Nano- and Pico-Scale Transport Phenomena in Fluids

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A new theoretical approach to describe pre-hydrodynamic stages of evolution in nonequilibrium fluids is presented. The local density, velocity, and temperature fields are expressed as integrals over Green's functions that depend on initial-state ensemble averages of dynamical quantities. For systems in which the initial states are nonuniform in only one spatial direction, explicit expressions for the Green's functions are derived in terms of initial-state ensemble averages of moments of particle displacements and products of particle velocities and particle displacements.

1. INTRODUCTION

Recent computer simulations of self diffusion[1] and heat transport[2] indicate that on the nanometer length scale and picosecond time scale there are significant deviations from hydrodynamic behavior in moderately dense fluids with initial states that are far removed from equilibrium. For instance, the initial decay of a rectangular heat pulse[2] was observed to be slower than the decay predicted by hydrodynamics or the telegrapher's equation,[3] and during the earliest stage of the decay the kinetic energy was not equipartitioned. In as much as local equipartition of the kinetic energy is a necessary condition for the definition of a local hydrodynamic temperature, it appears that hydrodynamic variables are not sufficient to describe this earliest stage of evolution, nor does it seem appropriate to try to correct the hydrodynamic equations by adding higher-order space

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and/or time derivatives to the equations. The current interest in nano-scale systems and the use of femtosecond-pulsed lasers to "observe" and modify these systems[4] will, no doubt, require a deeper understanding of transport on these very short scales.

In this paper we develop a new theoretical approach for the description of the pre-hydrodynamic stage of evolution of nonequilibrium fluids. The theory is formally exact and gives explicit expressions for the local density, velocity, and temperature fields in the fluid, as a function of position and time, in terms of Green's functions. The precise range of applicability of this theory, however, is in general unknown.

When the initial states have nonuniformities (which remove the system from equilibrium) confined to a single spatial direction, e.g., the heat pulse of ref. 2, the Green's functions can be written as an infinite series of *dynamical* quantities, such as those composed of products of powers of the displacement in position and the velocity of a particle at time t. The series expansion of the Green's functions are ordered such that the leading term is dominant as $t \to 0$ and as $t \to \infty$; the remaining terms appear to be small, making significant contributions only for the brief interval of time that separates the initial dynamical stage from the hydrodynamic stage of evolution. These leading terms contain a gaussian with a time dependent variance. As $t \to 0$ the variance is proportional to t^2, characteristic of free-particle motion, and as $t \to \infty$ they are proportional to t, characteristic of hydrodynamic relaxation. The short time expansions of these averages show that the basic physical mechanism for the initial stage of the decay takes place by the free streaming of particles as well as local exchange of kinetic and potential energy through "collisional transfer."

We begin, in Section 2, by defining variables and stating important assumptions. The Green's functions are formally defined in Section 3. These formal expressions, valid for a broad range of nonequilibrium systems, are not particularly useful for explicit calculations. In Section 4 we show how the Green's functions can be re-expressed in a manner that allows us to describe the pre-hydrodynamic stage of relaxation. The method shown there is valid for the heat-pulse case, as well as many other cases in which the non-uniformities of the initial state are confined to a single spatial direction. In Section 5 we make some final remarks.

2. DEFINITIONS AND ASSUMPTIONS

The initial phase-point of a system of N indistinguishable particles in a volume V is denoted by $\Gamma = (\vec{r}_1, \vec{v}_1, ..., \vec{r}_N, \vec{v}_N)$, where $\vec{r}_i$ and $\vec{v}_i$ are the position and velocity of particle i; the phase-space density function of the ensemble of initial states is $f(\Gamma)$. We shall assume that the Hamiltonian

for this system of particles is given by $H = \sum_i \frac{1}{2} m \vec{v}_i^2 + \Phi$, with $\Phi = \sum_{i > j} \varphi(|\vec{r}_i - \vec{r}_j|)$, where $\varphi(r)$ is a conservative, short-ranged, interparticle pair potential and m is the particle mass.

As the initial phase point evolves in time the particle positions and velocities will change; the phase point of the system at the time t is denoted by $\Gamma_t = (\vec{r}_1(t), \vec{v}_1(t),..., \vec{r}_N(t), \vec{v}_N(t))$. The phase-space density function for these phase-points Γ_t is denoted by $\hat{f}(\Gamma_t)$.

The local number density at position $\vec{r}$ and time t is given by

$$n(\vec{r}, t) = \int d\Gamma_t \, \hat{f}(\Gamma_t) \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i(t)). \qquad (2.1)$$

The local particle flux at the position $\vec{r}$ and time t is given by

$$\vec{j}(\vec{r}, t) = n(\vec{r}, t) \, \vec{v}(\vec{r}, t) = \int d\Gamma_t \, \hat{f}(\Gamma_t) \sum_{i=1}^{N} \vec{v}_i \delta(\vec{r} - \vec{r}_i(t)), \qquad (2.2)$$

where $\vec{v}(\vec{r}, t)$ is the local fluid velocity. In anticipation of the possibility that the kinetic energy might not be equipartitioned we define the local α-component kinetic energy density at position $\vec{r}$ and time t by

$$n(\vec{r}, t) \, e_\alpha^K(\vec{r}, t) = \frac{m}{2} \int d\Gamma_t \, \hat{f}(\Gamma_t) \sum_{i=1}^{N} v_{i\alpha}^2 \delta(\vec{r} - \vec{r}_i(t)), \qquad (2.3)$$

where $\alpha = x$, y, or z. The local α-component temperature is defined in terms of the α-component kinetic energy in the local center of mass reference frame

$$\frac{1}{2} k_{\rm B} T_\alpha(\vec{r}, t) = e_\alpha^K(\vec{r}, t) - \frac{1}{2} m v_\alpha(\vec{r}, t)^2, \qquad (2.4)$$

where $k_{\rm B}$ is the Boltzmann constant. When the kinetic energy is equipartitioned $T_x = T_y = T_z$, and if local or global equilibrium has been established $T = \frac{1}{3}(T_x + T_y + T_z)$ is the thermodynamic temperature. Expressions for the potential energy density and the total energy are not required with this definition of temperature.

3. THE NONEQUILIBRIUM GREEN'S FUNCTIONS

Given the assumptions described above, the local density, particle flux, and kinetic energy densities can be expressed in terms of the Green's functions $G(\vec{r}, \vec{r}', t)$, $\vec{J}(\vec{r}, \vec{r}', t)$, and $K_\alpha(\vec{r}, \vec{r}', t)$, respectively. Since the particles are indistinguishable and $d\Gamma \, f(\Gamma) = d\Gamma_t \, \hat{f}(\Gamma_t)$ we have from (2.1)

$$n(\vec{r}, t) = N \int d\Gamma \, f(\Gamma) \, \delta(\vec{r} - \vec{r}_1(t))$$

$$= nV \int d\vec{r}' \int d\Gamma \, f(\Gamma) \, \delta(\vec{r} - \vec{r}_1(t)) \, \delta(\vec{r}' - \vec{r}_1)$$

$$= n \int d\vec{r}' \left\{ V \int d\Gamma \, f(\Gamma) \, \delta(\vec{r} - \vec{r}_1(t)) \, \delta(\vec{r}' - \vec{r}_1) \right\}. \quad (3.1)$$

Thus

$$n(\vec{r}, t) = n \int d\vec{r}' \, G(\vec{r}, \vec{r}', t), \quad (3.2)$$

where

$$G(\vec{r}, \vec{r}', t) = V \int d\Gamma \, f(\Gamma) \, \delta(\vec{r} - \vec{r}_1(t)) \, \delta(\vec{r}' - \vec{r}_1) \quad (3.3)$$

and $n = N/V$.

Let the displacement of particle 1, $\Delta\vec{r}_1(t)$, be defined by $\vec{r}_1(t) = \vec{r}_1 + \Delta\vec{r}_1(t)$. $\Delta\vec{r}_1(t)$ does not depend on $\vec{r}_1$ because the forces acting on particle 1 depend only on the distance between other particles in the system. $\Delta\vec{r}_1(t)$ is a function of the initial particle velocities and of $\vec{s}_2, \vec{s}_3,..., \vec{s}_N$, where $\vec{s}_i = \vec{r}_i - \vec{r}_1$. Thus

$$G(\vec{r}, \vec{r}', t) = V \int d\vec{r}_1 \, d\vec{v}_1 \, d\vec{s}_2 \cdots f(\vec{r}_1, \vec{v}_1, \vec{s}_2 + \vec{r}_1, \vec{v}_2,...) \, \delta(\vec{r} - \vec{r}_1 - \Delta\vec{r}_1(t)) \, \delta(\vec{r}' - \vec{r}_1). \quad (3.4)$$

By integrating over $\vec{r}_1$, replacing V with an integral over $\vec{r}_1$, and then changing variables back to Γ we find

$$G(\vec{r}, \vec{r}', t) = V \int d\vec{v}_1 \, d\vec{s}_2 \cdots f(\vec{r}', \vec{v}_1, \vec{s}_2 + \vec{r}', \vec{v}_2,...) \, \delta(\vec{r} - \vec{r}' - \Delta\vec{r}_1(t))$$

$$= \int d\vec{r}_1 \, d\vec{v}_1 \, d\vec{s}_2 \cdots f(\vec{r}', \vec{v}_1, \vec{s}_2 + \vec{r}', \vec{v}_2,...) \, \delta(\vec{r} - \vec{r}' - \Delta\vec{r}_1(t))$$

$$= \int d\Gamma \, f(\Gamma_{r'}) \, \delta(\vec{r} - \vec{r}' - \Delta\vec{r}_1(t))$$

$$= \langle \delta(\vec{r} - \vec{r}' - \Delta\vec{r}_1(t)) \rangle_{r'}, \quad (3.5)$$

where $\Gamma_{r'} = (\vec{r}', \vec{v}_1, \vec{r}_2 - \vec{r}_1 + \vec{r}', \vec{v}_2, \vec{r}_3 - \vec{r}_1 + \vec{r}', \vec{v}_3,...)$.

In the same manner we find

$$\vec{j}(\vec{r}, t) = n \int d\vec{r}' \; \vec{J}(\vec{r}, \vec{r}', t), \tag{3.6}$$

and

$$n(\vec{r}, t) \, e_\alpha^K(\vec{r}, t) = \frac{m}{2} \, n \int d\vec{r}' \; K_\alpha(\vec{r}, \vec{r}', t), \tag{3.7}$$

where

$$\vec{J}(\vec{r}, \vec{r}', t) = \langle \vec{v}_1(t) \, \delta(\vec{r} - \vec{r}' - \Delta\vec{r}_1(t)) \rangle_{r'} \tag{3.8}$$

and

$$K_\alpha(\vec{r}, \vec{r}', t) = \langle v_{1\alpha}^2(t) \, \delta(\vec{r} - \vec{r}' - \Delta\vec{r}_1(t)) \rangle_{r'}. \tag{3.9}$$

Note that

$$\langle \cdots \rangle_{r'} \equiv \int d\Gamma \, f(\Gamma_{r'})..., \tag{3.10}$$

and thus the average over initial states is performed using a phase-space density function that has been modified by the variable $\vec{r}'$; $\langle \cdots \rangle_{r'}$ is a complicated function of $\vec{r}'$.

4. EVALUATION OF THE GREEN'S FUNCTIONS

The utility of this formal description for systems out of equilibrium depends on the extent to which techniques for evaluating the theory can be developed. We show, in this section, that the Green's functions can be written in a form that highlights the early, pre-hydrodynamic stage of system evolution. In particular, Eqs. (3.5), (3.8), and (3.9) can be rewritten in forms that depend on averages of dynamical quantities such as $\langle \Delta r_1^2(t) \rangle_{r'}$ and $\langle \vec{v}_1^2(t) \, \Delta r_1^2(t) \rangle_{r'}$. To do this we first determine the Fourier transforms of G, $\vec{J}$, and K_α, make a powerseries expansion of the transforms in the transform variable $\vec{k}$, rearrange the expansions, and invert the transforms. The rearrangements of the $\vec{k}$ expansions are made by factoring out gaussians so that they and the first one or two terms in the remaining series give the correct behavior as $t \to 0$ and $t \to \infty$. In other words, the $\vec{k}$-expansions are "rearranged" in a manner that factors out the Green's

functions in a form such that their variances, in the limit of long times, have a time dependence characteristic of hydrodynamic Green's functions. [See Sections 4.1 and 4.2 later.]

Assuming that the non-uniformity of the initial states is confined to the x-direction so that $f(\Gamma_{r'})$ depends only on r'_x and that $f(\Gamma_{r'})$ is such that $j_y(\vec{r}, t) = j_z(\vec{r}, t) = 0$ then $n(\vec{r}, t) = n(r_x, t)$, $\vec{j}(\vec{r}, t) = j_x(r_x, t)\,\hat{\imath}$, and $e_\alpha^K(\vec{r}, t) = e_\alpha^K(r_x, t)$—conditions that apply to the heat pulse of ref. 2, as well as the self-diffusion case of ref. 1—we find, using the method described above, that

$$G(r_x, r'_x, t) = g(r_x - r'_x, \rho) \left\{ 1 + \sum_{j=2}^{\infty} \frac{\rho_j}{\rho^j} j! \, S_{-1/2}^{(j)}(w^2) \right\}$$
$$+ \frac{\langle \Delta r_{1x}(t) \rangle_{r'}}{\sqrt{\rho'}} w' g(r_x - r'_x, \rho') \left\{ 1 + \sum_{j=2}^{\infty} \frac{\rho'_j}{\rho'^j} j! \, S_{1/2}^{(j)}(w'^2) \right\}, \quad (4.1)$$

$$J_x(r_x, r'_x, t) = \frac{\langle v_{1x}(t)\, \Delta r_{1x}(t) \rangle_{r'}}{\sqrt{\rho}} w g(r_x - r'_x, \rho) \left\{ 1 + \sum_{j=1}^{\infty} \frac{\bar{\rho}_{jx}}{\rho^j} j! \, S_{1/2}^{(j)}(w^2) \right\}$$
$$+ \langle v_{1x}(t) \rangle_{r'} g(r_x - r'_x, \bar{\rho}) \left\{ 1 + \sum_{j=2}^{\infty} \frac{\bar{\gamma}_{jx}}{\bar{\rho}^j} j! \, S_{-1/2}^{(j)}(\bar{w}^2) \right\}, \quad (4.2)$$

$$K_\alpha(r_x, r'_x, t) = \langle v_{1\alpha}^2(t) \rangle_{r'} g(r_x - r'_x, \rho) \left\{ \left[1 - \frac{\hat{\eta}_\alpha}{\rho} S_{-1/2}^{(1)}(w^2) \right] \right.$$
$$+ \sum_{j=2}^{\infty} \frac{\hat{\rho}_{j\alpha}}{\rho^j} \left(j! \, S_{-1/2}^{(j)}(w^2) - \frac{\hat{\eta}_\alpha}{\rho} (j+1)! \, S_{-1/2}^{(j+1)}(w^2) \right) \right\}$$
$$+ \frac{\langle v_{1\alpha}^2(t)\, \Delta r_{1x}(t) \rangle_{r'}}{\sqrt{\hat{\rho}_\alpha}} \hat{w}_\alpha g(r_x - r'_x, \hat{\rho}_\alpha) \left\{ 1 + \sum_{j=2}^{\infty} \frac{\hat{\gamma}_{j\alpha}}{\hat{\rho}_\alpha^j} j! \, S_{1/2}^{(j)}(\hat{w}_\alpha^2) \right\}. \quad (4.3)$$

Here

$$g(r_x - r'_x, a) = \frac{1}{\sqrt{4\pi a}} \exp\left[-\frac{(r_x - r')^2}{4a} \right], \quad (4.4)$$

where "a" may be ρ, ρ', $\bar{\rho}$, or $\hat{\rho}_\alpha$, and

$$\rho = \frac{1}{2} \langle \Delta r_{1x}^2(t) \rangle_{r'}, \qquad w = \frac{(r_x - r'_x)}{2\sqrt{\rho}}, \quad (4.5)$$

$$\rho' = \frac{1}{3!} \frac{\langle \Delta r_{1x}^3(t) \rangle_{r'}}{\langle \Delta r_{1x}(t) \rangle_{r'}}, \qquad w' = \frac{(r_x - r'_x)}{2\sqrt{\rho'}}, \quad (4.6)$$

$$\bar{\rho} = \frac{1}{2} \frac{\langle v_{1x}(t)\, \Delta r_{1x}^2(t)\rangle_{r'}}{\langle v_{1x}(t)\rangle_{r'}}, \qquad \bar{w} = \frac{(r_x - r'_x)}{2\sqrt{\bar{\rho}}}, \tag{4.7}$$

$$\hat{\rho}_\alpha = \frac{1}{3!} \frac{\langle v_{1\alpha}^2(t)\, \Delta r_{1x}^3(t)\rangle_{r'}}{\langle v_{1\alpha}^2(t)\, \Delta r_{1x}(t)\rangle_{r'}}, \qquad \hat{w}_\alpha = \frac{(r_x - r'_x)}{2\sqrt{\hat{\rho}_\alpha}}. \tag{4.8}$$

$S_m^{(n)}(x)$ are the Sonine polynomials[5] defined by

$$S_m^{(n)}(x) = \sum_{p=0}^n (-x)^p \frac{(n+m)_{n-p}}{p!(n-p)!}, \tag{4.9}$$

where $(j)_k = j(j-1)\cdots(j-k+1)$, $k \leqslant j$, and $(j)_0 = 1$. Additional moments of the particle displacement and velocity that occur in these equations have a form similar to the cumulants of the displacement introduced in ref. 1; they approach zero as $t \to 0$ and as the system approaches equilibrium. For the self-diffusion and heat-pulse cases they are quite small at intermediate times too. They are defined by

$$\rho_i = \frac{1}{(2i)!}\left[(-1)^i \langle \Delta r_{1x}^{2i}(t)\rangle_{r'} - (2i)! \sum_{j=1}^i \frac{(-1)^j}{j!} \rho^j \rho_{i-j} \right], \qquad i \geqslant 1 \tag{4.10}$$

$$\rho'_i = \left[(-1)^i \frac{1}{(2i+1)!} \frac{\langle \Delta r_{1x}^{2i+1}(t)\rangle_{r'}}{\langle \Delta r_{1x}(t)\rangle_{r'}} - \sum_{j=1}^i \frac{(-1)^j}{j!} \rho'^j \rho'_{i-j} \right], \qquad i \geqslant 1 \tag{4.11}$$

$$\bar{\gamma}_{ix} = \frac{1}{(2i)!}\left[(-1)^i \frac{\langle v_{1x}(t)\, \Delta r_{1x}^{2i}(t)\rangle_{r'}}{\langle v_{1x}(t)\rangle_{r'}} - (2i)! \sum_{j=1}^i \frac{(-1)^j}{j!} \bar{\rho}^j \bar{\gamma}_{(i-j)\,x} \right], \qquad i \geqslant 1 \tag{4.12}$$

$$\bar{\rho}_{ix} = \left[(-1)^i \frac{1}{(2i+1)!} \frac{\langle v_{1x}(t)\, \Delta r_{1x}^{2i+1}(t)\rangle_{r'}}{\langle v_{1x}(t)\, \Delta r_{1x}(t)\rangle_{r'}} - \sum_{j=1}^i \frac{(-1)^j}{j!} \rho^j \bar{\rho}_{(i-j)\,x} \right], \qquad i \geqslant 1 \tag{4.13}$$

$$\hat{\eta}_\alpha = \frac{1}{2} \frac{\langle v_{1\alpha}^2(t)\, \Delta r_{1x}^2(t)\rangle_{r'}}{\langle v_{1\alpha}^2(t)\rangle_{r'}} - \rho \tag{4.14}$$

$$\hat{\rho}_{i\alpha} = \frac{(-1)^i}{(2i)!} \frac{\langle v_{1\alpha}^2(t)\, \Delta r_{1x}^{2i}(t)\rangle_{r'}}{\langle v_{1\alpha}^2(t)\rangle_{r'}} + \hat{\eta}_\alpha \hat{\rho}_{(i-1)\,\alpha} - \frac{(-1)^i}{i!} \rho^i$$
$$- \sum_{j=1}^{i-1} \frac{(-1)^{i-j}}{(i-j)!} \rho^{i-j}(\hat{\rho}_{j\alpha} - \hat{\eta}_\alpha \hat{\rho}_{(j-1)\,\alpha}), \qquad i \geqslant 2 \tag{4.15}$$

$$\hat{\gamma}_{i\alpha} = \left[(-1)^i \frac{1}{(2i+1)!} \frac{\langle v_{1\alpha}^2(t)\, \Delta r_{1x}^{2i+1}(t)\rangle_{r'}}{\langle v_{1\alpha}^2(t)\, \Delta r_{1x}(t)\rangle_{r'}} - \sum_{j=1}^i \frac{(-1)^j}{j!} \hat{\rho}_\alpha^j \hat{\gamma}_{(i-j)\,\alpha} \right], \qquad i \geqslant 1 \tag{4.16}$$

with $\rho_0 = \rho'_0 = \bar{\gamma}_{0x} = \bar{\rho}_{0x} = \hat{\rho}_{0\alpha} = \hat{\gamma}_{0\alpha} = 1$ and $\rho_1 = \rho'_1 = \bar{\gamma}_{1x} = \hat{\gamma}_{1\alpha} = \hat{\rho}_{1\alpha} = 0$.

Although these general equations appear quite complicated, we find that for the self-diffusion and heat-pulse cases referred to earlier only a few of the terms in these expansions make any appreciable contribution to the Green's functions, and the leading terms dominate at very short and very long times, as shown in the next two sub-sections.

4.1. Behavior at Short Times

As $t \to 0$ the dynamical averages $\langle \cdots \rangle_{r'}$ may be expressed as power-series in t. The function g, however, becomes singular in this limit because the functions $\rho(t)$, $\rho'(t)$, $\bar{\rho}(t)$, and $\hat{\rho}_\alpha(t)$ are, to lowest order in t, proportional to t^2. For instance, $\rho(t) = \frac{1}{2} \langle v_{1x}^2 \rangle_{r'} t^2 + \cdots$. Although we cannot expand g as a powerseries in t it is nevertheless useful to order the Green's functions by the ordering the terms that multiply g. To "lowest order" in t

$$G^{(0)}(r_x, r'_x, t) = g(r_x - r'_x, \rho) \tag{4.17}$$

$$J_x^{(0)}(r_x, r'_x, t) = \frac{(r_x - r'_x)}{t} g(r_x - r'_x, \rho) \tag{4.18}$$

$$K_x^{(0)}(r_x, r'_x, t) = \frac{(r_x - r'_x)^2}{t^2} g(r_x - r'_x, \rho) \tag{4.19}$$

$$K_\perp^{(0)}(r_x, r'_x, t) = \langle v_{1\perp}^2 \rangle_{r'} g(r_x - r'_x, \rho), \tag{4.20}$$

where $\perp$ is y or z. As $t \to 0$, $\rho \to \frac{1}{2} \langle v_{1x}^2 \rangle_{r'} t^2$ and these "lowest order" Green's functions are those of an ideal fluid.

The next "order" of approximation has been examined for the case $\langle v_{1x} \rangle_{r'} = 0$ (which holds for the heat pulse examined earlier[2]) includes $O(t^2)$ contributions to the dynamical averages. For lack of space we can only remark here that these additional terms involve the interparticle potential and result in an exchange between kinetic and potential energy. Most important, at this order $K_\perp$ is given by $K_\perp^{(0)}$; only K_x includes potential energy changes and thus, at this order, equipartition of kinetic energy is lost—even if the initial ensemble was equipartitioned. It is clear, therefore, that there is some time interval, however brief, over which local equilibrium, and therefore hydrodynamics, cannot apply.

4.2. Behavior at Long Times

For very large t all of the ρ's grow as t and therefore the Green's functions become (spatially) flatter and flatter, implying that systems properties become uniform. In the $t \to \infty$ limit $n(r_x, \infty) = n$, $v_x(r_x, \infty) = 0$,

and the kinetic energy is equipartitioned and equal to its equilibrium value. When this Green's function approach was applied to the case of self diffusion the relaxation to hydrodynamics could explicitly be demonstrated and the usual Green–Kubo relation for the self-diffusion coefficient was obtained.[1] To obtain the analogous result for the heat pulse case turned out to be much more involved; however, the linear in t growth of the ρ's is consistent with hydrodynamic relaxation, as are the preliminary computer-simulation results of the theory.[6]

4.3. A Molecular Dynamics Evaluation

The relative importance of the many terms in the equations for the Green's functions is difficult to determine analytically, except in the long- and short-time limits. For an initial, rectangular, heat pulse (non-uniformity in the x-direction only), the low-order dynamical averages have been computed using molecular dynamics.[6] Most of these averages were of negligible magnitude; we found that the pre-hydrodynamic stage could be described using only the first few terms in Eqs. (4.1)–(4.3) [this approximation is denoted by a superscript (A)]:

$$G^{(A)}(r_x, r'_x, t) = g(r_x - r'_x, \rho) = \frac{1}{\sqrt{4\pi\rho}} \exp\left[-\frac{(r_x - r'_x)^2}{4\rho} \right] \qquad (4.21)$$

$$J_x^{(A)}(r_x, r'_x, t) = \frac{\langle v_{1x}(t)\,\Delta r_{1x}(t)\rangle_{r'}}{\sqrt{\rho}}\, wg(r_x - r'_x, \rho)\left\{ 1 + \frac{\bar{\rho}_{1x}}{\rho}\left(\frac{3}{2} - w^2\right) \right\}, \qquad (4.22)$$

$$K_\alpha^{(A)}(r_x, r'_x, t) = \langle v_{1\alpha}^2(t)\rangle_{r'}\, g(r_x - r'_x, \rho)\left[1 - \frac{\hat{\eta}_\alpha}{\rho}\left(\frac{1}{2} - w^2\right) \right]. \qquad (4.23)$$

The temperature $T(r_x, t) = \frac{1}{3}\left(T_x(r_x, t) + T_y(r_x, t) + T_z(r_x, t)\right)$ as a function of r_x calculated using these equations is compared to the molecular dynamics results and a solution of the hydrodynamic equations in Fig. 1. The agreement with the molecular dynamics calculation is very good. As $t \to 0$ Eqs. (4.21)–(4.23) reduce to Eqs. (4.17)–(4.20).

5. FINAL REMARKS

The Green's function approach described here, coupled with molecular dynamics evaluation of the dynamical averages, gives a useful description of the pre-hydrodynamic stage of relaxation in two simple cases: self diffusion and a heat pulse. Extension to other classes of initial states will require a more complete understanding of the relative importance of the many dynamical averages that appear in Eqs. (4.1)–(4.3) as well as the development
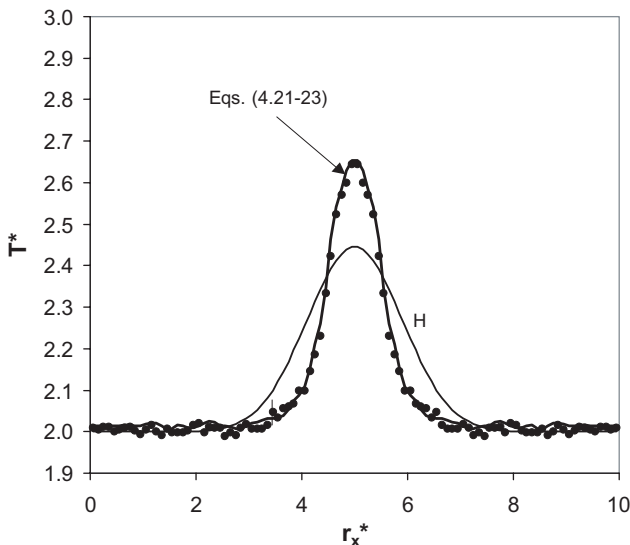
Fig. 1. The reduced temperature $T^* = k_B T/\varepsilon$ as a function of reduced distance $r_x^* = r_x/\sigma$ for a fluid of density $n\sigma^3 = 0.5$ at time $0.1\sigma\sqrt{m/\varepsilon}$. ($\bullet$ molecular dynamics,[6] H hydrodynamics[6]) At $t = 0$, $T^* = 3.0$ for r_x^* in (4.5, 5.5) and $T^* = 2$ otherwise. Here ε and σ are the usual Lennard-Jones parameters.

of techniques for determining the phase-space density function of the ensemble of initial states for a broad class in interesting cases.[7] In this respect, perhaps one should consider the approach here as a tentative first step toward a more general solution; a step for which a limited class of non-trivial transport problems may be studied in detail, particularly the transition from the dynamical stage to the hydrodynamic stage.

In the heat-pulse case we note that the telegrapher's equation, based as it is on the local equilibrium temperature, does not describe the pre-hydrodynamic stage any better than does hydrodynamics.[6] There does, however, seem to be some validity to Maxwell's observation[8] that the temperature field should not relax, over all time intervals, in the purely diffusive manner implicit in the parabolic heat equation. At times of the order 0.01 ps, our molecular dynamics heat-pulse calculations show that heat "propagates" by a combination of free streaming and collisional energy transfer that is purely dynamical rather than dissipative.

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