Fluctuations close to equilibrium

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We studied the fluctuations of well-defined nonequilibrium molecular dynamics systems by performing accurate computer simulations at constant volume and temperature. We monitored the internal energy, the color current, and the heat flow vectors and the pressure tensor in equilibrium and under the impact of "color" or shear fields of different size. Fluctuations of the previous quantities are the smallest under equilibrium conditions. In the case of the current generated by the external field, however, the relative fluctuations become smaller with increasing external field. We discuss the implications of these results and make comparisons with theoretical predictions. We point out problems related to the proof of the principle of maximum hardness by Parr and Chattaraj [J. Am. Chem Soc. **113**, 1854 (1991)].

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I. INTRODUCTION

All thermodynamic systems undergo continual local fluctuations. The values of state variables not fixed by external constraints exhibit incessant and rapid changes. This spontaneous exploration of nearby states tests the stability of the thermodynamic state. Thus, in thermodynamics fluctuations and stability conditions are closely related. This inherent connection suggests that fluctuation amplitudes might reveal information about the relative stability of nearby states. We propose that the equilibrium state of a system has the smallest fluctuations relative to nearby nonequilibrium states.

The purpose of the study reported in the following is to provide numerical evidence about the size of fluctuations in equilibrium and nearby nonequilibrium states to support this proposed extremum principle. Although it would be intriguing to test the validity of this extremum principle in general, we have to restrict our study to well-defined cases where the concept of "nearby nonequilibrium states" is clearly specified. These are the dissipative nonequilibrium steady states not very far from equilibrium.

In the linear regime, where one can use linear response theory, there is no difference between the fluctuations of an equilibrium and a nonequilibrium system because to leading order the change in the fluctuations is a quadratic function of the perturbing field. This is the reason thermostated and unthermostated linear responses are identical [1]. Thus, by the term "not very far from equilibrium" we mean conditions where the nonlinearity of the responses is detectable but not very large.

The so-called Sllod algorithm of planar Couette flow (so called because of its close relationship to the Dolls tensor algorithm) is an excellent model for this purpose because it is considered to be exact even outside of the linear regime [1]. This is not true in the case of the so-called color conductivity nonequilibrium molecular dynamics (NEMD) algorithm, which was created to calculate self-diffusion. The color current generated by an artificial external field can be related to the self-diffusion coefficient of the liquid only in the zero-field limit [1]. This algorithm, however, is an analog of an ionic liquid (alkali-halide melt, for instance) in the presence of a static electric field. The only difference is that the interparticle interactions "do not see" the plus or minus "color" charges; they are "visible" only to the external field. Thus, the calculated nonzero field color currents are analogous to real electric currents. This similarity makes our calculation relevant to real systems even outside the linear regime. (It should be noted here that from a computational point of view it is advantageous to use a model system where only short-range interactions are present.)

In the following section we describe the characteristics and present the results of our computer simulations. Then in Sec. III we compare our numerical findings to predictive theories present in the literature. Finally, our conclusions are presented in Sec. IV.

II. NONEQUILIBRIUM MOLECULAR DYNAMICS SIMULATIONS

In the field of molecular dynamics simulations it was a revolutionary step to introduce synthetic thermostats in the form of a feedback scheme in order to control the temperature of the system [2–4]. This was mandatory for NEMD calculations because the heat produced by the work of the external field on the system had to be removed to maintain steady-state conditions. In the case of equilibrium calculations there is a consensus in the literature with regard to the theoretical justification of such algorithms. In the Nosé-Hoover scheme the constant temperature condition is elegantly related to Gibbs' ensemble theory in statistical mechanics [5].

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Since there is no counterpart of Gibbs' ensemble theory for nonequilibrium steady-state systems, the thermostats applied in NEMD simulations are the same as that under equilibrium conditions. Far from equilibrium, however, the adoption of the equilibrium temperature concept is questionable. There are theoretical considerations and numerical evidence obtained from NEMD calculations showing that the kinetic temperature defined by the random velocities of particles and the thermodynamic temperature given as the partial derivative of the free energy with respect to entropy differ for systems far from equilibrium [6–9]. This means that there is little point in studying the fluctuations of NEMD systems far from equilibrium because their relevance to real systems is still in doubt.

In fact, the concept of temperature even close to equilibrium but outside of global equilibrium should be used cautiously. As it was shown by Ernst [10] that the use of the kinetic temperature as *the* temperature violates the Gibbs relations and gives false transport coefficients for the related scalar currents such as bulk viscosity or chemical rate constants. Unfortunately, we cannot avoid the problem of using some kind of temperature definition in order to have well-defined states of our systems. We have no other option than to use the kinetic temperature, defined as $T_K \equiv (1/3mkN)\sum_{i=1}^{N} p_i^2$, for this purpose because this is the only easily measurable and controllable temperaturelike variable in our simulation. We assume, however, that the qualitative characteristics of our findings remain valid in the low-field limit where the problems caused by improper temperature definitions become negligible.

The external fields applied in our NEMD simulations need to be quite large in order to have a good signal/noise ratio [1]. (This is obvious if one converts the usual reduced units into real units by identifying our simple spherically symmetric particles with liquid argon. Then the typical strain rate in NEMD planar Couette flow simulations corresponds to 10^{12} Hz. Using simple NEMD we cannot obtain statistically meaningful viscosities for strain rates below 10^{10} Hz.) However, all the evidences collected so far by NEMD simulations—including the so-called subtraction technique [11] which for a short time is capable of measuring the response of the system to very small fields (10^4 Hz)—indicate that up to moderate external fields there is no extremum behavior in terms of the strength of the external field. Therefore, we assume that the response of the liquid can be extrapolated towards smaller external fields.

The Sllod equations of motion for planar Couette flow supplemented with a Nosé-Hoover thermostat are as follows [1]:

$$\begin{aligned} \dot{\mathbf{q}}_i &= \mathbf{p}_i/m + \mathbf{i}\gamma y_i \ , \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \mathbf{i}\gamma p_y - \alpha \mathbf{p}_i \ , \\ \dot{\alpha} &= \frac{1}{Q}\left[\frac{T(t)}{T_0} - 1\right] , \end{aligned} \tag{1}$$

where $\mathbf{q}_i$, $\mathbf{p}_i$, and $\mathbf{F}_i$ are the position, momentum, and intermolecular force of particle i ($i=1,2,\ldots,N$), m is the mass, $\gamma \equiv \partial u_x/\partial y$ is the shear rate, $\mathbf{i}$ represents a unit vector in the x direction, α is the thermostating multiplier, $T(t)$ the actual kinetic temperature at time t, T_0 is the preset kinetic temperature, and Q is a constant.

The equations of color conductivity are the following [1]:

$$\begin{aligned} \dot{\mathbf{q}}_i &= \mathbf{p}_i/m \ , \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i + \mathbf{i}c_i F - \alpha(\mathbf{p}_i - \mathbf{i}c_i J_x/\rho) \ , \end{aligned} \tag{2}$$

where c_i is the color charge on particle i, $c_i=(-1)^i$, and J_x is the color current defined as

$$J_x = \frac{1}{V}\sum_{i=1}^{N} c_i \frac{p_{xi}}{m} \ . \tag{3}$$

It is straightforward to show that in the canonical ensemble the color current is related to the velocity autocorrelation function [1],

$$\langle J_x(t)J_x(0)\rangle_c = \frac{N}{m^2V^2}\langle p_x(t)p_x(0)\rangle_c \ , \tag{4}$$

where V is the volume of the system.

The microscopic definition of the internal energy, the pressure tensor, and the heat flow vector are well known and given in Refs. [1] and [12], for example.

We consider a system of 500 particles interacting via the so-called WCA potential. This spherically symmetric, pairwise additive short-range interaction is defined in terms of the interparticle separation r as follows:

$$\phi(r) = \begin{cases} 4[r^{-12} - r^{-6}] + 1, & r \le 2^{1/6}, \\ 0, & r > 2^{1/6}. \end{cases}$$

Here and throughout the paper we use the usual reduced units of computer simulations [distances made dimensionless by dividing by the molecular diameter σ, energies made dimensionless by dividing by the characteristic interaction energy ε, temperature made dimensionless by multiplying by k/ε where k is Boltzmann's constant, number densities made dimensionless by multiplying by σ^3, strain rates made dimensionless by multiplying by $(m\sigma^2/\varepsilon)^{1/2}$, and times made dimensionless by dividing by $(m\sigma^2/\varepsilon)^{1/2}$] [12]. The state point of the system is also given in reduced units. The temperature, $T=0.722$, and the number density, $\rho=0.8442$, correspond to triple-point conditions of liquid argon. We used only the half of the usual time step, $\Delta t=0.002$, in order to have higher accuracy. A fifth-order Gear algorithm integrated the equations of motion. The length of each run was 2×10^6 time steps, i.e., 4000 time units. In the case of the single equilibrium simulations we collected data from 4×10^6 time steps. It should be noted here that contrary to mean values the fluctuations are quite sensitive to the length of "equilibration" periods. While we need at most a couple of thousand time steps for the system to attain steady conditions in terms of mean values, in the case of fluctuations this time is longer by an order of magnitude.

The errors in our results were calculated by dividing each simulation run into 10 blocks (after discarding the

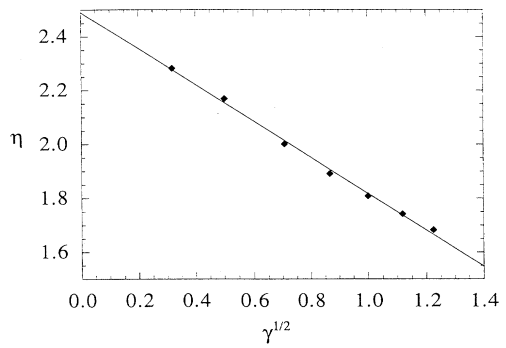

FIG. 1. Viscosity as a function of the square root of the shear rate ($N=500$, $T=0.722$, $\rho=0.8442$, WCA particles).

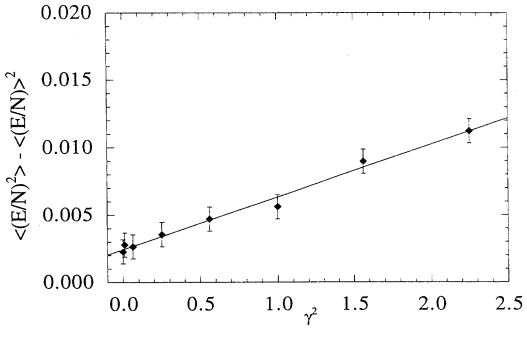

FIG. 3. Internal energy fluctuations in terms of the square of the shear rate.

initial period). The error bars correspond to one standard deviation of the block averages. In the figures the error bars shown are the same for each data point because the average of the error bars is shown rather than the individual error bars for each shear rate. This simplification could be made because individual error bar values were found to be close to one another. The variance of a quantity (required in Figs 3–7) was obtained by calculating the quantity $\langle A^2\rangle-\langle A\rangle^2$ in each block from the individual time steps in the block, then analyzing the block averages to obtain the overall average value and the standard deviation in this quantity.

In Fig. 1 we show the viscosity of the model fluid as a function of the square root of the shear rate. The linear relation between these two quantities is supported by both theoretical [13] and numerical calculations [1]. In Fig. 2 we show the internal energy per particle of the fluid in terms of $\gamma^{3/2}$. The relationship is linear again because the work done by the external field on the system is proportional to $P_{12}\gamma$, where P_{12} is the xy element of the pressure tensor, i.e., the dissipative flux. The results presented in these two graphs are not new. They were first shown by Evans, Morriss, and Hood [14] as the result of very accurate calculations on large systems. We show them here as a consistency check of our result with those of previous workers.

In Fig. 3 the variance of the energy is shown in terms of the *square* of the shear rate. The linearity of this relationship is less certain than in the previous two cases because of much larger estimated errors. The same can be said about the variance of the shear stress shown in Fig. 4, although it seems that the accuracy is somewhat better. Both figures support the notion that the fluctuations are at a minimum at equilibrium. The independent variable of these plots was chosen to be γ^2 simply because of the reasonable linear fit of the data.

In Fig. 5 we present the *relative* variance of the dissipative flux, which asymptotically approaches zero as the external field increases. Understandably, the relative fluctuations become smaller because of the ordering work of the external force. Thus, the external field can decrease the fluctuations of the generated flux but only in relative terms. We do not show the relative variance of the internal energy because this quantity has basically the same qualitative behavior as the absolute internal energy presented in Fig. 3.

Away from equilibrium correlations between quantities of different time-reversal parity do not vanish. In Fig. 6 we present the cross correlations between shear stress and internal energy. The results fit reasonably well to $\gamma^{3/2}$.

We performed the same calculations in the case of color conductivity. We found the same qualitative effects as in the case of the shear flow. The only difference is that the extrapolation of the color flux to zero field is not as well defined as in the planar Couette flow case. In most published simulation studies a linear dependence is assumed, although for higher fields the generated current

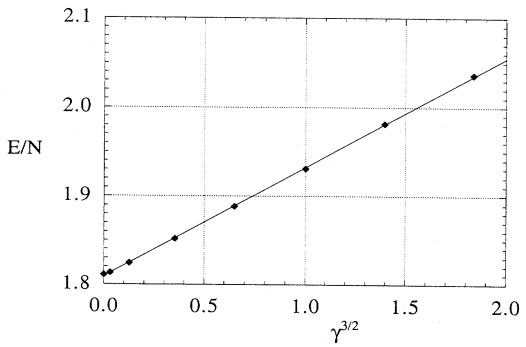

FIG. 2. Internal energy per particle as a function of $\gamma^{3/2}$. The system is the same as in Fig. 1.

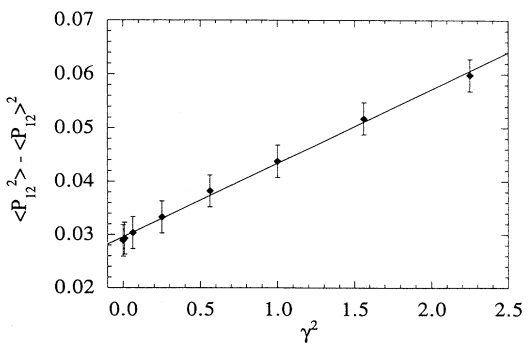

FIG. 4. Shear stress fluctuations in terms of the square of the shear rate.

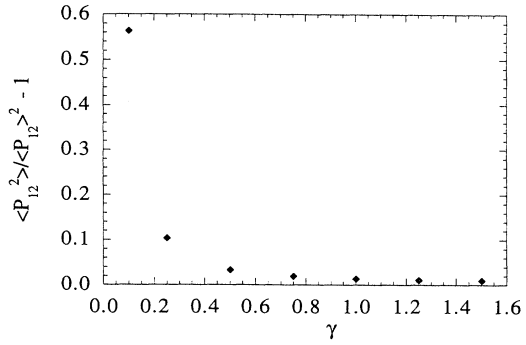

FIG. 5. Relative shear stress fluctuations in terms of the shear rate.

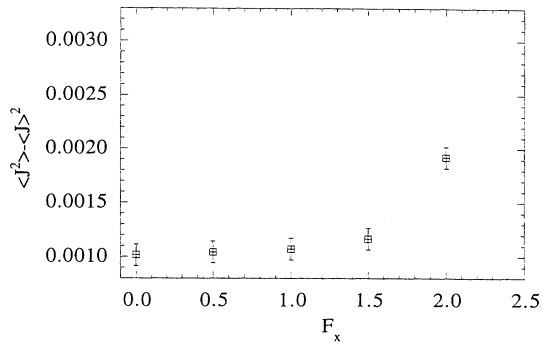

FIG. 7. Fluctuations in the color current in terms of the color field.

contains substantial higher-order contributions as well. For example, in Fig. 7 where we show the fluctuations in the color current in terms of the color field, the data point obtained at the highest field implies high-order field dependence.

III. THEORETICAL APPROACHES

We begin by recalling the famous hypothesis of Onsager, which claims that the relaxation of a macroscopic nonequilibrium disturbance is governed by the same laws as the regression of spontaneous microscopic fluctuations in an equilibrium system [15]. As the mathematical expression of this statement Chandler gives the following equation [16].

$$\frac{\Delta\overline{A}(t)}{\Delta\overline{A}(0)}=\frac{C(t)}{C(0)}\ , \tag{5}$$

where $C(t)$ is the autocorrelation function of the phase variable $A(t)\equiv A(\mathbf{p}^N(t),\mathbf{q}^N(t))$ defined as

$$C(t)=\langle[A(0)-\langle A\rangle][A(t)-\langle A\rangle]\rangle\ , \tag{6}$$

where $\langle A\rangle$ is the ensemble average of A at equilibrium and $\langle\ \rangle$ indicates an ensemble average. The meaning of $\Delta\overline{A}(t)$ is

$$\Delta\overline{A}(t)=\overline{A}(t)-\langle A\rangle\ , \tag{7}$$

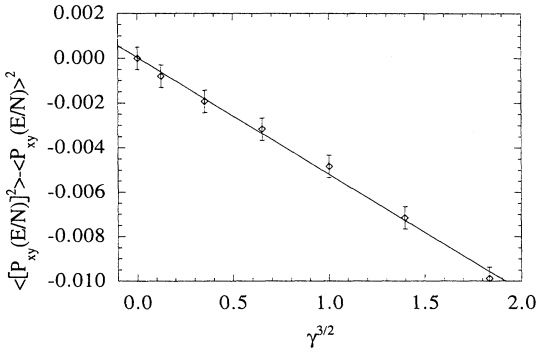

FIG. 6. Cross correlation between the energy and the shear stress in terms of $\gamma^{3/2}$.

where $\overline{A}(t)$ is the ensemble average value of A at time t if at $t=0^-$ we perturbed the system in a systematic way. Expression (5) can be easily obtained applying linear response theory [1].

As exercise 8.3 on page 242, Chandler claims in his book that the following relationship can also be shown to be valid [16]:

$$C(t)=\langle A\rangle\Delta\overline{A}(t)\ , \tag{8}$$

provided the nonequilibrium distribution of the system is given by

$$F(\mathbf{q}^N,\mathbf{p}^N)=\langle A\rangle^{-1}f(\mathbf{q}^N,\mathbf{p}^N)A(\mathbf{q}^N,\mathbf{p}^N)\ , \tag{9}$$

where $f(\mathbf{q}^N,\mathbf{p}^N)$ is the equilibrium phase-space distribution function. Equation (8) might seem appealing because the acceptance of Eq. (8) makes it trivial to show that if the time average of A is positive then the average nonequilibrium value, $\overline{A}(0)$, is larger than the equilibrium mean value, $\langle A\rangle$. From Eq. (8) it follows immediately that

$$\overline{A}(0)-\langle A\rangle=\langle A\rangle^{-1}\langle[A(0)-\langle A\rangle]^2\rangle\ , \tag{10}$$

where the right-hand side of Eq. (10) cannot be negative if $\langle A\rangle$ is positive. This was derived by Parr and Chattaraj who showed that in an equilibrium electronic system the chemical softness (which is proportional to the fluctuation in the number of electrons in the system) is a minimum [17]. Analogously, if A is the variance of any property unconstrained by the thermodynamic boundary conditions, Eq. (8) shows that the fluctuations in equilibrium are minimal relative to nearby nonequilibrium states of the same system [18]. Thus, if Eq. (8) had been a general result, this would have provided a convenient route to proving the extremum principle about fluctuations for which we have provided simulation evidence in the preceding section. This was our original motivation for examining this approach.

Evidently, Parr and Chattaraj did not realize that Eq. (8) is not a generally valid expression, unlike Eq. (5). For example, Eq. (9), and thus Eqs. (5) and (10), obviously fail if the mean value of A is zero in equilibrium. The none-

quilibrium phase-space distribution of (9) represents a peculiar case when the relative occurrence of phase-space points are weighted by their A value. This property of the phase-space distribution ensures that points with larger absolute value of A give enhanced contribution to the average, thereby increasing the fluctuations of A in the nonequilibrium phase. In general, Eq. (8) does not follow from Eq. (5).

Other approaches to determining the size of fluctuations away from equilibrium come from theories of nonequilibrium thermodynamics. Since the initial formulation of linear irreversible thermodynamics, there has been an ongoing effort to generalize it beyond the linear regime. The most comprehensive theoretical study of fluctuations away from equilibrium was carried out by Keizer [19]. Formal generalizations of equilibrium fluctuation expressions have also been derived by Evans and Morriss in the framework of Kawasaki distributions or the transient time-correlation formalism [1]. These formulas are of general validity for nonequilibrium steady-state systems, but provide no *a priori* predictions in terms of the size of the fluctuations.

To predict the fluctuations of nonequilibrium steady-state systems one needs to generalize Einstein's expression of equilibrium fluctuations [19]. This has been done in the framework of the so-called extended irreversible thermodynamics (EIT) theory, which puts a generalized entropy (which away from equilibrium is also a function of the steady-state fluxes) in the Einstein relation to calculate nonequilibrium steady-state fluctuations [20]. For ideal gases, in the case of planar Couette flow, for instance, the steady-state fluctuation in the dissipative flux can be given in terms of well-defined quantities [20]

$$\langle \delta P_{12} \delta P_{12} \rangle = \frac{\eta k T}{\tau V} (1 + \tfrac{20}{3} \tau^2 \gamma^2) , \tag{11}$$

where τ is the characteristic relaxation time of the flux and η is the shear viscosity. For ideal gases the cross correlation between energy and stress is the following:

$$\langle \delta E \delta P_{12} \rangle = -2kT\eta\gamma / M , \tag{12}$$

where E is the internal energy and M is the mass of the system.

Comparing the theoretical derivations of Eqs. (11) and (12) to our numerical results presented in Figs. 4 and 6, it appears that the predictions of EIT are not contradicted by our calculations, although the theoretical formulas are not perfectly reproduced in their functional forms. Taking into account the $\eta = \eta_0 - \eta_1 \gamma^{1/2}$ dependence of the viscosity ($\eta_0 = 2.49; \eta_1 = 0.67$) the predictions of Eq. (12) due to the dominant linear term ($\eta_0 \gamma$) do not give a perfect fit to our simulated results. The discrepancy, although systematic, is not very large. In the case of Eq. (11) the plot in terms of the square of the shear rate gives a reasonable fit to a linear relationship, suggesting that the smaller additional term proportional to $\gamma^{5/2}$ does not play a significant role over this range of shear rates.

IV. CONCLUSIONS

We have presented a study of the size of fluctuations in nonequilibrium steady-state fluids in order to test the validity of our proposal that the equilibrium fluctuations are the smallest relative to nearby nonequilibrium states of the system. We used well-defined NEMD systems for this purpose. For these systems the validity of this proposition is confirmed. The size of energy and flux fluctuations at constant density and temperature increases roughly as quadratic functions of the external field, which is in qualitative agreement with the predictions of EIT. The relative fluctuations in the fluxes are decreasing, as one would assume, if the conjugate thermodynamic forces are increasing.

No matter how small, the applied external field introduces a certain amount of anisotropy in the liquid. A manifestation of this anisotropy is the different values of the *kinetic* temperature components in the three directions. (Note that we have no way to control temperature definition other than that. Thus, the following discussion refers to this quantity without defining its relationship to other temperature concepts.) There is a straightforward consequence of temperature anisotropy that can be understood most trivially in the case of color conductivity. The zero-field limit value of the color current is proportional to half of the average reduced temperature in that direction [see Eq. (4)]. The fluctuations of the color current are proportional to the square of the temperature. If the temperature is not uniform in the three directions, then the sum of the squares of temperature components will always be larger than the sum of squares with the same average but uniform temperature. Since the anisotropy becomes larger for stronger external fields, this effect increases the fluctuations of the color current.

This behavior seems to be valid for the fluctuations in general. Although the heat flux was zero in the presence of a color field, the fluctuations of the heat flux vector increased quadratically in terms of the external field due to the anisotropy of the system. The same was observed in the case of the pressure tensor in the presence of the color field and the heat and color flux vectors showed enhanced fluctuations in the presence of the shear field.

We provided numerical evidence supported by the predictions of the existing theory that the fluctuations are the smallest in equilibrium relative to nearby (dissipative) nonequilibrium steady states of the system. We believe that this extremum property of the equilibrium state is valid with respect to any well-defined nonequilibrium state under the same macroscopic constraints. Unfortunately, it is quite difficult to devise such states in a thought experiment and to prove using statistical mechanics that their fluctuation is larger than the equilibrium value. One has to move beyond linear response theory. We pointed out that Parr and Chattaraj [17], in attempting to prove much the same thing, apparently based their proof on a simple misinterpretation of Chandler's book [16].

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