AIP | The Journal of Chemical Physics

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Citation: J. Chem. Phys. **70**, 4660 (1979); doi: 10.1063/1.437249
View online: http://dx.doi.org/10.1063/1.437249
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v70/i10
Published by the American Institute of Physics.

Master equation derivation of Keizer's theory of nonequilibrium thermodynamics with critical fluctuations

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(Received 22 December 1978)

A master equation derivation of Keizer's theory of nonequilibrium thermodynamics is presented. It reduces the number of independent postulates in Keizer's theory from three to one, clarifies delicate questions regarding "scaling", and extends Keizer's theory to include fluctuations at a critical point. The critical fluctuations are not Gaussian, like the noncritical fluctuations, but still possess a universal character exhibited in a distribution function which is the exponential of a quartic form. Both Fokker–Planck and nonlinear Langevin formulations are utilized.

INTRODUCTION

A phenomenological theory of nonequilibrium thermodynamic fluctuations has been promulgated in recent years by Joel Keizer.[1] The theory has surprising generality, and has been applied by Keizer to (1) chemical reactions, (2) diffusion, (3) electrode kinetics, (4) thermionic emission, (5) internal state relaxation, (6) heat transport, (7) the Boltzmann equation, (8) the Gunn oscillator,[2] and (9) hydrodynamics.[3] It appears that just about any type of nonlinear transport process in a macroscopic system falls within the scope of the theory.

The theory is phenomenological because it is based upon three postulates which Keizer formulated after he had made a detailed study of the processes mentioned above as well as many other processes. A growing literature[4–6] dealing with "macrovariable" fluctuations as described by "master equations" has also exhibited surprising generality in recent years. Indeed, a striking similarity exists between the structure of Keizer's theory and the structure of master equation theories. It is the purpose of the present paper to show that Keizer's theory may be derived from a master equation. This will unify the two approaches to fluctuations in macroscopic systems and clarify the reasoning in each.

As a bonus for engaging in these formal considerations, the unified view yields a theory for fluctuations at critical points. These fluctuations, like the noncritical fluctuations, exhibit universal character, although of a distinctly different kind. The noncritical fluctuations are always Gaussian in the macroscopic limit,[6] whereas the critical fluctuations are characterized by a distribution function which is the exponential of a quartic form. These properties suggest the existence of "critical Brownian motion" described by a cubically nonlinear Langevin equation.

KEIZER'S PHENOMENOLOGICAL POSTULATES

The structure of Keizer's theory follows from three postulates which characterize the stochastic properties of the transport processes.[1] The description is given in terms of N extensive macrovariables denoted by n_i for $i=1, 2, \ldots, N$. The system is also characterized by a "largeness" parameter V which is often the volume in concrete situations. The macrovariables are thought of in terms of a "deterministic" portion $\bar{n}_i$ and a fluctuating deviation μ_i related to each other by

$$n_i = \bar{n}_i + V^{-\alpha}\mu_i \ , \tag{1}$$

in which α is the "scaling" parameter. The scaling parameter α is introduced here in order to make the connection with master equation results, to be given in the next section, much clearer. In fact, no such parameter appears in Keizer's theory, and his theory may be viewed as simply the $\alpha=0$ special case of Eq. (1).

The rate of change of $\bar{n}_i$ is given by the macroscopic transport law which is determined empirically. Keizer[1] has shown in many different cases that these transport laws may always be expressed in terms of "elementary processes" which are labelled by $k=1, 2, \ldots, m$. Associated with each elementary process is a "forward" rate V_k^+ and a "backward" rate, V_k^-. During the kth elementary process, $\bar{n}_i$ changes by a microscopic amount ω_{ki} in the forward direction, and by $-\omega_{ki}$ in the backward direction. The rates of change V_k^+ and V_k^- are each functions of all the $\bar{n}_i$'s.

Keizer's postulates are

$$\text{(I)}\ \frac{d}{dt}\bar{n}_i = \sum_{k=1}^{m} \omega_{ki}(V_k^+ - V_k^-) \ ; \tag{1}$$

$$\text{(II)}\ \frac{d}{dt}\mu_i = \sum_{j=1}^{N} H_{ij}(t)\mu_j + \tilde{f}_i(t) \ , \tag{2}$$

in which $H_{ij}(t)$ is defined by

$$H_{ij}(t) \equiv \frac{\partial}{\partial \bar{n}_j} \sum_{k=1}^{m} \omega_{ki}[V_k^+(\mathrm{n}) - V_k^-(\mathrm{n})] \tag{3}$$

and $\tilde{f}_i(t)$ is a Gaussian, Markov stochastic force with zero mean and correlation formula

$$\langle \tilde{f}_i(t)\tilde{f}_j(s)\rangle = \gamma_{ij}(t)\,\delta(t-s) \ ; \tag{4}$$

and

$$\text{(III)}\ \gamma_{ij}(t) \equiv \sum_{k=1}^{m} \omega_{ki}\left\{V_k^+[\bar{\mathrm{n}}(t)] + V_k^-[\bar{\mathrm{n}}(t)]\right\}\omega_{kj} \ . \tag{5}$$

These postulates provide a closed description because the $\bar{n}_i$'s are determined by Eq. (1) alone, and both $H_{ij}(t)$ and $\gamma_{ij}(t)$ are determined directly from the $\bar{n}_i$'s. The fluctuations satisfy a nonstationary but linear Langevin description. The linearity of Eq. (2) reflects the fact that the $\bar{n}_i$'s are macroscopic, extensive variables,

 0021-9606/79/104660-04$01.00

whereas the μ_i's are fluctuations in the $\bar{n}_i$'s and are of a much smaller scale, even in the critical fluctuation case where the fluctuations are very large relative to noncritical fluctuations.

MASTER EQUATION FLUCTUATIONS

The appropriate variables for master equation descriptions are most conveniently taken to be the intensive macrovariables

$$c_i = \frac{1}{V} n_i \ . \tag{6}$$

This choice simplifies the presentation of the limit theorem[7,8] results which are characteristic of the master equation procedure. A probability distribution $P(\mathbf{c}, t)$ for the values of the c_i's satisfies the "master equation"

$$\frac{\partial}{\partial t} P(\mathbf{c}, t) = \int d^N c' [W(\mathbf{c}, \mathbf{c}') P(\mathbf{c}', t) - W(\mathbf{c}', \mathbf{c}) P(\mathbf{c}, t)], \tag{7}$$

in which $W(\mathbf{c}, \mathbf{c}')$ is the "transition distribution," which is generally *not* symmetric in $\mathbf{c}$ and $\mathbf{c}'$.

The moments of the transition distribution are given by

$$K^{(p)}_{i_1 i_2 \cdots i_p}(\mathbf{c}) \equiv \int d^N c' \prod_{j=1}^{p} (c'_{i_j} - c_{i_j}) W(\mathbf{c}', \mathbf{c}) \ . \tag{8}$$

In particular,

$$K^{(1)}_i(\mathbf{c}) = \int d^N c' (c'_i - c_i) W(\mathbf{c}', \mathbf{c}) \text{ and}$$

$$K^{(2)}_{ij}(\mathbf{c}) = \int d^N c' (c'_i - c_i)(c'_j - c_j) W(\mathbf{c}', \mathbf{c}) \ . \tag{9}$$

For properly behaved transition distributions, the master equation (7) may be equivalently expressed

$$\frac{\partial}{\partial t} P(\mathbf{c}, t) = \sum_{p=1}^{\infty} \frac{(-1)^p}{p!} \left(\prod_{j=1}^{p} \sum_{i_j=1}^{N} \frac{\partial}{\partial c_{i_j}} \right) \times [K^{(p)}_{i_1 i_2 \cdots i_p}(\mathbf{c}) P(\mathbf{c}, t)] \tag{10}$$

and the $K^{(p)}_{i_1 i_2 \cdots i_p}$'s are observed to be of order $V^{-(p-1)}$ in many specific cases.[8] Cases in which the $K^{(p)}$'s show a compatible monotonic dependence on p but of a more complicated nature are also known.[9]

As in Eq. (1), c_i is thought of in terms of a deterministic portion $\bar{c}_i$ and a fluctuating derivation μ_i related by

$$c_i = \bar{c}_i + V^{-\alpha} \mu_i \ , \tag{11}$$

where again α, the scaling parameter, appears. The normal values for α are $0 \le \alpha \le 1$.

The deterministic portion $\bar{c}_i$ satisfies the macroscopic limit $V \to \infty$ behavior of Eq. (10).

$$\frac{\partial}{\partial t} P_\infty(\bar{\mathbf{c}}, t) = -\frac{\partial}{\partial \bar{c}_i} [K^{(1)\infty}_i(\bar{\mathbf{c}}) P(\bar{\mathbf{c}}, t)] \ , \tag{12}$$

which has the self-consistent solution

$$P(\bar{\mathbf{c}}, t) = \delta[\bar{\mathbf{c}} - \bar{\mathbf{c}}(t)] \ , \tag{13}$$

in which $\bar{\mathbf{c}}(t)$ is the solution to

$$\frac{d}{dt} \bar{c}_i(t) = K^{(1)\infty}_i [\bar{\mathbf{c}}(t)] \ . \tag{14}$$

For any particular transport law, the first criterion to be satisfied by a master equation which putatively gives an equivalent deterministic description is that Eq. (14) is identically the macroscopic transport law.

In order to obtain the macroscopic limit $V \to \infty$ behavior of the fluctuating deviations μ_i, it is necessary to introduce the probability distribution for fluctuations $\phi(\mu, t)$ and the transformations[6]

$$P(\mathbf{c}, t) \to \phi(\mu, t) \ ,$$

$$\frac{\partial}{\partial c_i} \to V^{-\alpha} \frac{\partial}{\partial \mu_i} \ ,$$

$$\frac{\partial}{\partial t} \to \frac{\partial}{\partial t} - V^{\alpha} \sum_{i=1}^{N} \frac{d}{dt} \bar{c}_i(t) \frac{\partial}{\partial \mu_i} \ . \tag{15}$$

If, in addition, the $K^{(p)}(\mathbf{c})$'s are Taylor expanded around the deterministic motion, then the following equation is equivalent with Eq. (10):

$$\begin{aligned}
&\frac{\partial}{\partial t}\phi(\mu, t) - V^{\alpha} \sum_{i=1}^{N} \left[\frac{d}{dt} \bar{c}_i(t)\right] \frac{\partial}{\partial \mu_i} \phi(\mu, t) = -V^{\alpha} \sum_{i=1}^{N} \frac{\partial}{\partial \mu_i} \Bigg(K^{(1)}_i[\bar{\mathbf{c}}(t)]\phi[\mu, t] \\
&\quad - V^{\alpha} \sum_{i=1}^{N} \frac{\partial}{\partial \mu_i} \left\{ \sum_{q=1}^{\infty} V^{-q\alpha} \left(\prod_{j=1}^{q} \sum_{i_j=1}^{N} \mu_{i_j} \frac{\partial}{\partial \bar{c}_{i_j}} \right) K^{(1)}_i[\bar{\mathbf{c}}(t)] \phi[\mu, t] \right\} \Bigg) \\
&\quad + \tfrac{1}{2} V^{2\alpha} \sum_{i_1 i_2}^{N} \frac{\partial^2}{\partial \mu_{i_1} \partial \mu_{i_2}} \left(\left\{ K^{(2)}_{i_1 i_2}[\bar{\mathbf{c}}(t)] + \sum_{q=1}^{\infty} V^{-q\alpha} \left(\prod_{j=1}^{q} \sum_{i_j=1}^{N} \mu_{i_j} \frac{\partial}{\partial \bar{c}_{i_j}} \right) K^{(2)}_{i_1 i_2}[\bar{c}(t)] \right\} \phi(\mu, t) \right) + \cdots \\
&\quad + \frac{(-1)^p}{p!} V^{p\alpha} \sum_{i_1 i_2 \cdots i_p}^{N} \frac{\partial^p}{\partial \mu_{i_1} \partial \mu_{i_2} \cdots \partial \mu_{i_p}} \left(\left\{ K^{(p)}_{i_1 i_2 \cdots i_p}[\bar{\mathbf{c}}(t)] + \sum_{q=1}^{\infty} V^{-q\alpha} \left(\prod_{j=1}^{q} \sum_{i_j=1}^{N} \mu_{i_j} \frac{\partial}{\partial \bar{c}_{i_j}} \right) K^{(p)}_{i_1 i_2 \cdots i_p}[\bar{\mathbf{c}}(t)] \right\} \phi(\mu, t) \right) + \cdots .
\end{aligned} \tag{16}$$

Because of Eq. (14), the two V^{α} terms in Eq. (16) cancel identically. Recalling that $K^{(p)}$ is of order $V^{-(p-1)}$ justifies the conclusion that, in the macroscopic limit $V \to \infty$, the terms which survive in Eq. (16) are

$$\frac{\partial}{\partial t} \phi_\infty(\mu, t) = -\sum_{i=1}^{N} \frac{\partial}{\partial \mu_i} \left\{ \sum_{l=1}^{N} \frac{\partial}{\partial \bar{c}_l} K^{(1)\infty}_i[\bar{\mathbf{c}}(t)] \mu_l \phi_\infty(\mu, t) \right\} + \frac{1}{2} \sum_{i_1 i_2}^{N} \frac{\partial^2}{\partial \mu_{i_1} \partial \mu_{i_2}} \{ R^{(2)}_{i_1 i_2}[\bar{c}(t)] \phi_\infty(\mu, t) \} \ , \tag{17}$$

where

$$R_{ij}^{(2)}[\bar{\mathbf{c}}(t)] \equiv \lim_{V\to\infty} VK_{ij}^{(2)}[\bar{\mathbf{c}}(t)] ,$$

provided $\alpha = \frac{1}{2}$ is chosen.

This description of the fluctuations given by Eq. (17) for the $\alpha = \frac{1}{2}$ scaling is a Gaussian description for which Eq. (17) is the Fokker–Planck equation. It is a nonstationary equation because both $K^{(1)\infty}$ and $R^{(2)}$ depend upon time through their $\bar{\mathbf{c}}(t)$ dependence.

A nonstationary Langevin description[6] equivalent with Eq. (17) exists and is

$$\frac{d}{dt}\mu_i = \sum_{j=1}^{N} H_{ij}^{\infty}(t)\,\mu_j + \tilde{f}_i(t) , \tag{18}$$

with $\tilde{f}_i(t)$ a Gaussian, Markov fluctuating force of zero mean and with correlation formula

$$\langle \tilde{f}_i(t)\tilde{f}_j(s)\rangle = \gamma_{ij}(t)\,\delta(t-s) , \tag{19}$$

with $H_{ij}^{\infty}(f)$ and $\gamma_{ij}(t)$ defined by

$$H_{ij}^{\infty}(t) \equiv \frac{\partial}{\partial \bar{c}_j} K_i^{(1)\infty}[\bar{\mathbf{c}}(t)], \quad \gamma_{ij}(t) \equiv R_{ij}^{(2)}[\bar{\mathbf{c}}(t)] . \tag{20}$$

The similarity between these results and the structure of Keizer's theory should now be evident.

DERIVATION OF KEIZER'S THEORY

Because Keizer's theory is given in terms of macroscopic, extensive variables n_i, the rate laws for the transport equations V_k^+ and V_k^- are extensive quantities of order V.

Choose as the transition distribution

$$W(\mathbf{c},\mathbf{c}') \equiv \sum_k \left[\hat{V}_k^+ \delta\left(\mathbf{c}' - \mathbf{c} + \frac{\omega_k}{V}\right) + \hat{V}_k^- \delta\left(\mathbf{c}' - \mathbf{c} - \frac{\omega_k}{V}\right)\right] . \tag{21}$$

The quantities $\hat{V}_k^+$ and $\hat{V}_k^-$ are not identically given by V_k^+ and V_k^-, which are given by the macroscopic rate laws. The master equation applies to a finite system characterized by finite V. Consequently, for this finite system, the rate laws involve corrections to V_k^+ and V_k^- of order $0(1/V)$:

$$\hat{V}_k^{\pm} = V_k^{\pm} + 0(1/V) ,$$

and in the limit $V\to\infty$, these corrections vanish yielding $V_k^{\pm}$. Starting from Keizer's theory which is macroscopic, it is impossible to determine explicitly the precise form of these correction terms. Because they do not contribute to the limit theorem results, it is unnecessary to specify them further. Our purpose here is not to deduce the details of an underlying master equation, but to demonstrate that such an equation leads to a consolidation of the three postulates for the theory. In the future, it will prove desirable to try to derive from a truly microscopic dynamical basis the form for the transition distribution given in Eq. (21), and then the explicit structure of the $0(1/V)$ terms will emerge.

It is convenient to introduce the intensive rates v_k^+ and v_k^- defined by

$$V_k^+ = Vv_k^+, \quad V_k^- = Vv_k^- . \tag{22}$$

Consequently, Eqs. (9), (14), (17), (18), and (20) yield

$$\text{(I)}\ \ K_i^{(1)\infty}[\bar{\mathbf{c}}(t)] = \sum_k \omega_{ki}(v_k^+ - v_k^-) , \tag{23}$$

with Eq. (14);

$$\text{(II)}\ \ H_{ij}^{\infty}(t) = \sum_k \omega_{ki}\frac{\partial}{\partial \bar{c}_j}[v_k^+(\bar{\mathbf{c}}) - v_k^-(\bar{\mathbf{c}})] ,$$

with Eqs. (17) and (18); and

$$\text{(III)}\ \ \gamma_{ij}(t) = \sum_k \omega_{ki}(v_k^+ + v_k^-)\,\omega_{kj} .$$

These are precisely Keizer's postulates, except for scaling.

The scaling for these Gaussian fluctuations is $\alpha = \frac{1}{2}$, and is needed in order to obtain the limiting behavior as $V\to\infty$. The physically measured scale is, of course, the scaling $\alpha = 0$, which is the Keizer scaling. It is always necessary to "unscale" the limit theorem results in order to compare theory with experiment. Consequently, the three identities in Eq. (23) along with their associated dynamical equations (14) and (18) are equivalent with Keizer's postulates given by Eqs. (1)–(5). It should be noticed in particular that both the Gaussian character of the fluctuations and the linear nature of postulate (II) have been clearly explained in terms of the macroscopic limit $V\to\infty$ *and* the proper scaling $\alpha = \frac{1}{2}$.

CRITICAL FLUCTUATIONS

An equilibrium state, or a steady state, is determined by

$$\frac{d}{dt}\bar{c}_i = K_i^{(1)\infty}(\bar{\mathbf{c}}) = 0 . \tag{24}$$

The solution to Eq. (24) will be denoted by the stationary quantity $\mathbf{s}$. The stationary behavior of Eq. (17) for either an equilibrium state or a steady state is characterized by the fluctuation–dissipation relation which may be derived from Eq. (17)[1,6]:

$$-\sum_l [H_{il}^{\infty}(\mathbf{s})\,C_{lj}^{\infty} + C_{il}^{\infty}H_{jl}^{\infty}(\mathbf{s})] = R_{ij}^{(2)\infty}(\mathbf{s}) , \tag{25}$$

where $C_{ij}^{\infty} = \langle \mu_i\mu_j\rangle \equiv \int_{-\infty}^{\infty} d^N\mu\,\mu_i\mu_j\,\phi(\mu, t=\infty)$ is the correlation matrix for the fluctuations.

Clearly, at a stationary state for which $H_{ij}^{\infty}(\mathbf{s}) = 0$ for all i and j, matrix elements of C^{∞} will have to diverge. This is the behavior of a "critical" state. The stationary critical fluctuation distribution according to Eq. (17) will be uniform when $t\to\infty$.

Using a more subtle choice of scaling, a more structured distribution may be obtained as $V\to\infty$. With scaling parameter $\alpha = \frac{1}{3}$, Eq. (16) yields, for $V\to\infty$,

$$\frac{\partial}{\partial\tau}\phi_{\infty}(\mu,\tau) = -\sum_{i=1}^{N}\frac{\partial}{\partial\mu_i}\times\left[\sum_{i_1i_2}^{N}\frac{\partial^2}{\partial s_{i_1}\partial s_{i_2}}K_i^{(1)\infty}(\mathbf{s})\,\mu_{i_1}\mu_{i_2}\,\phi_{\infty}(\mu,\tau)\right] + \frac{1}{2}\sum_{i_1i_2}^{N}\frac{\partial^2}{\partial\mu_{i_1}\partial\mu_{i_2}}[R_{i_1i_2}^{(2)}(\mathbf{s})\,\phi_{\infty}(\mu,\tau)] , \tag{26}$$

in which $\tau = V^{-1/3}t$, the rescaled time. The rescaling of time manifests the fact that the time scale for relaxation of fluctuations is much longer than the relaxation time scale for the deterministic solution's approach to the stationary state **s**. This is the behavior of "critical slowing down." When $\tau \to \infty$, the stationary critical fluctuation distribution according to Eq. (26) is the exponential of a cubic form in the quantities μ_i. With such a distribution, the first moments of the μ_i's will diverge and render the stationary state unstable.

Therefore, a critical stationary state will remain stable only if, in addition to $H^{\infty}_{ij}(\mathbf{s}) = 0$ for all i and j, it is also true that

$$\frac{\partial^2}{\partial s_{j_1} \partial s_{j_2}} K^{(1)\infty}_i(\mathbf{s}) = 0, \quad \text{for all } i,\ j_1, \text{ and } j_2 . \tag{27}$$

In this case, the scaling parameter $\alpha = \frac{1}{4}$ may be used and Eq. (16) yields, for $V \to \infty$,

$$\frac{\partial}{\partial \tau}\phi_\infty(\mu,\tau) = -\sum_{i=1}^{N} \frac{\partial}{\partial \mu_i}\left[\sum_{i_1 i_2 i_3}^{N} \frac{\partial^3}{\partial s_{i_1}\partial s_{i_2}\partial s_{i_3}} K^{(1)\infty}_i(\mathbf{s})\mu_{i_1}\mu_{i_2}\mu_{i_3}\phi_\infty(\mu,\tau)\right] + \frac{1}{2}\sum_{i_1 i_2}^{N} \frac{\partial^2}{\partial \mu_{i_1}\partial \mu_{i_2}} R^{(2)}_{i_1 i_2}\phi_\infty(\mu,\tau)] , \tag{28}$$

in which $\tau = V^{-1/2} t$ is the rescaled time. Stability of the stationary state is now possible and the stationary distribution is the exponential of a quartic form which is negative definite.

The foregoing considerations become transparent in the case of a one component system. Equation (28) becomes

$$\frac{\partial}{\partial \tau}\phi_\infty(\mu,\tau) = -\frac{\partial}{\partial \mu}\left[\frac{\partial^3}{\partial s^3} K^{(1)\infty}(s)\,\mu^3\,\phi_\infty(\mu,\tau)\right] + \frac{1}{2}\frac{\partial^2}{\partial \mu^2}\left[R^{(2)}(s)\,\phi_\infty(\mu,\tau)\right] , \tag{29}$$

which has the normalized stationary distribution

$$\phi_\infty(\mu) = \frac{2\lambda^{1/4}}{\Gamma(\frac{1}{4})}\exp(-\lambda\mu^4) , \tag{30}$$

where

$$\lambda \equiv -\frac{1}{2}\,\frac{\frac{\partial^3}{\partial s^3} K^{(1)\infty}(s)}{R^{(2)}(s)} .$$

λ is positive if $(\partial^3/\partial s^3)K^{(1)\infty}(s)$ is negative, which is the condition for stability in this one component case. Such a distribution occurs in critical density fluctuations in fluids.[10] It also appeared in a remark by van Kampen[11] concerning chemical reactions.

An explicit example[12] of a one component system has recently been worked out and exhibits the behavior in Eq. (30). This example is the Schlögl model[13,14] of a chemical reaction involving a third order reaction step. The reaction is characterized by a cubic equation which, through the adjustment of the relative size of the rate constants, makes a transition from a unique real root to three real roots, two of which correspond to stable states. The point at which the transition occurs is the critical point and critical fluctuations of the type in Eq. (30) are found there, whereas at all noncritical points, Gaussian fluctuations are obtained.

The Fokker–Planck description given by Eq. (29) has associated with it a nonlinear Langevin equation

$$\frac{d}{dt}\mu(t) = \frac{\partial^3}{\partial s^3} K^{(1)\infty}(s)\,\mu^3(t) + \tilde{f}(t) , \tag{31}$$

where $\tilde{f}(t)$ is Gaussian, with zero mean, and correlation formula

$$\langle \tilde{f}(t)\tilde{f}(t')\rangle = R^{(2)}(s)\,\delta(t-t') . \tag{32}$$

It would be of considerable interest if such cubically nonlinear "Brownian motion" could be observed experimentally in a system which has been allowed to age sufficiently long at its critical point.

ACKNOWLEDGMENT

This work was supported by NSF grant PHY77-07372.

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