

## Finite-size effects in nonequilibrium correlation functions

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(Received 27 March 1990; revised manuscript received 16 October 1990)

We have shown that finite-size effects in the correlation functions away from equilibrium may be introduced through dimensionless numbers: the Nusselt numbers, accounting for both the nature of the boundaries and the size of the system. From an analysis based on fluctuating hydrodynamics, we conclude that the mean-square fluctuations satisfy scaling laws, since they depend only on the dimensionless numbers in addition to reduced variables. We focus on the case of diffusion modes and describe some physical situations in which finite-size effects may be relevant.

### I. INTRODUCTION

It is well known that nonequilibrium correlation functions exhibit a number of properties that are not present at equilibrium, such as, for example, long-range behavior, time-reversal symmetry breaking, or the lack of translational invariance.<sup>1</sup> The analysis of correlation functions involves two characteristic lengths, namely, the penetration depth of fluctuations and the size of the system. One may show that when dealing with diffusion modes it is possible to avoid boundary effects by choosing conveniently the orientation between the external gradients and the wave vectors.<sup>2</sup> Light-scattering (Rayleigh) experiments support this assumption.<sup>3</sup> The situation is not the same for sound modes. Consequently, to reproduce the Brillouin spectrum boundary effects should be considered in the derivation of the correlation functions.<sup>4</sup>

Our aim in this paper is to show that finite-size effects in the correlation functions are not only due to the fact that the penetration depth for the perturbations is at least of the same order as the size of the system, but to the nature of the boundaries themselves. Then the stationary solutions may be modified by this fact and the overall transport coefficients may depend on parameters related to the boundaries. As a consequence, the correlation functions will be also affected by this feature. We will show that boundary effects enter the analysis through Nusselt numbers comparing the nature of the boundaries, the size of the system, and the thermal properties of the bulk.

Crucial in our analysis will be the calculation of mean-square fluctuations. As we will see later on, these quantities are obtained after averaging the corresponding correlation functions and provide all the information about the relevance of both boundary and nonequilibrium effects. In the absence of external gradients they reduce to the well-known equilibrium result which follows from the study of fluctuations of thermodynamical variables. These quantities will therefore constitute the nonequilibrium

version of the thermodynamical result.

The paper is organized as follows. In Sec. II we discuss the stationary solutions for diffusion processes with Neumann-Dirichlet boundary conditions in the presence of external gradients. The nature of the steady states depends on Nusselt numbers, the steady profiles also being linear. In Sec. III and IV we shall be concerned with the explicit calculation of the correlation functions for two particular diffusion processes, namely heat conduction and mass diffusion. In both cases, we consider that in addition to the stochastic bulk sources, used when dealing with fluctuations away from equilibrium, there exists stochastic surface sources which also satisfy fluctuation-dissipation theorems. The correlation functions are then influenced by both bulk and surface sources of noise. It is interesting to realize that in the absence of external gradients the surface terms are not present. From the general expression of the correlation functions we then calculate averaged correlations. These quantities satisfy scaling laws since they only depend on reduced variables and dimensionless functions of the Nusselt numbers. We analyze in detail the correlations in some particular limiting cases. In Sec. V we stress our main results.

### II. STATIONARY STATES FOR NEUMANN-DIRICHLET BOUNDARY CONDITIONS

In this section we will analyze the nature of the stationary states for the most general boundary conditions, namely the Neumann-Dirichlet ones. As a first example we will consider a fluid between two parallel plates located at  $y=0$  and  $L$ , which are in contact with thermal reservoirs at temperatures  $T_0$  and  $T_L$ , respectively. In the case in which the product of the Reynolds and Prandtl numbers is very small, the convective term of the temperature evolution equation can be neglected, therefore that equation simply reads

$$\frac{\partial T(\mathbf{r}, t)}{\partial t} = \alpha \nabla^2 T(\mathbf{r}, t), \quad (2.1)$$

where  $T(\mathbf{r}, t)$  is the temperature and  $\alpha$  the thermal diffusivity. As a consequence, thermal modes are not coupled to viscous modes and can be treated independently.

The boundary conditions come from the fact that the heat fluxes given through Fourier law and the Newton law of cooling<sup>5</sup> should be equal at the surfaces. We then obtain

$$\lambda \hat{\mathbf{n}} \cdot \nabla T = \epsilon_0 (T - T_0) \quad \text{at } y = 0, \quad (2.2)$$

$$\lambda \hat{\mathbf{n}} \cdot \nabla T = \epsilon_L (T - T_L) \quad \text{at } y = L, \quad (2.3)$$

Here  $\lambda$  is the heat conductivity of the fluid,  $\hat{\mathbf{n}}$  the unit vector normal to the boundaries, pointing inward to the system, and  $\epsilon_0$  and  $\epsilon_L$  heat transfer coefficients. The particular cases  $\epsilon_0, \epsilon_L \rightarrow \infty$  and 0 will correspond to perfectly conducting and perfectly insulating boundaries, respectively. Both limits can be also reproduced if one introduces the Nusselt numbers

$$N_0 \equiv \frac{\epsilon_0 L}{\lambda}, \quad N_L \equiv \frac{\epsilon_L L}{\lambda}. \quad (2.4)$$

Then perfectly conducting boundaries will correspond to the limits  $N_0, N_L \rightarrow \infty$ , whereas perfectly insulating boundaries to  $N_0, N_L \rightarrow 0$ .

The diffusion equation (2.1) can be solved using the general boundary conditions (2.2) and (2.3) and the definitions (2.4). One arrives at

$$T_s(\mathbf{r}) = \frac{N_0 N_L}{N_0 + N_L + N_0 N_L} \mathbf{r} \cdot \nabla T + \frac{N_0 T_0 + N_L T_L + N_0 N_L T_0}{N_0 + N_L + N_0 N_L}, \quad (2.5)$$

where the external the external gradient is  $\nabla T = \hat{\mathbf{y}}(T_L - T_0)/L$ ,  $\hat{\mathbf{y}}$  being the unit vector along the  $y$  coordinate. The following cases will be under consideration.

(i) Both Nusselt numbers are equal to  $N$ . In this case (2.5) becomes

$$T_s(\mathbf{r}) = \frac{N}{2+N} \mathbf{r} \cdot \nabla T + \frac{(1+N)T_0 + T_L}{2+N}. \quad (2.6)$$

Therefore the temperature gradient in the system does not coincide with the imposed external gradient. One then arrives at the relation

$$\nabla T_s = \frac{N}{2+N} \nabla T, \quad (2.7)$$

showing that the temperature gradient clearly depends on the Nusselt number. If the plates are perfectly conducting ( $N_0, N_L \rightarrow \infty$ ), the stationary temperature reduces to

$$T_s(\mathbf{r}) = \mathbf{r} \cdot \nabla T + T_0, \quad (2.8)$$

which corresponds to the reference state that is habitual taken as the reference state in many analyses of nonequilibrium fluctuations. In the case in which both plates are perfectly insulating ( $N_0, N_L \rightarrow 0$ ), (2.5) yields the homogeneous temperature

$$T_s = (T_0 + T_L)/2. \quad (2.9)$$

(ii) The Nusselt numbers are very different (say  $N_0 \ll N_L$ , with  $N_0 \ll 1$  and  $N_L \gg 1$ ). The stationary solution gives, in this case,

$$T_s(\mathbf{r}) = N_0 \mathbf{r} \cdot \nabla T + N_0 T_0 + T_L, \quad (2.10)$$

which in the extreme situation  $N_0 \rightarrow 0$  tends to the homogeneous temperature profile

$$T_s = T_L. \quad (2.11)$$

According to the former analysis we can conclude that transport coefficients are modified by the presence of the boundaries. In fact, we can define the overall heat conductivity  $\tilde{\lambda}$  through

$$\mathbf{J} \equiv \tilde{\lambda} \nabla T, \quad (2.12)$$

where  $\mathbf{J}$  is the heat flow. In view of (2.5) one then obtains

$$\tilde{\lambda} = \frac{N_0 N_L}{N_0 + N_L + N_0 N_L} \lambda. \quad (2.13)$$

This expression indicates that the system behaves as if heat conduction took place between perfectly conducting boundaries but with a different transport coefficient. Therefore  $\tilde{\lambda}$  plays the role of an effective or renormalized heat conductivity.

To end this section we will discuss the stationary solutions in the case of mass diffusion. The problem could be formulated in the following way. Let us assume the diffusion of a contaminant in a fluid between two parallel plates. Both plates are chemically active in the sense that chemical reactions producing or absorbing the contaminant take place. Our analysis could also be applied to describe a situation in which adsorption phenomena may occur at the boundaries. The basic equations are quite similar to the ones defining the heat conduction problem introduced above. In fact, when the Péclet number is very small, the number density  $\mathcal{N}(\mathbf{r}, t)$  evolves according to the diffusion equation

$$\frac{\partial \mathcal{N}(\mathbf{r}, t)}{\partial t} = D \nabla^2 \mathcal{N}(\mathbf{r}, t), \quad (2.14)$$

where  $D$  is the diffusion coefficient. On the other hand, the boundary conditions are now<sup>6</sup>

$$\hat{\mathbf{n}} \cdot \nabla \mathcal{N} = \hat{N}_{0,L} \mathcal{N} \quad \text{at } y = 0, L. \quad (2.15)$$

These equations come from the fact that diffusion and reaction fluxes counterbalance each other at the boundary. Now the Nusselt numbers are defined as

$$\hat{N}_{0,L} \equiv \frac{\kappa_{0,L} L}{D}, \quad (2.16)$$

where  $\kappa_{0,L}$  are the reaction rates at  $y = 0, L$ , respectively. Therefore the limit  $\hat{N}_0, \hat{N}_L \rightarrow 0$  corresponds to the case in which chemical reactions at the boundaries are very slow, whereas very fast reactions will take place for  $\hat{N}_0, \hat{N}_L \rightarrow \infty$ . Because of the similarity to the former case, the stationary solution obtained in (2.5) will now be formally the same, taking into account the characteristic variables of this second problem.

### III. CORRELATION FUNCTIONS IN THE CASE OF HEAT CONDUCTION

Our purpose in this section is to study the propagation of thermal fluctuations in the system. In accordance with the Onsager regression hypothesis, fluctuation evolution equations are precisely the differential equations of nonequilibrium thermodynamics. Their stochastic character is due to the presence of random currents satisfying appropriate fluctuation-dissipation theorems. In our case, we are only considering thermal modes, therefore the corresponding stochastic differential equation is

$$\frac{\partial \delta T(\mathbf{r}, t)}{\partial t} = \alpha \nabla^2 \delta T(\mathbf{r}, t) - (\rho c)^{-1} \nabla \cdot \mathbf{J}^R, \quad (3.1)$$

where  $\rho$  is the density,  $c$  the specific heat, and  $\mathbf{J}^R$  the stochastic current. To solve for  $\delta T$  we must specify the boundary conditions. In view of (2.2) and (2.3) one has<sup>7,8</sup>

$$-\lambda \hat{\mathbf{n}} \cdot \nabla \delta T = -\epsilon_0 \delta T + J_0 \quad \text{at } y=0, \quad (3.2)$$

$$-\lambda \hat{\mathbf{n}} \cdot \nabla \delta T = -\epsilon_L \delta T + J_L \quad \text{at } y=L, \quad (3.3)$$

where we have assumed that the temperatures of the baths do not fluctuate. In (3.2) and (3.3)  $J_0$  and  $J_L$  act as stochastic currents at the boundaries; hence both equations become stochastic boundary conditions.

To analyze the fluctuations it is convenient to Fourier transform (3.1) in time and in the coordinates  $x$  and  $z$ . Then, one may define the following boundary-value problem:

$$(i\bar{\omega} + \alpha \partial_y^2) \delta T = (\rho c)^{-1} \nabla \cdot \mathbf{J}^R, \quad y \in (0, L) \quad (3.4)$$

$$(-\lambda \partial_y + \epsilon_0) \delta T = J_0, \quad y = 0 \quad (3.5)$$

$$(\lambda \partial_y + \epsilon_L) \delta T = J_L, \quad y = L \quad (3.6)$$

where use has been made of the definition  $\bar{\omega} \equiv \omega + i\alpha k_{\parallel}^2$ , with  $\mathbf{k}_{\parallel} = (k_x, k_z)$ .

The former boundary value problem defines the Green problem for Neumann-Dirichlet boundary conditions.<sup>9</sup> The Green function  $G(y, y'; \bar{\omega})$  is the solution of the equation

$$(i\bar{\omega} + \alpha \partial_y^2) G(y, y'; \bar{\omega}) = \delta(y - y'), \quad y \in (0, L) \quad (3.7)$$

and is subject to boundary conditions similar to (3.5) and (3.6)

$$(-\lambda \partial_y + \epsilon_0) G(y, y'; \bar{\omega}) = 0, \quad y = 0 \quad (3.8)$$

$$(\lambda \partial_y + \epsilon_L) G(y, y'; \bar{\omega}) = 0, \quad y = L. \quad (3.9)$$

Moreover, the adjoint Green function  $\bar{G}$  satisfies the time-reversed equation

$$(-i\bar{\omega}^* + \alpha \partial_y^2) \bar{G}(y, y'; \bar{\omega}) = \delta(y - y'), \quad y \in (0, L) \quad (3.10)$$

where the symbol  $*$  denotes complex conjugation. Hence the reciprocity relation consistent with (3.7) and (3.10) reads

$$\bar{G}^*(y, y'; \bar{\omega}) = G(y', y; \bar{\omega}). \quad (3.11)$$

The solution of (3.7)–(3.9) is found to be

$$G(y, y'; \bar{\omega}) = -\frac{\bar{\gamma}}{\alpha} \frac{K_2^0(y_<) K_2^L(L - y_>)}{K_2^L(L) + (\lambda/\bar{\gamma} \epsilon_0) K_1^L(L)}, \quad (3.12)$$

where  $y_> \equiv \max\{y, y'\}$  and  $y_< \equiv \min\{y, y'\}$ . Moreover, we have also used the definitions

$$\bar{\gamma} \equiv (i\alpha/\bar{\omega})^{1/2}, \quad (3.13)$$

$$K_1^{0,L}(x) \equiv \cosh(x/\bar{\gamma}) + (\lambda/\bar{\gamma} \epsilon_{0,L}) \sinh(x/\bar{\gamma}), \quad (3.14)$$

$$K_2^{0,L}(x) \equiv \sinh(x/\bar{\gamma}) + (\lambda/\bar{\gamma} \epsilon_{0,L}) \cosh(x/\bar{\gamma}). \quad (3.15)$$

Notice that the quantity  $\bar{\gamma}$  can be interpreted as a penetration depth for thermal fluctuations, consequently  $\bar{\gamma} \epsilon_{0,L} / \lambda$  is the Nusselt number related to that length.

The formal solution for the temperature fluctuations follows from the Green theorem and is given by

$$\delta T(y, \mathbf{k}_{\parallel}; \omega) = \frac{\alpha}{\lambda} \left[ \int_0^L d\tau G(y, \tau; \bar{\omega}) \nabla_{\tau} \cdot \mathbf{J}^R(\tau, \mathbf{k}_{\parallel}; \omega) - G(y, L; \bar{\omega}) J_L(\mathbf{k}_{\parallel}; \omega) - G(y, 0; \bar{\omega}) J_0(\mathbf{k}_{\parallel}; \omega) \right]. \quad (3.16)$$

This expression clearly exhibits the different contributions due to the surface  $J_{0,L}$  and bulk  $\mathbf{J}^R$  sources of noise. Such stochastic currents are assumed to satisfy the following fluctuation-dissipation theorems:

$$\begin{aligned} \langle J_i^R(y, \mathbf{k}_{\parallel}; \omega) J_j^R(y', \mathbf{k}'_{\parallel}; \omega') \rangle \\ = 2(2\pi)^3 k_B \lambda T_s^2(y) \delta(y - y') \delta(\omega + \omega') \delta(\mathbf{k}_{\parallel} + \mathbf{k}'_{\parallel}) \delta_{ij}, \end{aligned} \quad (3.17)$$

$$\begin{aligned} \langle J_0^R(\mathbf{k}_{\parallel}; \omega) J_0^R(\mathbf{k}'_{\parallel}; \omega') \rangle \\ = 2(2\pi)^3 k_B \sigma_0 T_s^2(0) \delta(\omega + \omega') \delta(\mathbf{k}_{\parallel} + \mathbf{k}'_{\parallel}), \end{aligned} \quad (3.18)$$

$$\begin{aligned} \langle J_L^R(\mathbf{k}_{\parallel}; \omega) J_L^R(\mathbf{k}'_{\parallel}; \omega') \rangle \\ = 2(2\pi)^3 k_B \sigma_L T_s^2(L) \delta(\omega + \omega') \delta(\mathbf{k}_{\parallel} + \mathbf{k}'_{\parallel}), \end{aligned} \quad (3.19)$$

where the quantities  $\sigma_0$  and  $\sigma_L$  will be specified later on. In addition to these theorems, the random currents are chosen in such a way that their cross correlations vanish since surface  $J_{0,L}$  and bulk  $\mathbf{J}^R$  sources of noise are assumed to be statistically independent. The temperature correlation function then follows from the formal solution (3.16) by means of reiterative application of the Green theorem. Taking into account the fluctuation-dissipation theorems (3.17)–(3.19) one obtains

$$\begin{aligned}
\langle \delta T(y, \mathbf{k}_{\parallel}; \omega) \delta T(y', \mathbf{k}'_{\parallel}; \omega') \rangle &= 2(2\pi)^3 k_B \frac{\alpha}{\lambda} \delta(\omega + \omega') \delta(\mathbf{k}_{\parallel} + \mathbf{k}'_{\parallel}) \\
&\times \left[ -\frac{1}{2} [G(y, y'; \bar{\omega}) T_s^2(y') + G(y', y; \bar{\omega}') T_s^2(y)] \right. \\
&\quad + i \frac{\alpha}{4\omega} [\partial_{\tau}^2 T_s^2(\tau)] [G(y, y'; \bar{\omega}) - G(y', y; \bar{\omega}')] \\
&\quad - \frac{\alpha}{2} \{ [\partial_{\tau} T_s^2(\tau)] G(y, \tau; \bar{\omega}) G(y', \tau; \bar{\omega}') \}_{\tau=0}^{\tau=L} \\
&\quad \left. + \frac{\alpha}{\lambda} [(\sigma_{\tau} - \epsilon_{\tau}) T_s^2(\tau) G(y, \tau; \bar{\omega}) G(y', \tau; \bar{\omega}') ]_{\tau=0, L} \right]. \quad (3.20)
\end{aligned}$$

The last term in this expression must vanish due to the time-reversal symmetry requirement of the correlation function for a system at equilibrium, therefore we have to impose  $\sigma_{0,L} = \epsilon_{0,L}$ .<sup>7,8,10</sup> Expression (3.20) constitutes the explicit expression of the correlation function. From it we conclude that the temperature correlation function depends on the external gradient and on the Nusselt numbers.

To analyze the nonequilibrium and finite-size contributions we have defined the following quantity:

$$\langle (\delta T)^2 \rangle \equiv \frac{1}{(2\pi L)^2} \int_0^L dy dy' \int_{-\infty}^{\infty} d\omega d\omega' \langle \delta T(y, \mathbf{k}_{\parallel} = \mathbf{0}; \omega) \delta T(y', \mathbf{k}'_{\parallel} = \mathbf{0}; \omega') \rangle, \quad (3.21)$$

which is the average of the equal-time correlation function for the case  $\mathbf{k}_{\parallel} = \mathbf{0}$ . Its corresponding expression for wave vectors different from zero has been analyzed in detail in the Appendix. The main conclusion is that when  $k_{\parallel} L < 1$ , the consideration of nonvanishing wave vectors only introduces small corrections in the correlation function (3.21).

The main usefulness of  $\langle (\delta T)^2 \rangle$  comes from the fact that it provides information about the averaged behavior of the system in a clear and scaling way, analogous to its equilibrium counterpart. Inserting (3.20), with  $\mathbf{k}_{\parallel} = \mathbf{k}'_{\parallel} = \mathbf{0}$ , into (3.21) one arrives at

$$\langle (\delta T)^2 \rangle = \frac{k_B T_0^2}{\rho c L} [1 + A(N_0, N_L) \beta + B(N_0, N_L) \beta^2], \quad (3.22)$$

where the quantity  $k_B T_0^2 / \rho c L$  corresponds to the averaged equilibrium temperature correlation function  $\langle (\delta T)^2 \rangle_{\text{eq}}$ , which coincides with the thermodynamical result.<sup>11</sup> This limiting value holds when the nonequilibrium parameter or reduced temperature

$$\beta \equiv \frac{T_L - T_0}{T_0} \quad (3.23)$$

vanishes, irrespective of the values of  $N_0$  and  $N_L$ . This fact must be emphasized, since it indicates that at equilib-

rium the presence of the imperfectly conducting boundaries only affects the spectrum of the correlation function, but not its averaged intensity. Clearly, this behavior fails out of equilibrium, due to the lack of translational invariance produced by the external gradients. On the other hand, the dimensionless functions  $A(N_0, N_L)$  and  $B(N_0, N_L)$ , introduced in (3.22), are defined by

$$A(N_0, N_L) = a \left[ 1 + \frac{2}{N_0} + \frac{2}{\pi} (I_0 - I_L) \right], \quad (3.24)$$

$$\begin{aligned}
B(N_0, N_L) = a^2 \left[ \frac{2}{3} + \frac{1}{N_0^2} + \frac{1}{N_0} + a \left[ \frac{1}{N_0 N_L} - \frac{1}{4} \right] \right. \\
\left. + \frac{2}{\pi N_0} (I_0 - I_L - N_0 I_L) \right]. \quad (3.25)
\end{aligned}$$

Here  $a$  is the combination of the Nusselt numbers

$$a = \frac{N_0 N_L}{N_0 + N_L + N_0 N_L}, \quad (3.26)$$

which is simply the ratio between the overall heat conductivity and the actual heat conductivity of the fluid:  $\tilde{\lambda} / \lambda$ . Moreover,  $I_0$  and  $I_L$  are functions of the Nusselt numbers defined by the integrals

$$I_{\tau} \equiv \frac{1}{N_{\tau}^2} \int_0^{\infty} dx \left| \frac{\eta^{-1} [1 - \cosh(\eta) - N_{\tau}^{-1} \eta \sinh(\eta)]}{\sinh(\eta) + (N_0^{-1} + N_L^{-1}) \eta \cosh(\eta) + N_0^{-1} N_L^{-1} \eta^2 \sinh(\eta)} \right|^2, \quad (3.27)$$

where  $\tau = 0, L$  and  $\eta = (x/i)^{1/2}$ .

Expression (3.22) constitutes our main result. It has an interesting interpretation, since it enables us to clearly identify the roles on the correlation function of the nonequilibrium and boundary effects. The former enter

through  $\beta$ , whereas the latter are related to the functions  $A$  and  $B$ .

Now we will proceed to study the averaged temperature correlation for the cases introduced in Sec. II.

(i) Both Nusselt numbers are equal to  $N$ . In this case

$I_0 = I_L$  and  $A(N) = 1$ , whereas  $B$  remains Nusselt dependent. For perfectly conducting and perfectly insulating boundaries one has, respectively,

$$B(N \gg 1) = \frac{5}{12}, \quad (3.28)$$

$$B(N \ll 1) = \frac{1}{4} - \frac{1}{2\pi} N^2 I_0 \approx \frac{1}{4}. \quad (3.29)$$

This second limit has been computed numerically and the value of  $NI_0$  has been represented in Fig. 1 as a function of  $N$ . Consequently, the averaged temperature correlation is given in both limits by

$$\langle (\delta T)^2 \rangle_{N \gg 1} = \langle (\delta T)^2 \rangle_{\text{eq}} (1 + \beta + \frac{5}{12} \beta^2), \quad (3.30)$$

$$\langle (\delta T)^2 \rangle_{N \ll 1} = \langle (\delta T)^2 \rangle_{\text{eq}} (1 + \beta + \frac{1}{4} \beta^2), \quad (3.31)$$

Therefore the difference between both correlations, normalized to the equilibrium value, will be equal to  $\beta^2/6$ . In Fig. 2 we have plotted the quantity

$$\frac{\mathcal{F}(N)}{\beta^2} \equiv \frac{\langle (\delta T)^2 \rangle_{N \gg 1} - \langle (\delta T)^2 \rangle}{\beta^2 \langle (\delta T)^2 \rangle_{\text{eq}}} = \frac{5}{12} - B(N) \quad (3.32)$$

versus the Nusselt number. Such a function gives us global information about the influence of the boundary conditions on the correlation function. In fact, from (3.28) and (3.29) one has

$$\mathcal{F}(N \gg 1) = 0, \quad (3.33)$$

$$\mathcal{F}(N \ll 1) = \frac{1}{6} \beta^2. \quad (3.34)$$

From our analysis we then conclude that the correction introduced by the presence of identical walls in the system will be maximum for  $N \ll 1$  and its value is  $\beta^2/6$ .

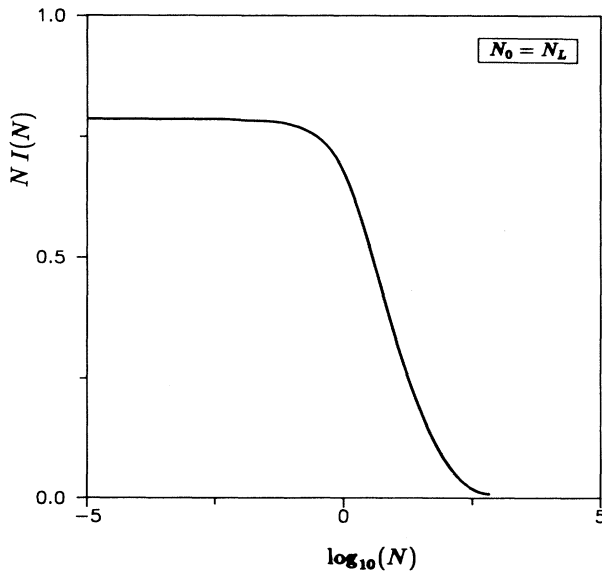


FIG. 1. We represent the product  $NI(N)$  as a function of the  $\log_{10}$  of the Nusselt number, for  $N_0 = N_L \equiv N$ . In this case  $I_0 = I_L \equiv I$ .

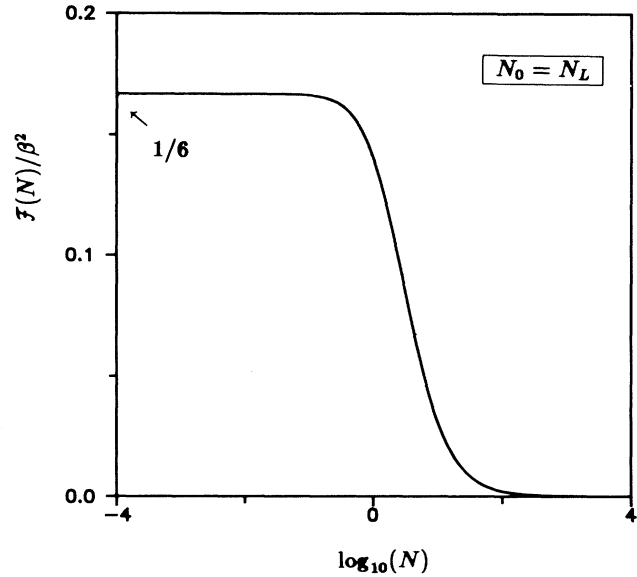


FIG. 2. The function  $\mathcal{F}(N)/\beta^2$ , accounting for the influence of the finite size of the system in the correlation function, is plotted vs  $\log_{10}(N)$ . In this case  $N_0 = N_L \equiv N$ .

On the other hand, the limiting case (3.33) corresponds to the case treated in Refs. 12 and 13, using perfectly conducting boundaries.

(ii) The Nusselt numbers are very different. First of all we will analyze the case  $N_0 \ll 1$ ,  $N_L \gg 1$ . In this case  $a \simeq N_0$  and  $I_0 \gg I_L$ . We then obtain

$$A \simeq N_0 \left[ \frac{2}{N_0} + \frac{2}{\pi} I_0 \right] \simeq 2, \quad (3.35)$$

$$B \simeq N_0^2 \left[ \frac{1}{N_0^2} + \frac{2}{\pi N_0} I_0 \right] \simeq 1. \quad (3.36)$$

In these expressions use has been made of the fact that the quantity  $N_0 I_0$  is negligible, which is illustrated in Fig. 3. As in the former case, we can now define the quantity

$$\mathcal{G}(N_\tau, N_\nu) \equiv \frac{\langle (\delta T)^2 \rangle_{N_\tau \ll 1, N_\nu \gg 1} - \langle (\delta T)^2 \rangle_{N_\tau, N_\nu \gg 1}}{\langle (\delta T)^2 \rangle_{\text{eq}}}, \quad (3.37)$$

$\tau \neq \nu, \tau, \nu = 0, L$

accounting for the finite-size effects on the correlation function due to the presence of an insulating boundary at  $y = \tau$ . In view of (3.30), (3.35), and (3.36) one obtains

$$\mathcal{G}(N_0, N_L) \simeq \beta + \frac{7}{12} \beta^2. \quad (3.38)$$

This quantity contains a linear term in the reduced temperature  $\beta$  and therefore the correction to the correlation function due to the finite size of the system may be larger than in the former case. One may also discuss the opposite case in which  $N_0 \gg 1$  and  $N_L \ll 1$ . This implies that  $a \simeq N_L$  and  $I_0 \ll I_L$ . Hence  $A \simeq N_L$  and  $B \simeq N_L^2$ . Consequently,

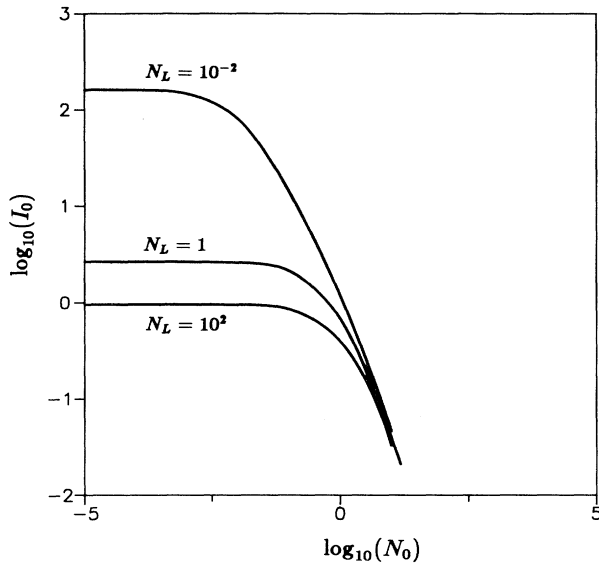


FIG. 3. Typical behavior of the integral  $I_0(N_0, N_L)$  as a function of  $N_0$ , for different values of  $N_L$ . The integral  $I_L$  behaves similarly.

$$\mathcal{G}(N_L, N_0) \simeq -\beta - \frac{5}{12}\beta^2, \tag{3.39}$$

which also exhibits a linear term in  $\beta$ . Notice that the function  $\mathcal{G}(N_L, N_0)$  is not a symmetric function of its arguments due to the presence, in the general expression (3.22), of a quadratic term in the reduced temperature. It is worth pointing out that the functions  $\mathcal{G}(N_\tau, N_\nu)$  compare the averaged correlations corresponding to two different stationary states, namely (2.8) and  $T_s = T_\nu$ ,

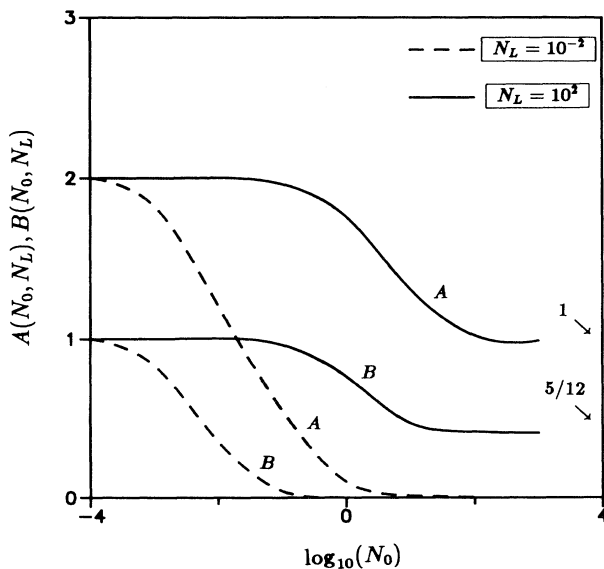


FIG. 4. The dimensionless functions  $A(N_0, N_L)$  and  $B(N_0, N_L)$  have been plotted vs  $N_0$  for  $N_L = 10^2$  and  $10^{-2}$ .

$\nu=0, L$ . For this reason they become linear in  $\beta$ .

Finally, to make it clear that the finite-size effects enter the mean-square fluctuation mainly due to the modification of the stationary state with respect to (2.8), we have computed that quantity in the case of “stick” boundary conditions for  $\delta T$ , but assuming (2.5) instead of (2.8). This is, of course, a nonconsistent approach, but it allows us to clearly illustrate the relevance of the modified reference state. Using the expression for the temperature correlation function<sup>7,12,13</sup> and taking the average (3.21), one obtains an expression similar to (3.22) but with

$$A'(N_0, N_L) = a \left[ 1 + \frac{2}{N_0} \right], \tag{3.40}$$

$$B'(N_0, N_L) = a^2 \left[ \frac{5}{12} + \frac{1}{N_0} + \frac{1}{N_0^2} \right]. \tag{3.41}$$

These functions differ from the expressions for  $A(N_0, N_L)$  and  $B(N_0, N_L)$ , given by (3.24) and (3.25), in some terms which are very small for  $N \gg 1$  and  $N \ll 1$ . For intermediate Nusselt numbers, however, these terms become relevant. In Fig. 4 we have represented the functions  $A(N_0, N_L)$  and  $B(N_0, N_L)$  appearing in the general expressions (3.24) and (3.25) for  $N_L = 10^2$  and  $N_L = 10^{-2}$ .

#### IV. CORRELATION FUNCTIONS IN THE CASE OF MASS DIFFUSION

The formalism developed in Sec. III can be extended to the case of mass diffusion. Due to the similarity with the case of heat diffusion, we do not repeat here the whole analysis but only indicate its main steps. We can also formulate the corresponding boundary value problem, as we did in (3.4)–(3.6) and solve for the number density fluctuations which depend also on the Green function and on the stochastic currents at both boundaries. To compute the correlation function, we should keep in mind the different nature of this second problem. In fact, we must now formulate the fluctuation-dissipation theorems

$$\begin{aligned} \langle \hat{J}_j^R(y, \mathbf{k}_\parallel; \omega) \hat{J}_l^R(y', \mathbf{k}'_\parallel; \omega') \rangle \\ = 2(2\pi)^3 D \mathcal{N}_s(y) \delta(y - y') \delta(\omega + \omega') \delta(\mathbf{k}_\parallel + \mathbf{k}'_\parallel) \delta_{jl}, \end{aligned} \tag{4.1}$$

$$\begin{aligned} \langle \hat{J}_0^R(\mathbf{k}_\parallel; \omega) \hat{J}_0^R(\mathbf{k}'_\parallel; \omega') \rangle \\ = 2(2\pi)^3 \kappa_0 \mathcal{N}_s(0) \delta(\omega + \omega') \delta(\mathbf{k}_\parallel + \mathbf{k}'_\parallel), \end{aligned} \tag{4.2}$$

$$\begin{aligned} \langle \hat{J}_L^R(\mathbf{k}_\parallel; \omega) \hat{J}_L^R(\mathbf{k}'_\parallel; \omega') \rangle \\ = 2(2\pi)^3 \kappa_L \mathcal{N}_s(L) \delta(\omega + \omega') \delta(\mathbf{k}_\parallel + \mathbf{k}'_\parallel), \end{aligned} \tag{4.3}$$

where  $\tilde{\omega} \equiv \omega + iDk_\parallel^2$ , and  $\hat{J}^R$  and  $\hat{J}_{0,L}^R$  are the stochastic currents corresponding to the diffusion and chemical reaction processes. The form of (4.2) and (4.3) also follows to guarantee the time-reversal symmetry of the number-density correlation function for a system at equilibrium.

The formal solution for the number density together with the fluctuation-dissipation theorems (4.1)–(4.3) lead to the correlation function

$$\begin{aligned} \langle \delta\mathcal{N}(y, \mathbf{k}_\parallel; \omega) \delta\mathcal{N}(y', \mathbf{k}'_\parallel; \omega') \rangle &= 2(2\pi)^3 \delta(\omega + \omega') \delta(\mathbf{k}_\parallel + \mathbf{k}'_\parallel) \\ &\times \left[ -\frac{1}{2} [G(y, y'; \bar{\omega}) \mathcal{N}_s(y') + G(y', y; \bar{\omega}') \mathcal{N}_s(y)] \right. \\ &\quad \left. - \frac{D}{2} \{ [\partial_\tau \mathcal{N}_s(\tau)] G(y, \tau; \bar{\omega}) G(y', \tau; \bar{\omega}') \}_{\tau=0}^{\tau=L} \right], \end{aligned} \quad (4.4)$$

where the Green function is analogous to the one given in (3.12). The first term on the right-hand side of (4.4) comes from the bulk noise, whereas the second is due to surface noise. Due to the linear character of the stationary profile, the surface term in (4.4) will be proportional to the density gradient  $\nabla \mathcal{N}_s$ . We will now compute the quantity  $\langle (\delta\mathcal{N})^2 \rangle$ , defined through an expression similar to (3.21). One arrives at

$$\langle (\delta\mathcal{N})^2 \rangle = \langle (\delta\mathcal{N})^2 \rangle_{\text{eq}} [1 + \hat{A}(\hat{N}_0, \hat{N}_L) \hat{\beta}] \quad (4.5)$$

in which  $\langle (\delta\mathcal{N})^2 \rangle_{\text{eq}} = n_0/L$ .<sup>11</sup> Here the nonequilibrium parameter  $\hat{\beta}$  is also the reduced number density

$$\hat{\beta} \equiv \frac{\mathcal{N}_L - \mathcal{N}_0}{\mathcal{N}_0} \quad (4.6)$$

and  $\hat{A}(\hat{N}_0, \hat{N}_L)$  is the dimensionless function

$$\hat{A}(\hat{N}_0, \hat{N}_L) = \hat{a} \left[ \frac{1}{2} + \frac{1}{\hat{N}_0} + \frac{\hat{I}_0 - \hat{I}_L}{\pi} \right], \quad (4.7)$$

where  $\hat{I}_0$ ,  $\hat{I}_L$ , and  $\hat{a}$  are defined as they were in (3.26) and (3.27). It is worth pointing out that in this case the averaged correlation is linear in the reduced concentration  $\hat{\beta}$ . When both Nusselt numbers are equal ( $\hat{N}_0 = \hat{N}_L \equiv \hat{N}$ ), one has  $\hat{a} = \hat{N}/(2 + \hat{N})$ ,  $\hat{I}_0 = \hat{I}_L$ , and

$$\hat{A}(\hat{N}_0, \hat{N}_L) = \frac{1}{2}; \quad (4.8)$$

consequently  $\langle (\delta\mathcal{N})^2 \rangle$  does not depend on the Nusselt number  $\hat{N}$ . On the contrary, when the Nusselt numbers are very different we arrive at

$$\hat{G}(\hat{N}_0, \hat{N}_L) \simeq \frac{1}{2} \hat{\beta}, \quad (4.9)$$

$$\hat{G}(\hat{N}_L, \hat{N}_0) \simeq -\frac{1}{2} \hat{\beta}, \quad (4.10)$$

where  $\hat{G}(\hat{N}_L, \hat{N}_0)$  is defined as it was in (3.37). Notice that in this case the relevance of the finite-size effects is directly related to the different nature of the boundaries.

## V. DISCUSSION

In the light of the results obtained in the preceding sections the following comments are in order.

We have computed and analyzed the correlation functions in systems away from equilibrium, due to the presence of external gradients. Instead of assuming "stick" boundary conditions for the hydrodynamic and fluctuating fields, as usually done in previous analyses, we have considered general Neumann-Dirichlet boundary conditions. These boundary conditions introduce Nusselt numbers which are also present in the final form of the correlation functions. This fact allows us to include the

nature of the surfaces and the size of the system in the whole analysis. We conclude that the boundary effects will be important for  $N \ll 1$ , whereas bulk noise dominates for  $N \gg 1$ .

We have analyzed diffusion processes, in particular thermal conduction and mass diffusion. Both problems are quite similar, and the associated averaged correlations depend on the reduced temperature and concentration, respectively. For thermal modes one obtains corrections due to the presence of the boundaries which are quadratic in the reduced temperature, in the case in which the Nusselt numbers relative to the boundaries are equal, whereas for different Nusselt numbers the corrections become linear. Therefore finite-size effects are more important when the boundaries are different or, in other words, for very different Nusselt numbers. Essentially, this feature is due to the modification of the stationary temperature profile with respect to the case  $N_0, N_L \gg 1$ . Notice also that the Nusselt number defined through (2.4) or (2.16) can be interpreted as the ratio between the size of the system and the effective thickness  $\lambda/\epsilon$ . This would explain the saturation effect of the function  $\mathcal{F}(\mathcal{N})$ , which occurs for  $N \ll 1$ , as showed in Fig. 2.

In experiments with fluids under large temperature gradients at room temperature,  $\nabla T$  is typically of the order  $10^2 \text{K/cm}$ ,  $L \simeq 10^{-1} \text{cm}$ , and  $T_0 \simeq 10^2 \text{K}$ , therefore  $\beta \simeq 10^{-1}$ . This introduces small corrections in case (i), whereas the corrections in case (ii) are of the order of 10%. Moreover, the smaller the reference temperature, the larger the correction.

Our formalism may be applied to a wide variety of real situations. For instance, we could study the case in which thermal contacts are not perfect due to the presence of impurities or small skins of poor conductors. To be precise, when the fluid is water or toluene and there exists a layer of air or oxide between the fluid and the thermal reservoir, one may use the equality between the fluxes

$$-\lambda \frac{\partial T}{\partial y} = \frac{\lambda'}{d} (T - T_B), \quad (5.1)$$

where  $\lambda'$  is the heat conductivity of the layer and  $d$  its thickness. According to (2.2) and (2.4) the heat transfer coefficient is  $\lambda'/d$  and the Nusselt number is

$$N = \frac{\lambda' L}{\lambda d}, \quad (5.2)$$

therefore boundary effects depend on the ratio between both conductivities and the aspect ratio.

Numerical simulations of the temperature and concentration correlation functions<sup>14</sup> or light-scattering experiments<sup>3,15</sup> could be performed to check the validity of our

results. In particular it is possible to compute the structure factor  $S(k_{\perp}, t=0)$  for wave vectors perpendicular to the plates,  $k_{\perp} = 2\pi n/L$ ,  $n \in \mathbb{Z}$ . We have shown that this quantity is quite insensitive to variations of  $n$ . Therefore the intensity  $I$  under the Rayleigh peak

$$I \simeq S(n, t=0) \simeq S(n=0, t=0) \simeq \langle (\delta T)^2 \rangle \quad (5.3)$$

is basically proportional to  $\langle (\delta T)^2 \rangle$ , which follows from (3.22) and in principle could be measured.

Our analysis could also be extended to more general and interesting situations in which viscous or sound modes are present. For instance, a similar treatment could be carried out to arrive at scaling laws for the density correlation function following the expression given by Satten and Ronis in Ref. 4. We ultimately predict

$$\langle (\delta T)^2 \rangle_{k_{\parallel}} \equiv \frac{1}{(2\pi L)^2} \int_0^L dy dy' \int_{-\infty}^{\infty} d\omega d\omega' \langle \delta T(y, \mathbf{k}_{\parallel}; \omega) \delta T(y', \mathbf{k}'_{\parallel}; \omega') \rangle \quad (A1)$$

Substituting (3.20) into expression (A1) yields

$$\langle (\delta T)^2 \rangle_{k_{\parallel}} = \frac{k_B T_0^2}{\rho c L} [1 + \tilde{A}(N_0, N_L; \xi) \beta + \tilde{B}(N_0, N_L; \xi) \beta^2], \quad (A2)$$

where use has been made of the definitions

$$\tilde{A}(N_0, N_L; \xi) \equiv a \left[ 1 + \frac{2}{N_0} + \frac{2}{\pi} (\tilde{I}_0 - \tilde{I}_L) \right], \quad (A3)$$

$$\tilde{B}(N_0, N_L; \xi) \equiv a^2 \left[ \frac{1}{3} + \frac{1}{N_0^2} + \frac{1}{N_0} + \frac{2}{\pi N_0} (\tilde{I}_0 - \tilde{I}_L - N_0 \tilde{I}_L) \right] + \tilde{H}(N_0, N_L; \xi), \quad (A4)$$

the function  $\tilde{H}$  being

$$\tilde{H}(N_0, N_L; \xi) = a^2 \left[ \frac{1}{\xi^2} - \frac{1}{\xi^3} \frac{(1-a)\xi \sinh(\xi) + 2a[\cosh(\xi) - 1]}{a(1+N_0^{-1}N_L^{-1}\xi^2)\sinh(\xi) + (1-a)\xi \cosh(\xi)} \right]. \quad (A5)$$

In these expressions  $\xi \equiv k_{\parallel} L$  and the integrals  $\tilde{I}_0$  and  $\tilde{I}_L$  correspond to (3.27) with  $\eta \equiv (\xi^2 - ix)^{1/2}$ .

We will analyze the behavior of  $\tilde{H}$ ,  $\tilde{I}_0$ , and  $\tilde{I}_L$  in the cases  $\xi < 1$  and  $\xi > 1$ . When  $\xi < 1$  we can expand the function  $\tilde{H}$  in powers of  $\xi$ . One arrives at

$$\tilde{H}(N_0, N_L; \xi < 1) \simeq \left[ \frac{1}{12} + \frac{1}{N_0 N_L} + \frac{1-a}{3a} \right] a^3 + \xi^2 \left[ -\frac{2}{15} + \frac{5}{24} a - \frac{a^2}{12} - \frac{a^2}{N_0^2 N_L^2} + \frac{1}{N_0 N_L} \left[ \frac{7}{12} a^2 - \frac{a}{2} \right] \right] a^2 + \dots \quad (A6)$$

In the case  $N_0 \gg 1$ ,  $N_L \gg 1$  (perfectly conducting boundaries), this expression gives

$$\tilde{H}(N_0 \gg 1, N_L \gg 1; \xi < 1) \simeq \frac{1}{12} - \frac{1}{5!} \xi^2 + \dots \quad (A7)$$

Furthermore it is possible to show by numerical analysis that  $\tilde{I}_{0,L}(\xi \ll 1) \simeq \tilde{I}_{0,L}(\xi=0) = I_{0,L}$ . Then one concludes that  $\tilde{A}(\xi \ll 1) \simeq \tilde{A}(\xi=0) = A$  and  $\tilde{B}(\xi \ll 1) \simeq \tilde{B}(\xi=0) = B$ .

On the other hand, when  $\xi \gg 1$  the function  $\tilde{H}$  behaves as

modifications in the critical behavior of nonequilibrium systems when boundary effects are taken into account.<sup>16</sup>

### ACKNOWLEDGMENTS

This work has been supported by the Comisión Interministerial de Ciencia y Tecnología Grant No. PB87-0782, and by the European Economic Community under Grant No. ST2\*0246.

### APPENDIX

Our aim in this appendix is to analyze the averaged equal time correlation function (3.21) for nonzero wave vectors  $\mathbf{k}_{\parallel}$ . To this end we start from the generalized version of (3.21)

$$\tilde{H}(N_0, N_L; \xi \gg 1) \sim \frac{1}{\xi^2} \quad (A8)$$

and the integrals  $\tilde{I}_{0,L}(\xi \gg 1)$  are negligible. This result may be interpreted as follows. Notice that the functions  $\tilde{H}$ ,  $\tilde{I}_0$ , and  $\tilde{I}_L$  come from the long-range terms of the correlation function (3.20). In particular,  $\tilde{H}$  corresponds to the second term on the right-hand side of this expression, whereas  $\tilde{I}_{0,L}$  are related to the third term, which contains the Green functions evaluated at  $y=0, L$ . Therefore, when  $\xi \gg 1$  the leading terms in the correlation function (A1) are the local ones, related to the first term in the large parentheses of (3.20), and long-range correlations are negligible.<sup>17</sup> Then, finite-size effects are only due to the modification of the stationary tempera-



ture profile. However, one has  $\tilde{A}(\zeta \gg 1) = A'$  [Eq. (3.40)], but  $\tilde{B}(\zeta \gg 1) \neq B'$  [Eq. (3.41)], the reason being the fact that  $B'$  contains a long-range contribution that disappears in the situation  $\zeta \gg 1$ .

On the contrary, when  $\zeta < 1$ ,  $\tilde{A}$  and  $\tilde{B}$  are practically insensible to the value of  $\zeta$ , consequently, the long-range contributions become important. Our analysis over the relevance of finite-size effects clearly applies to this case.

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