

Linear response theory for thermal conductivity and viscosity in terms of boundary fluctuations

Janka Petravac and Peter Harrowell

School of Chemistry, The University of Sydney NSW 2006, Australia

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Boundary driven shear flows and wall thermostats are being used in computer simulations of materials with increasing frequency. One attraction is that such boundary constraints offer a more realistic representation of the physical constraints imposed experimentally than the widely employed homogeneous constraints. In this paper we derive the linear response expressions for shear viscosity and thermal conductivity based on the fluctuations associated with boundary constraints. We demonstrate that our approach provides an effective method of describing the rheology in interfaces as well as bulk samples.

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I. INTRODUCTION

In recent years, an increasing interest in the behavior of materials in confined geometries (e.g., the marked difference between the transport properties in the bulk and in confinement [1] and transport across interfaces in layered systems [2–4]) has been a strong motivator in the development of simulation methods for heterogeneous systems. While equilibrium molecular dynamics simulations have been widely used to address structural properties and spatially dependent diffusion coefficients in confined systems, the spatial dependence of thermal conductivity [4,5] and viscosity [6–8] are invariably computed in nonequilibrium molecular dynamics (NEMD) simulations. The reason for this is that equilibrium methods for calculating transport coefficients rely on linear response theory and, currently, there is no implementation of this theory that will allow one to calculate the local value of a transport coefficient in a heterogeneous system. In this paper we present a treatment of linear response based on localized fluctuations that directly addresses this problem.

In the conventional Green-Kubo linear response theory [9] a transport coefficient is expressed in terms of a time integral of the autocorrelation function of the associated flux. There is no obstacle to applying this same method to a heterogeneous material at equilibrium such as the case when two phases are in coexistence. The result is a transport coefficient averaged over the entire system. The difficulty comes if one is interested in the transport coefficient associated with a specific part of such a heterogeneous sample, a layer containing an interface, for example. The theory we present here is a generalization of the Green-Kubo formalism describing the transport between two arbitrarily located parallel planes within a sample. The expressions we derive for shear viscosity and thermal conductivity can be applied to a material of arbitrary heterogeneity.

The knowledge of spatially dependent linear response is the prerequisite for a complete statistical theory of friction or thermal conductivity at a general interface. An interfacial layer of a multiphase system can undergo a structural change for much weaker driving fields (e.g., shear stress or temperature gradient) than a uniform bulk system. Since the weakest driving fields accessible to NEMD simulations are large compared to the largest experimental gradients, the extrapolation of “weak field” results can lead to incorrect conclu-

sions about the equilibrium, i.e., the experimental weak field, limit. It is impossible to determine which part of the interfacial friction or thermal conductivity can be determined from the equilibrium structure and fluctuations, and which effects observed in simulation are nonlinear consequences of driving forces.

In this paper, we focus on the linear response theory for boundary-driven systems of finite extension in one Cartesian direction. Mechanical and thermal constraints establishing shear or heat flow in a liquid or gas are physically imposed upon a material at its surfaces. In the case of fluids, these constraints are typically applied via the walls that serve to contain the material. Boundary constraints on stress, strain, and temperature, similar in principle to the experimental constraints, are now frequently employed in simulations of confined systems [3,4]. They avoid the artificialities and ambiguities of uniformly applied driving fields and homogeneous temperature constraints [10] in heterogeneous systems such as coexisting phases or banded flows.

The approach we develop in this paper involves determining the response of materials to an applied boundary constraint through recording the response of the very boundaries at which the constraint is imposed. An appealing feature of this approach is that it closely resembles the experimental situation. Consider, for example, the specific heat measurements of Birge and Nagel [11]. In this 1985 experiment, a supercooled liquid was heated using a hot wire. The resulting temperature was monitored by measuring the change in resistivity of the same wire used in heating.

Our expressions for shear viscosity and thermal conductivity of a material are completely in terms of the fluctuations occurring in localized layers of the sample. This theory provides the basis for a general microscopic description of interfacial friction and thermal transport. To see this, consider the problem as sketched in Fig. 1. To determine the transport coefficients for momentum and energy transport across an interface we need to be able to study the linear response of just that portion of the sample lying between the planes marked 1' and 2'. To apply constraints of some type at these planes would run the risk of perturbing the very response we would like to measure. In this paper we have solved this problem by deriving expressions for the transport coefficients between these internal planes in which no form of constraint is applied at the planes themselves. Instead, the

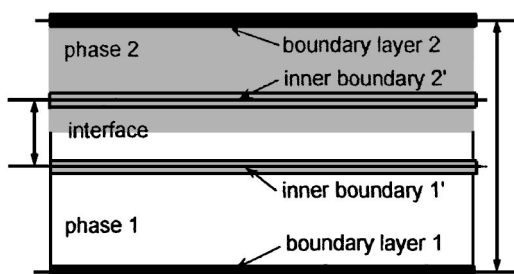


FIG. 1. A schematic representation of a two-phase system and the various layers referred to in the text. Black layers 1 and 2 are the boundary layers at which constraints are applied while the inner layers 1' and 2', that bracket the interfacial region, exert no constraint.

state of the sample is determined by constraints applied to boundaries 1 and 2 that can be well removed from the local region of interest.

We consider an N -particle system. As shown in Fig. 1, we separate it into two parallel planar boundary layers 1 and 2 consisting of N_1 and N_2 atoms, respectively, and the rest of the system referred to as “bulk” and consisting of $N_b = N - N_1 - N_2$ particles (see Fig. 2). The average separation of the centers of mass of the boundary layers is L . Constraints are applied only to the boundary layer atoms, which are assumed to stay confined to the boundary regions of the system's volume V . This assumption is not an essential requirement, but one made in order to simplify the treatment of the boundary by removing the fluctuations in particle number. The reader should note that the boundary we introduce does not necessarily have to correspond to an actual interface between different phases. Later in this paper we shall provide an example of boundaries designed to closely match the bulk properties of a sample. The flexibility provided by these generalized boundaries allows one to study a physical interface without perturbing its properties by imposing constraints.

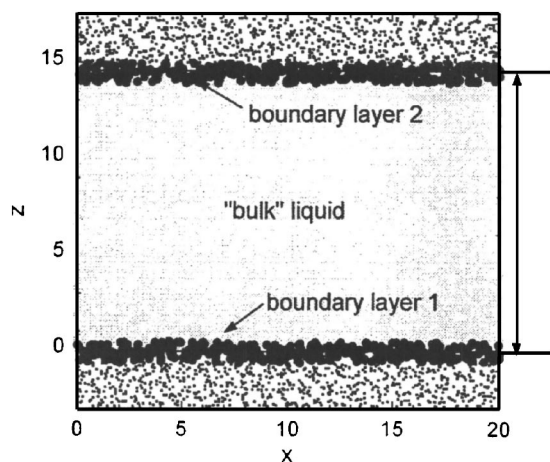


FIG. 2. A y - z projection of a configuration of the simulated Lennard-Jones liquid showing the boundary layer atoms tethered to disordered “liquid” sites (full black circles) and bulk liquid atoms (full grey circles). The stationary external atomic layers used in thermal conductivity simulations are plotted as black dots.

II. THERMAL CONDUCTIVITY

To begin, we derive an expression for the thermal conductivity of a system. The temperature at each boundary $T_0 \pm \Delta T$, respectively, is imposed using the Nosé equations of motion [12], i.e.,

$$\dot{\mathbf{r}}_{i,2} = \mathbf{p}_{i,2} / m_{1,2} s_{1,2}^2,$$

$$\dot{\mathbf{p}}_{i,2} = \mathbf{F}_{i,2},$$

$$\dot{s}_{1,2} = p_{s1,2} / Q,$$

$$\dot{\mathbf{p}}_{s1,2} = \sum_{i,2} \frac{p_{i,2}}{m_{1,2} s_{1,2}^3} - \frac{3N_{1,2} k_B (T_0 \pm \Delta T)}{s_{1,2}},$$

and the bulk equations of motion are

$$\dot{\mathbf{r}}_{i_b} = \mathbf{p}_{i_b} / m_{i_b},$$

$$\dot{\mathbf{p}}_{i_b} = \mathbf{F}_{i_b}.$$

In Eqs. (1) and (2), \mathbf{r}_i , \mathbf{p}_i , and m_i are, respectively, the position, momentum, and mass of the atom i . The index i_1 goes over all N_1 atoms of the first layer, i_2 goes over N_2 , and i_b goes over N_b . \mathbf{F}_i is the total force on the atom i from its interaction with the other particles of the system. In Eq. (1), $s_{1,2}$ and $p_{s1,2}$ are the thermostat degrees of freedom, and the variable Q can be interpreted as the “thermostat inertia.”

The equilibrium ($\Delta T = 0$) system conserves the Nosé Hamiltonian [12],

$$H_0 = \sum_{i=1}^N \frac{p_i^2}{2m_i} + \Phi + \frac{p_{s1}^2 + p_{s2}^2}{2Q} + 3k_B T_0 (N_1 \ln s_1 + N_2 \ln s_2) + \sum_{i_1=1}^{N_{w_1}} \frac{p_{i_1}}{m_1 s_1^2} + \sum_{i_2=1}^{N_{w_2}} \frac{p_{i_2}}{m_2 s_2^2}, \quad (3)$$

which can be interpreted as the internal energy of the system [the first two terms on the right-hand side of Eq. (3)] and environment (the remaining terms). The rate of change of internal energy according to Eqs. (1) and (2) defines the dissipative flux J created by maintaining a temperature gradient $2\Delta T/L$ between the boundary layers [13], $H_0' = -(2\Delta T/L)JV$. Using the perturbed equations of motion Eq. (1) and Eq. (2), we obtain the rate of change of the equilibrium Hamiltonian,

$$\dot{H}_0 = \frac{3k_B \Delta T}{Q} \left(N_1 \frac{p_{s1}}{s_1} - N_2 \frac{p_{s2}}{s_2} \right) = -JV \frac{2\Delta T}{L}, \quad (4)$$

defining the dissipative flux conjugate to the temperature gradient $2\Delta T/L$ as

$$J = \frac{3k_B}{2QS} \left(N_2 \frac{p_{s2}}{s_2} - N_1 \frac{p_{s1}}{s_1} \right), \quad (5)$$

where $S=V/L$ is the surface area of the system.

Using the substitution

$$\frac{P_{s_{1,2}}}{s_{1,2}} = Q \frac{\dot{s}_{1,2}}{s_{1,2}} = Q\alpha_{1,2}, \quad (6)$$

the equations of motion (1) reduce to a much simpler Nosé-Hoover form [14],

$$\begin{aligned} \dot{\mathbf{r}}_{i,2} &= \mathbf{p}_{i,2}/m_{1,2}, \\ \dot{\mathbf{p}}_{i,2} &= \mathbf{F}_{i,2} - \alpha_{1,2}\mathbf{p}_{i,2}, \end{aligned} \quad (7)$$

$$\dot{\alpha}_{1,2} Y' = [2K_{1,2} - 3N_{1,2}k_B(T_0 \pm \Delta T)]/Q,$$

where K_1 and K_2 are total kinetic energies of the boundary layer 1 and 2, respectively, and α_1 and α_2 deterministically adjust the kinetic energy of the respective boundaries so that the average kinetic energy of each corresponds to the desired temperature. The variable Q determines the time scale of fluctuations in α_1 and α_2 . After substitution Eq. (6), the flux in Eq. (5) conjugate to temperature gradient is given by

$$J = \frac{3k_B}{2S}(N_2\alpha_2 - N_1\alpha_1). \quad (8)$$

If the boundary layers on average consist of no more than one molecular layer, the energy flux J_q through the system described by Eqs. (7) and (2) is half the difference of fluxes through each of the boundaries,

$$J_q = (\alpha_2 K_2 - \alpha_1 K_1)/S,$$

which is in equilibrium equal to

$$J_q = 3k_B T_0 (\alpha_2 N_2 - \alpha_1 N_1)/2S = T_0 J. \quad (9)$$

The dissipative flux is equal to the energy flux multiplied by temperature T_0 , just as it appears in the conventional bulk Green-Kubo relationships for thermal conductivity.

The expression for thermal conductivity can now be obtained by following the transient time-correlation formalism (TTCF) [13]. In general, the linear transport coefficient χ associated with the variable A under external perturbation F_{ext} “switched on” at $t=0$ is obtained from the ratio $\langle A(t) \rangle / F_{\text{ext}}$ by taking the limit $F_{\text{ext}} \rightarrow 0$ followed by the limit $t \rightarrow \infty$,

$$\chi = \lim_{F_{\text{ext}} \rightarrow 0} \lim_{t \rightarrow \infty} \frac{\langle A(t) \rangle}{F_{\text{ext}}} = - \frac{V}{k_B T} \int_0^\infty ds \langle A(s) J(0) \rangle_{\text{EQ}}, \quad (10)$$

providing that $\langle A(0) \rangle$ vanishes, and that the perturbed equations of motion conserve the phase space volume (phase space incompressibility [13]). Note that J refers to the flux conjugate to the field F_{ext} . After taking the limits, the integrand on the right-hand side becomes the equilibrium correlation function, hence the subscript “EQ.”

The phase space incompressibility condition [13],

$$\sum_{i=1}^N \frac{\partial}{\partial \mathbf{r}_i} \cdot \dot{\mathbf{r}}_i + \sum_{i=1}^N \frac{\partial}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i + \frac{\partial \dot{\alpha}_1}{\partial \alpha_1} + \frac{\partial \dot{\alpha}_2}{\partial \alpha_2} = 0,$$

is satisfied in the extended phase space of nonequilibrium equations of motion (7) and (2) spanned by Cartesian components of positions and momenta of all particles ($\mathbf{r}_i, \mathbf{p}_i, i=1, \dots, N$) and α_1 and α_2 [one can verify this by substituting $\dot{\mathbf{r}}_i, \dot{\mathbf{p}}_i$, and $\dot{\alpha}_{1,2}$ from Eqs. (7) and (2) and differentiating].

Thermal conductivity λ (as appears in the Fourier heat law $J_q = -\lambda \Delta T/L$ [15]) is in our system the ratio of the energy flux Eq. (9) and the temperature gradient,

$$\begin{aligned} \lambda &= \lim_{\Delta T \rightarrow 0} \lim_{t \rightarrow \infty} \frac{J_q}{2\Delta T/L} = \lim_{\Delta T \rightarrow 0} \lim_{t \rightarrow \infty} \frac{T_0 J}{2\Delta T/L} \\ &= \frac{9Vk_B}{4} \int_0^\infty dt \left\langle \frac{\Delta\alpha(t)}{S} \frac{\Delta\alpha(0)}{S} \right\rangle, \end{aligned} \quad (11)$$

where $\Delta\alpha = N_1\alpha_1 - N_2\alpha_2$. In deriving Eq. (11), we have chosen the energy flux Eq. (9) as the phase variable A in Eq. (10), while the role of the external driving field F_{ext} is played by the temperature gradient, and J is the dissipative flux conjugate to $F_{\text{ext}} = 2\Delta T/L$. Equation (11) is the major result of this paper. It is remarkable in that it describes a transport property of the bulk sample through the fluctuations in the boundaries alone.

An alternative expression for thermal conductivity follows from imposing a constant energy flux through the system. If the particles in the boundary layers satisfy the equations of motion

$$\dot{\mathbf{r}}_{i,2} = \mathbf{p}_{i,2}/m_{1,2}, \quad (12)$$

$$\dot{\mathbf{p}}_{i,2} = \mathbf{F}_{i,2} + \alpha \mathbf{p}_{i,2}/N_{1,2},$$

where α is now held constant. If T_0 is the average temperature of the system, the heat flux J_q imposed by Eq. (12) is $3k_B\alpha T_0/S$. The rate of change of the equilibrium Hamiltonian

$$H_0 = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \Phi$$

is $3k_B(T_2 - T_1)$. If we take the external field to be $F_{\text{ext}} = J_q/T_0 = 3k_B\alpha/S$, the dissipative flux J associated with this external field is the temperature gradient $\Delta T/L$, where $\Delta T = T_2 - T_1$ is the temperature difference between two boundary layers. The phase space incompressibility of the system described by Eqs. (12) and (2),

$$\sum_{i=1}^N \frac{\partial}{\partial \mathbf{r}_i} \cdot \dot{\mathbf{r}}_i + \sum_{i=1}^N \frac{\partial}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i = 0 \quad (13)$$

is easily verified. The inverse thermal conductivity in the linear response limit $\alpha \rightarrow 0$ is obtained from Eq. (10) by substituting J_q/T_0 for external field, $\Delta T/L$ as the dissipative flux, and $\Delta T/T_0 L$ as the phase variable A . It is determined from the fluctuations of the average temperature difference between the two boundaries,

$$\frac{1}{\lambda} = \lim_{\alpha \rightarrow 0} \lim_{t \rightarrow \infty} \frac{1}{T_0} \frac{\Delta T/L}{J_q/T_0} = - \frac{V}{k_B T_0^2} \int_0^\infty dt \left\langle \frac{\Delta T(t)}{L} \frac{\Delta T(0)}{L} \right\rangle. \quad (14)$$

The expression for $1/\lambda$ in Eq. (14) can be generalized in a useful fashion. Consider a planar interface for which we would like to calculate the interfacial conductivity, let us call it λ' . The situation is sketched in Fig. 1. Since the heat flux imposed at the boundaries is constant throughout the system, one can obtain the inverse thermal conductivity $1/\lambda'$ of an arbitrary film of width L' within the system, between the layers 1' and 2' shown in Fig. 1 as

$$\frac{1}{\lambda'} = - \frac{V}{k_B T_0^2} \int_0^\infty dt \left\langle \frac{\Delta T'(t)}{L'} \frac{\Delta T(0)}{L} \right\rangle, \quad (15)$$

where $\Delta T'$ is the temperature difference between boundary layers 1' and 2'. Equation (15) represents, to our knowledge, the first general Green-Kubo-type expression for the thermal conductivity across an arbitrary interface.

III. SHEAR VISCOSITY

We now consider the shear viscosity η in terms of boundary fluctuations. Let the z direction lie parallel to the normal to the boundaries. We apply the force \mathbf{F} in the x direction on the center of mass of the first external boundary layer and the force $-\mathbf{F}$ on the center of mass of the second layer. If S is the surface area of the layers, F/S is shear stress. The equations of motion for the layer atoms are

$$\begin{aligned} \mathbf{r}_{i,2} Y' &= \mathbf{p}_{i,2} / m_{i,2}, \\ \mathbf{p}_{i,2} Y' &= \mathbf{F}_{i,2} \pm \mathbf{e}_x m_{i,2} F / M_{1,2}, \end{aligned} \quad (16)$$

The second term on the right-hand side of the momentum equation in Eq. (16) is the external force driving the shear flow, where \mathbf{e}_x is the unit vector in the x direction and $M_{1,2}$ is the total mass of the first or second layer. The bulk atoms still obey Newton equations (2). The phase space incompressibility of the system (16) is verified from Eq. (13).

The equilibrium of the system is characterized by $F=0$. The rate of change of internal energy according to Eqs. (16) and (2) defines the dissipative flux J created during shear [13], $\dot{H}_0 = -(F/S)JV$. The flux conjugate to shear stress is $J = \Delta v_{xCM}/L$, where Δv_{xCM} is the difference between the x components of the center-of-mass velocities of the boundary layers, so that the dissipative flux conjugate to shear stress is the average strain rate in the system. The ratio of $\Delta v_{xCM}/L$ and F/S in the limit $F \rightarrow 0$, $t \rightarrow \infty$ expresses the inverse average viscosity $1/\eta$ of the system between two layers as the integral of the equilibrium correlation function of strain rates,

$$\frac{1}{\eta} = - \frac{V}{k_B T} \int_0^\infty dt \left\langle \frac{\Delta v_{xCM}(t)}{L} \frac{\Delta v_{xCM}(0)}{L} \right\rangle. \quad (17)$$

As in Eq. (15), we can generalize this expression to obtain

the viscosity acting between any two layers 1' and 2' within our sample (see Fig. 1) separated by a distance L' ,

$$\frac{1}{\eta'} = - \frac{V}{k_B T} \int_0^\infty dt \left\langle \frac{\Delta v'_{xCM}(t)}{L'} \frac{\Delta v_{xCM}(0)}{L} \right\rangle, \quad (18)$$

where $\Delta v'_{xCM}$ is the difference in x components of the center-of-mass velocities of the inner boundaries 1' and 2'. This expression can be used to define the viscosity in an interfacial region or the friction coefficient across an interface.

An alternative expression can be obtained by constraining the centers of mass of the boundary layers to move at a fixed relative velocity Δv_{xCM} , so that the overall strain rate is $\Delta v_{xCM}/L$. In the limit $\Delta v_{xCM}/L \rightarrow 0$ we obtain viscosity in terms of correlations of surface forces,

$$\eta = - \frac{V}{k_B T} \int_0^\infty dt \left\langle \frac{\Delta F(t)}{2S} \frac{\Delta F(0)}{2S} \right\rangle. \quad (19)$$

IV. SIMULATIONS

In this section we shall test the validity of our expressions for λ and η by showing that the above theory can reproduce well-known results for thermal conductivity and viscosity of a uniform liquid. We compare the results from our theory, applied to a liquid film, with those from the standard Green-Kubo expressions for a uniform bulk liquid in periodic boundary conditions. To this end we shall introduce liquid-structured boundaries to avoid perturbing the homogeneous liquid. Such boundaries, consisting of particles pinned to liquidlike sites by anharmonic springs, have been used previously [16]. The springs are anharmonic in order to reduce the coupling to the Nosé-Hoover thermostat [14]. We demonstrate that, with this choice of boundary, the correlation integrals converge to the known bulk transport properties in the case of homogeneous liquid film. This result implies that, by matching the structure of the boundary layer to the structure of the bulk system adjacent to it we can study liquids without the disturbance from the solid walls.

We studied a Lennard-Jones liquid at the density $\rho=0.84$ and temperature $T=1.0$ in reduced units [17]. The equations of motions were integrated using fifth order Gear predictor-corrector scheme with the time step $dt=0.001$. Initially, a bulk liquid system of $N=6912$ atoms was equilibrated from fcc lattice in periodic boundary conditions for 10^6 steps. To generate the amorphous boundary layers (see Fig. 2), the atoms within layers of thickness $l=0.84$ at the lower and the upper boundary of the periodic cell [i.e., such that $0 < r_z(i) < l$ and $L-l < r_z(i)L$] were then tethered to their current sites $\mathbf{r}_{eq}(i)$ by anharmonic potentials of the form

$$\Phi_a(\mathbf{r}_i) = -k_4[\mathbf{r}_i - \mathbf{r}_{eq}(i)]^4 - k_6[\mathbf{r}_i - \mathbf{r}_{eq}(i)]^6$$

with $k_4=5 \times 10^3$ and $k_6=5 \times 10^6$. Production runs were of 5×10^6 time steps.

We left three amorphous layers of ‘‘frozen’’ immobile atoms below and above the tethered liquidlike boundary layers (Fig. 2), in order to prevent the escape of liquid atoms through the holes in the boundary layer, and the average

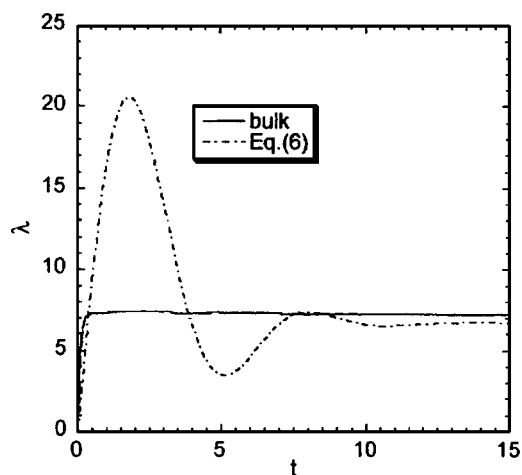


FIG. 3. The running thermal conductivity integral λ plotted against the size of the time window over which the associated correlation function is integrated. The results from Eq. (11) (dotted line) are compared with the Green-Kubo bulk thermal conductivity correlation integral (full line).

displacement of the tethered atoms away from the confined liquid causing the change in the liquid film density. The immobile atoms represent an additional static conservative external field term in the Nosé Hamiltonian that does not alter the derivation of thermal conductivity. In the shear viscosity simulation, the forces due to the immobile atoms were not included in the definition of shear stress as the total force per unit area acting on the boundary atoms in Eq. (19). Their role was to preserve the liquid structure close to the boundary without making an explicit contribution to friction.

In Figs. 3 and 4 we present the thermal conductivity calculated using Eqs. (11) and (4), respectively. The values are plotted against the size of the time interval used to integrate the respective correlation functions. The thermal conductivity calculated using the conventional Green-Kubo expression for a bulk liquid with periodic boundary conditions is pro-

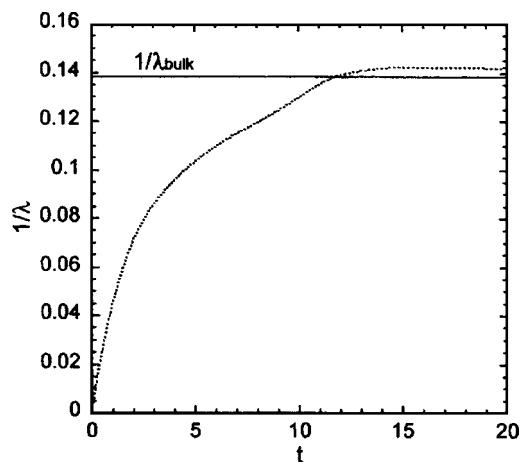


FIG. 4. The running inverse thermal conductivity integral λ^{-1} plotted against the time window over which the associated correlation function is integrated. The results from Eq. (14) (dotted line) are compared with the inverse value of the thermal conductivity obtained from the Green-Kubo bulk correlation integral (full line).

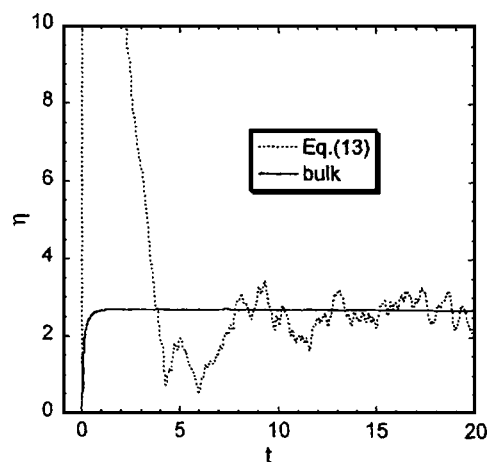


FIG. 5. The running shear viscosity integral η is plotted against the size of the time window over which the associated correlation function is integrated. The results from Eq. (19) (dotted line) are compared with those obtained from the Green-Kubo bulk shear viscosity correlation integral (full line).

vided for comparison. In Fig. 5 we present the analogous results for the shear viscosity calculated using Eq. (19). The height of the large initial peaks in the boundary correlation integrals in Figs. 3 and 5 depends on the pinning potential and the choice of Q in the Nosé-Hoover thermostat. It is known [18] that tethering of wall atoms reduces the heat transfer between wall and liquid. However, we have not seen the influence of this effect on the equilibrium simulation results.

In all three cases, we find that our boundary correlation results converge to the bulk values. These results both confirm our derivations and show that the pinned liquid walls do not alter the transport properties of a liquid in the linear limit.

While the standard Green-Kubo approach clearly represents a more efficient route for calculating transport coefficients in bulk liquids, we remind the reader that the boundary fluctuation method developed here can also be applied to problems such as interfacial transport in a localized region of a layered film, where the expressions based upon conventional Green-Kubo theory do not apply. Since even the equivalent expressions for transport in specified bands of the bulk are not known, our method is so far the only one which makes it possible to calculate the transport coefficients across a localized region containing an interface.

V. CONCLUSION

We have presented a linear response theory for transport in finite systems in terms of boundary fluctuations. The expressions we obtain for thermal conductivity and viscosity of the whole sample are remarkable in that they rely solely on fluctuations at the walls and contain no explicit reference to the material contained by the walls. It is this feature that enables us to apply these expressions to localized regions of a material of arbitrary heterogeneity.

By treating heat and shear flow in a completely analogous manner, this theory provides a statistical mechanical basis for

nonequilibrium simulations of layered and interfacial systems. In current wall-driven nonequilibrium simulations of shear flow [3], the averages of the driving boundary forces are used to specify shear stress across the system. Our theory makes it possible to formulate a nonequilibrium method for calculating thermal conductivity that makes use of fluctuations in boundary constraints [Eq. (9)], currently calculated and discarded in simulations involving wall thermostats, for the definition of the uniform heat flux.

We verified the theory on a homogeneous liquid film bounded by pinned liquid-structured boundaries. The equilibrium transport coefficients across the film evaluated using

our theory match the bulk liquid values. The theory developed here represents a general treatment with which to study linear transport across any type of interface (liquid-liquid, liquid-solid or solid-solid) without interference caused by driving boundary layers in equilibrium and nonequilibrium simulations.

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