0
−2.5
0
5
10
15
t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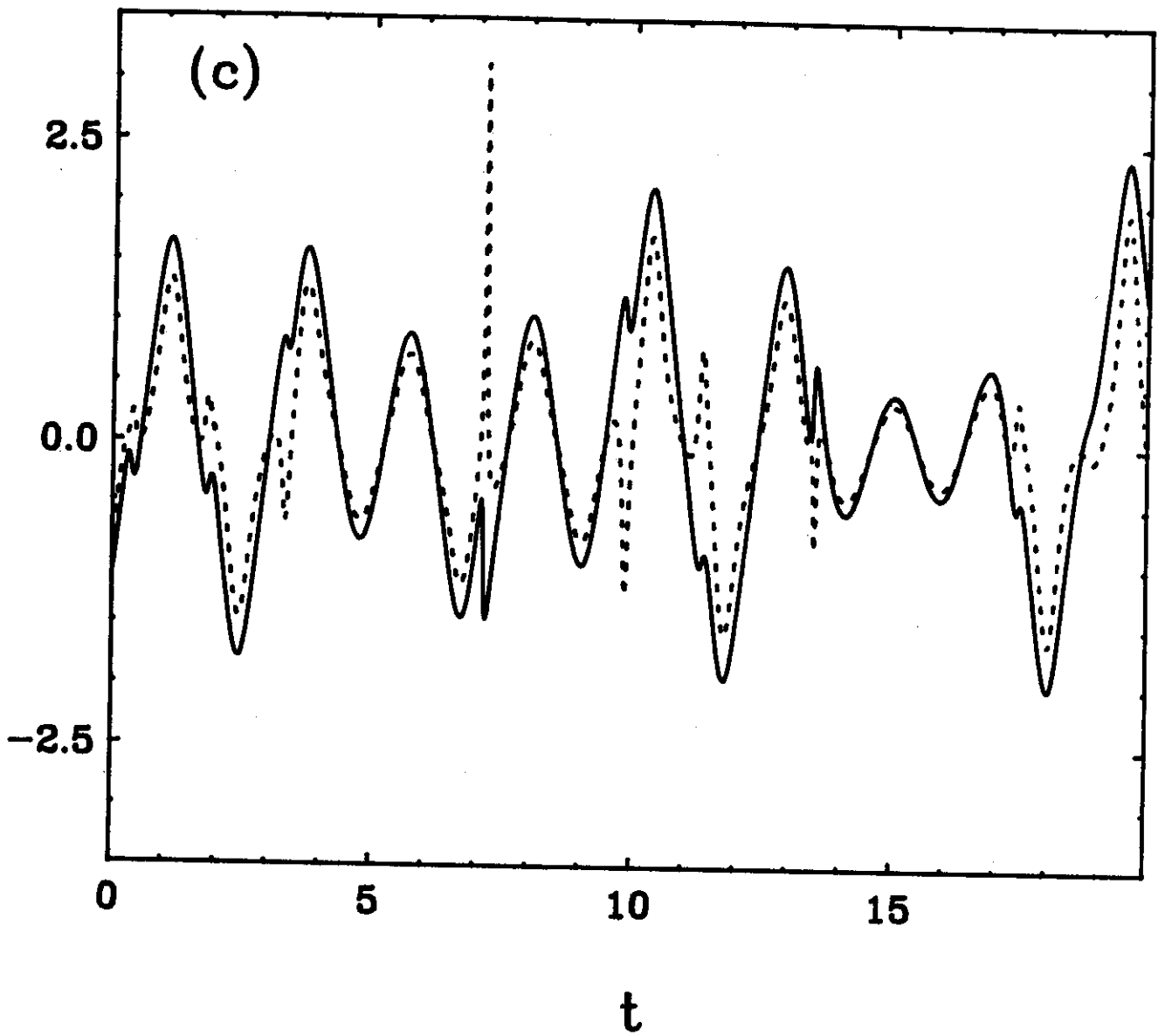
0
5
10
15
t


(c)
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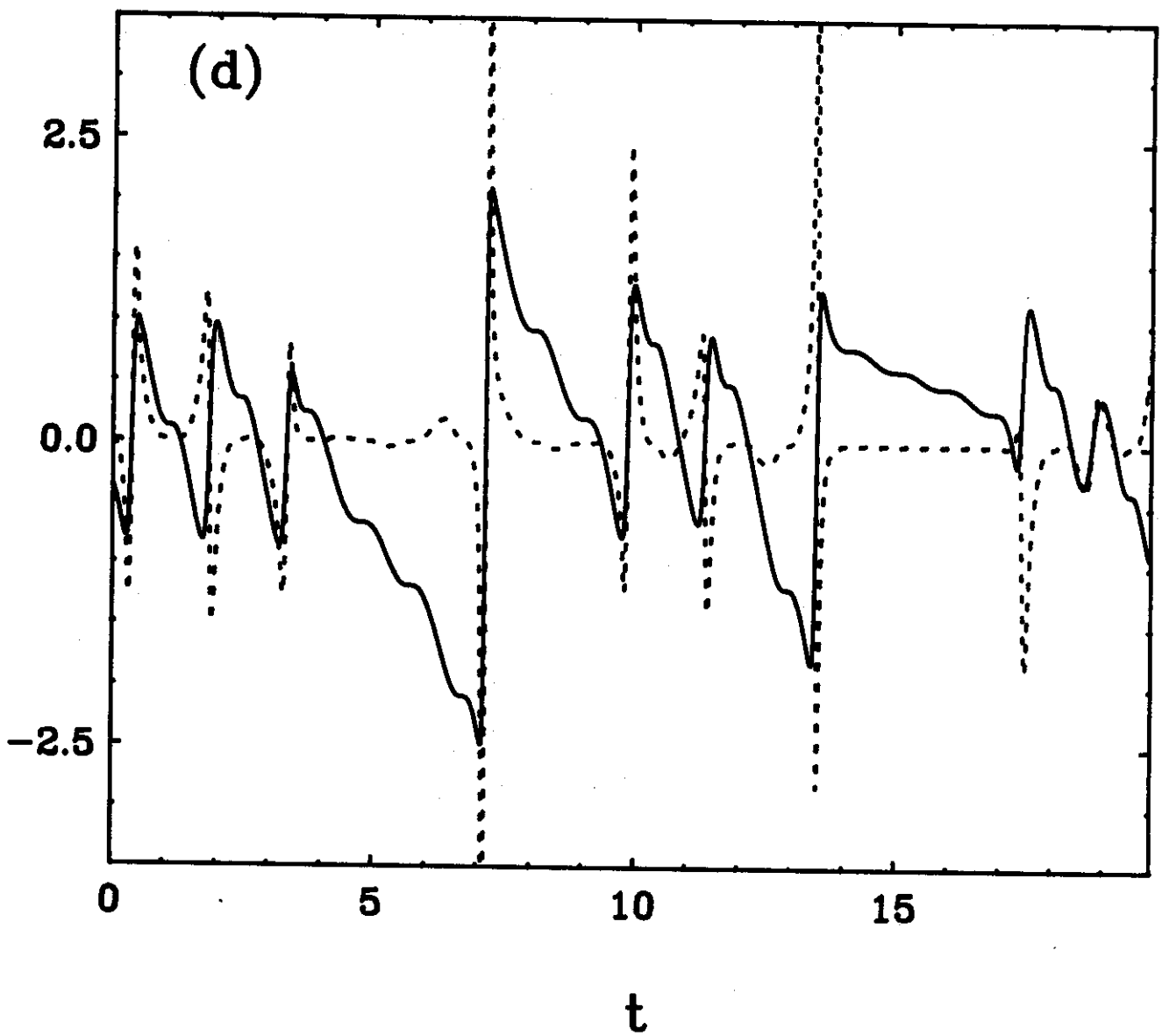
0.0
−2.5
0
5
10
15
t


(d)
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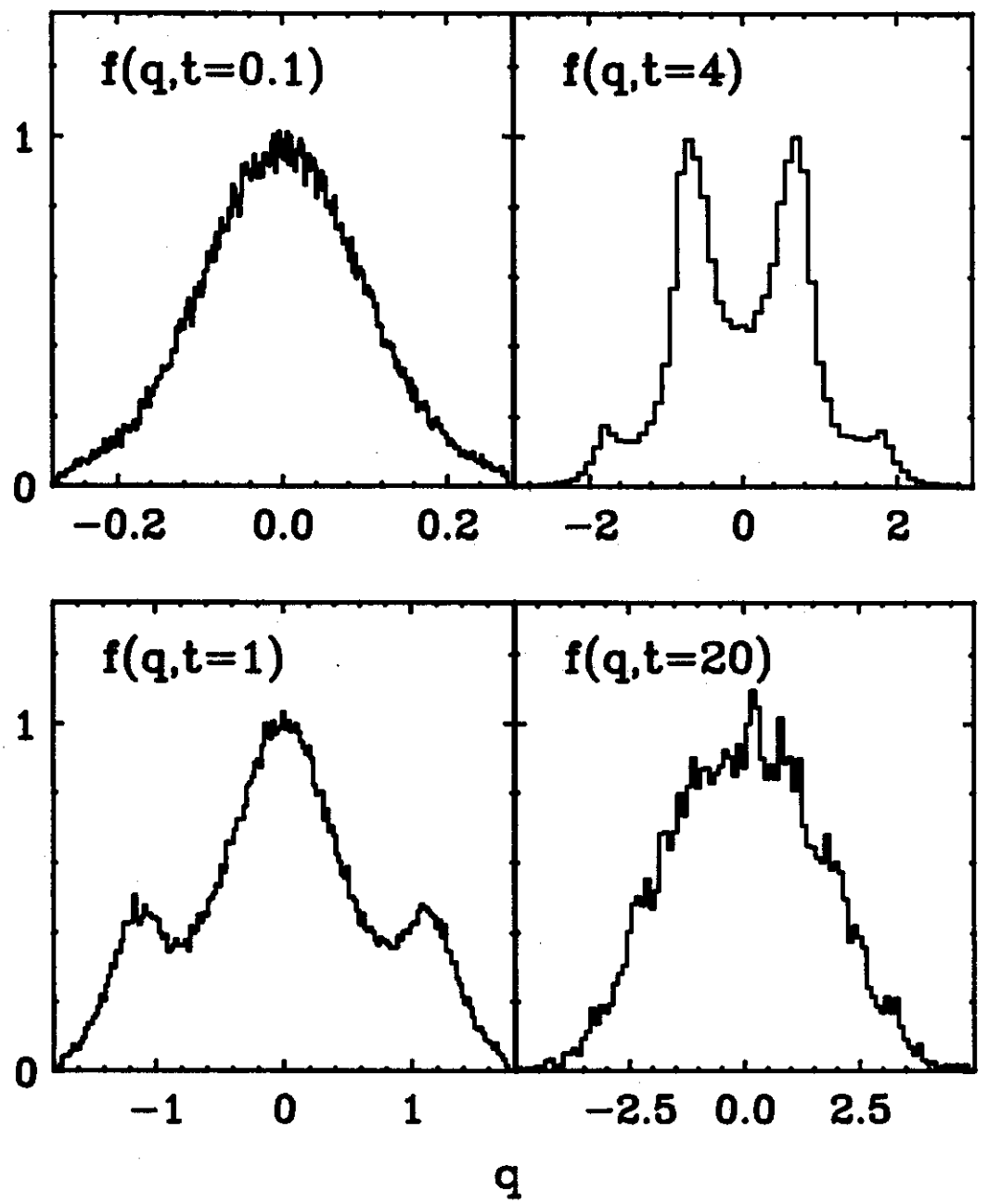
0.0
−2.5
0
5
10
15
t


f(q,t=0.1)
f(q,t=4)
f(q,t=1)
f(q,t=20)
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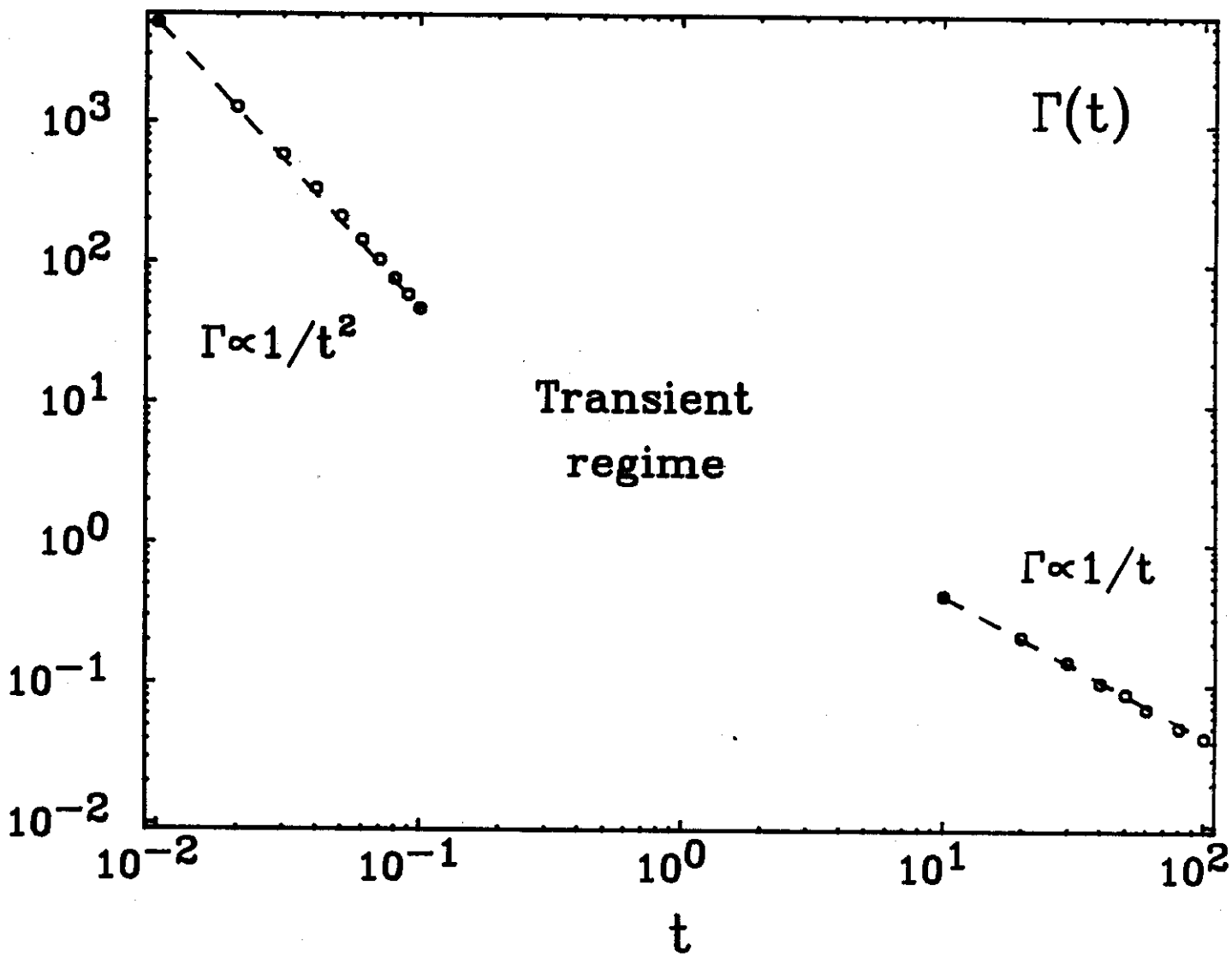
0.2
−2
0
2
−1
0
1
−2.5
0.0
2.5
q


Γ(t)
Γ∝1/t²
Transient
regime
Γ∝1/t
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10²
10¹
10⁰
10⁻¹
10⁻²
10⁻²
10⁻¹
10⁰
10¹
10²
t