Journal of Statistical Physics, Vol. 56, Nos. 5/6, 1989

Local *H*-Theorem for a Kinetic Variational Theory

Jerzy Bławzdziewicz[1,2] **and George Stell**[1,3]

Received December 1, 1988; final April 14, 1988

A local *H*-theorem is derived for a recently proposed extension of Enskog kinetic theory to a dense model fluid composed of particles with interactions extending beyond a hard core.

KEY WORDS: *H*-theorem; local *H*-theorem; entropy; entropy production; maximization of entropy; continuous attractive tail; variational kinetic theory.

1. INTRODUCTION

A long-standing problem in the kinetic theory of fluids at moderate and high densities is how to treat the effect of a range of molecular interaction that extends beyond the nearly impenetrable repulsive core that can reasonably be modeled as a hard-sphere core. The most obvious complications in this connection are as follows. First, for high densities, particles are most of the time interacting with several other particles simultaneously and it is typically not possible to represent the evolution of the system in terms of a sequence of binary collisions. Next, the potential energy density is not determined by the one-particle distribution function alone, and therefore even on the simplest level of approximation the one-particle distribution function alone is not sufficient to describe the state of the system.

A possible way of dealing with these difficulties was considered recently by Karkheck *et al.*$^{(1)}$ as part of a program proposed by Stell and co-workers to extend the Enskog theory in a way that takes into account the effect of the extended range of interactions. Following the terminology of Stell *et al.*$^{(2)}$ we will refer to the theory investigated by Karkheck *et al.*

---

[1] Department of Chemistry, State University of New York, Stony Brook, New York 11794.

[2] On leave from: Katedra Fizyki, Uniwersytetu Szczecinskiego, 70-451 Szczecin, Poland.

[3] Department of Mechanical Engineering, State University of New York, Stony Brook, New York 11794.

as kinetic variational theory, version III (KVT III). To avoid problems related to simultaneous multiple collisions, Karkheck *et al.* considered a model system of particles with a hard core of diameter d supplemented by an attractive square-well interaction of range R. The advantage of such a model is that the duration of partial collisions either at the hard core or at the square-well edge is equal to zero. Subsequently, KVT III was applied also to a more general interaction, with a slowly varying potential inside the well which was treated in a mean-field manner. In order to keep the treatment of a system tractable, the KVT III is formulated in such a way that correlations between repeated partial collisions are ignored. If the density is high enough, this assumption seems reasonable: Between two successive partial collisions of any pair of particles ij each of the particles i and j will usually suffer several collisions with other particles.

While ignoring dynamical correlations between colliding particles, Karkheck *et al.* retained correlations between particle positions. To approximate such static correlations, they assumed that for a given one-particle distribution F_1 and a given potential energy density u, the state of the system is described by a probability distribution which maximizes the informational entropy functional under the constraints that functions F_1 and u are reproduced correctly. The two-particle distribution function derived from such approximate ensemble, when inserted into the first BBGKY hierarchy, yields evolution equations for both F_1 and u.

KVT III has been tested for a square-well fluid against computer simulation data.(3) As might be expected, at low densities the theory yields poor estimates for the velocity autocorrelation function and the self-diffusion coefficient, due to the neglect of correlations between subsequent partial collisions of identical pairs. At intermediate densities the theory makes reasonable predictions. At high densities it provides too high values, due to the neglect of ring terms and other correlated collision sequences. KVT III was applied also in analysis of the transport properties of real fluids.(4) When supplemented by a phenomenological rule for approximating a pair potential by a hard-core part and an attractive tail, it can be used to obtain quite good predictions for transport coefficients for simple fluids such as noble gases.

KVT III has a number of features to be expected from any consistent approximate kinetic theory. First of all, the local energy conservation law is obeyed, as it was incorporated in a natural way into the theory. Earlier theories suffered from the problem that energy was not strictly conserved either on the global or on the local level.(2,5,6) Next, KVT III exactly describes equilibrium states of the system, both for uniform and non-uniform fluids, as is true of the revised Enskog equation(7,8) (REE) for a hard-sphere fluid. It has already been proved in ref. 1 (see also ref. 9) that

KVT III obeys a global *H*-theorem and thus it describes the approach of a system toward equilibrium.

The main objective of the present paper is to show that KVT III has not only a global, but also a local *H*-theorem for a rather general class of pair potentials with a hard core and a discontinuity in the soft tail. Such a local *H*-theorem is an important step in demonstrating that a system can be described in terms of irreversible thermodynamics after approaching a state of local equilibrium. (After this paper was completed we learned from Henk van Beijeren that he has independently considered such a local *H*-theorem for the square-well potential in unpublished work.) In what follows we will define the local "entropy density" for a system described by KVT III. Then we will go on to a derivation of a local entropy-balance equation with a positive-definite source term. We will present our results in a form explicitly invariant under Galilean transformations. In our analysis we apply techniques similar to those used in the recent derivation of a local *H*-theorem for the REE.(10) Despite apparent similarities, there are some important differences between the two derivations. These differences are due to the nontrivial role played by the potential energy density for KVT III. In particular, in the derivation of an *H*-theorem for KVT III we have to deal with quasiequilibrium correlations for a system in which both density and local temperature are nonuniform.

Our paper is organized as follows. In Section 2 we outline KVT III and introduce basic kinetic equations. In Section 3 we define a non-equilibrium entropy density for the system described by KVT III. Next, in Section 4 we derive the entropy-balance equation with the positive-definite entropy production. The paper concludes with some remarks in Section 5. Some details of our calculations are relegated to the appendices.

2. KINETIC EQUATIONS

We consider a system of identical particles of mass m, with phases $\mathbf{x}_i = (\mathbf{r}_i, \mathbf{v}_i)$, where $\mathbf{r}_i \equiv (i)$ is the position and $\mathbf{v}_i$ is the velocity of particle i. The relative position of the particles i and j is given by $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, and the relative velocity by $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$. The particles are subject to a time-independent external potential $\Phi(i)$ which includes a wall potential. They interact via a spherically symmetric pair potential $\phi(ij)$ which is a sum of a singular hard-core term $\phi^{\mathrm{HC}}(ij)$ and a finite part $\phi_f(ij)$ extending beyond the core,

$$\phi(ij) = \phi^{\mathrm{HC}}(ij) + \phi_f(ij) \tag{2.1}$$

with

$$\phi^{\mathrm{HC}}(ij) = \begin{cases} \infty, & r_{ij} \leqslant d \\ 0, & r_{ij} > d \end{cases} \tag{2.2}$$

where $r_{ij} = |\mathbf{r}_{ij}|$. We assume that the finite part ϕ_f consists of two terms: a square potential well of depth $\varepsilon > 0$ and a smooth and slowly varying potential tail ϕ_s:

$$\phi_f(ij) = -\varepsilon\theta(R - r_{ij}) + \phi_s(r_{ij}) \tag{2.3}$$

where $\theta(x)$ is the unit step function

$$\theta(x) = \begin{cases} 0, & x < 0 \\ 1, & x \geqslant 0 \end{cases}$$

The square-well edge yields a singular attractive force at $r_{ij} = R$. We note that (2.1)–(2.3) includes the case of a potential consisting of a hard-sphere core and a truncated Lennard-Jones tail. In contrast to the effect of instantaneous partial collisions at the hard core and at the square-well edge, the effect of the smooth part of the potential in the framework of KVT III is treated in a mean-field manner. The parameter ε in Eq. (2.3) can also take negative values, in which case appropriate modification of the description of collisions has to be made.

The time evolution of the one-particle distribution function $F_1(\mathbf{x}_1, t)$ and of the local potential energy density $u(1, t)$ is determined respectively by (note the difference in the definition of the operators $\bar{T}_{ij}$ here and in ref. 1):

$$\left\{\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} - \frac{1}{m}\frac{\partial \Phi(1)}{\partial \mathbf{r}_1} \cdot \frac{\partial}{\partial \mathbf{v}_1}\right\} F_1(\mathbf{x}_1; t)$$

$$= \int d\mathbf{x}_2 [\bar{T}(12) + \delta L(12)]\, F_2(\mathbf{x}_1, \mathbf{x}_2; t) \tag{2.4}$$

and

$$\frac{\partial}{\partial t} u(1, t) + \frac{1}{2}\frac{\partial}{\partial \mathbf{r}_1} \int d\mathbf{v}_1 \int d\mathbf{x}_2\, \mathbf{v}_1 \phi(12)\, F_2(\mathbf{x}_1, \mathbf{x}_2; t)$$

$$= \frac{1}{2} \int d\mathbf{v}_1 \int d\mathbf{x}_2 [\phi(12)\, \bar{T}(12) + \mathbf{v}_{12} \phi_s'(12)]\, F_2(\mathbf{x}_1, \mathbf{x}_2; t) \tag{2.5}$$

with the following notation:

$$F_1(\mathbf{x}; t) = \left\langle \sum_{i=1}^{N} \delta(\mathbf{x} - \mathbf{x}_i) \right\rangle \tag{2.6}$$

$$F_2(\mathbf{x}, \mathbf{x}'; t) = \left\langle \sum_{\substack{i, j = 1 \\ i \neq j}}^{N} \delta(\mathbf{x} - \mathbf{x}_i)\, \delta(\mathbf{x}' - \mathbf{x}_j) \right\rangle \tag{2.7}$$

$$u(1;t)=\frac{1}{2}\int d\mathbf{v}_1\int d\mathbf{x}_2\,\phi(12)\,F_2(\mathbf{x}_1,\mathbf{x}_2;t) \tag{2.8}$$

$$\langle A(\Gamma_N,N)\rangle=\sum_{N=0}^{\infty}\int d\Gamma_N\,\rho_N(\Gamma_N;t)\,A(\Gamma_N,N) \tag{2.9}$$

where A is an arbitrary function, t denotes time, $\Gamma_N=(\mathbf{x}_1,\dots,\mathbf{x}_N)$ is the point in the phase space, $\rho_N(\Gamma_N;t)$ is a probability density, and $d\Gamma_N=d\mathbf{x}_1\cdots d\mathbf{x}_N/h^3N!$, with h Planck's constant. The operator $\delta L(ij)$ describes the influence of the smooth part of the pair potential upon the evolution of the system and is defined as

$$\delta L(ij)=\phi_s'(ij)\frac{\partial}{\partial\mathbf{v}_{ij}} \tag{2.10}$$

where

$$\phi_s'(12)=\partial\phi_s(r_{12})/\partial\mathbf{r}_{12} \tag{2.11}$$

The binary collisional operator $\bar{T}(ij)$ for a pair i, j is most conveniently defined through its adjoint operator $T(ij))=\bar{T}^{\dagger}(ij)$, where

$$\int d\mathbf{v}_i\int d\mathbf{v}_j\,fT(ij)\,g=\int d\mathbf{v}_i\int d\mathbf{v}_j\,g\bar{T}(ij)\,f \tag{2.12}$$

for any functions f and g of variables $(\mathbf{x}_i,\mathbf{x}_j)$. Four different terms in

$$T(ij)=\sum_{l=1}^{4}T_l(ij) \tag{2.13}$$

describe collisions between particles i and j at the hard core $(l=1)$, entering $(l=2)$ and leaving $(l=3)$ the potential well, and rebounding at the inside potential-well edge $(l=4)$, respectively. Explicitly,

$$\begin{aligned}T_l(ij)&=d_l(ij)\,\delta(r_{ij}-R_l)\,|\mathbf{v}_{ij}\cdot\hat{\mathbf{r}}_{ij}|\,\theta_l(\mathbf{v}_{ij}\cdot\hat{\mathbf{r}}_{ij})\\&\quad\times[b_l(ij)\,d_l^{*}(ij)-d_l^{\dagger}(ij)]\end{aligned} \tag{2.14}$$

where

$$R_1=d,\qquad R_2=R_3=R_4=R,\qquad \hat{\mathbf{r}}_{ij}=\mathbf{r}_{ij}/r_{ij}$$

$$\theta_1(y)=\theta_2(y)=\theta(-y)$$

$$\theta_3(y)=\theta(y-v_e)$$

$$\theta_4(y)=\theta(y)\,\theta(v_e-y)$$

and $v_e = (2\varepsilon/m)^{1/2}$. The operators $b_l(ij)$ change the velocities of particles i and j according to the collisional dynamics. The center-of-mass velocity $(\mathbf{v}_i + \mathbf{v}_j)/2$ remains unchanged, while the relative velocity $\mathbf{v}_{ij}$ is changed according to

$$\begin{aligned} b_1(ij)\mathbf{v}_{ij} = b_4(ij)\mathbf{v}_{ij} &= \mathbf{v}_{ij} - 2\hat{\mathbf{r}}_{ij}(\mathbf{v}_{ij}\cdot\hat{\mathbf{r}}_{ij}) \\ b_2(ij)\mathbf{v}_{ij} &= \mathbf{v}_{ij} - \hat{\mathbf{r}}_{ij}\{[(\mathbf{v}_{ij}\cdot\hat{\mathbf{r}}_{ij})^2 + v_e^2]^{1/2} + \mathbf{v}_{ij}\cdot\hat{\mathbf{r}}_{ij}\} \\ b_3(ij)\mathbf{v}_{ij} &= \mathbf{v}_{ij} + \hat{\mathbf{r}}_{ij}\{[(\mathbf{v}_{ij}\cdot\hat{\mathbf{r}}_{ij})^2 - v_e^2]^{1/2} - \mathbf{v}_{ij}\cdot\hat{\mathbf{r}}_{ij}\} \end{aligned} \tag{2.15}$$

The operators $d_l(ij)$ are inserted in order to produce unique results when $T_l(ij)$ acts upon functions discontinuous at $r_{ij} = R_l$. We define the operators $d_\pm(ij)$ by the formula

$$f(\mathbf{r}_{ij})\, d_\pm(ij)\, g(\mathbf{r}_{ij}) = \lim_{\varepsilon \to 0^+} f(\mathbf{r}_{ij})\, g((1 \pm \varepsilon)\cdot\mathbf{r}_{ij})$$

valid for any functions f and g of the variable $\mathbf{r}_{ij}$, and we denote the adjoint operator $d_\pm^\dagger(ij) = d_\mp(ij)$. With this notation we have $d_1 = d_2 = d_-$, $d_3 = d_4 = d_+$, $d_l^* = d_l^\dagger$ for $l = 1, 4$, and $d_l^* = d_l$ for $l = 2, 3$. The adjoint $\bar{T}_l(ij)$ of $T_l(ij)$ follows from Eq. (2.14), relation

$$b_l^\dagger(ij) = b_l(ij) \tag{2.16a}$$

for $l = 1, 4$, and

$$[|\mathbf{v}_{ij}\cdot\hat{\mathbf{r}}_{ij}|\, \theta_2(\mathbf{v}_{ij}\cdot\hat{\mathbf{r}}_{ij})\, b_2(ij)]^\dagger = |\mathbf{v}_{ij}\cdot\hat{\mathbf{r}}_{ij}|\, \theta_3(-\mathbf{v}_{ij}\cdot\hat{\mathbf{r}}_{ij})\, b_3(ji) \tag{2.16b}$$

It follows from the definition of the operators T_l that for any function $f(ij)$ continuous at $r_{ij} = R$

$$T(ij)\, f(ij) = 0 \tag{2.17}$$

The action of the operators $T_l(ij)$ on functions discontinuous at $r_{ij} = R_l$ has been specified here in a different way than in ref. 1. This change does not effect the first BBGKY-hierarchy equation (2.4) and allows us to write the energy equation (2.5) and the expression for entropy-production density in a very compact way.

The closure of the hierarchy equations (2.4) and (2.5), which is given in KVT III, is obtained using the maximization-of-entropy procedure.$^{(1)}$ In this procedure it is assumed that for any t the phase-space density $\rho_N(\Gamma;\, t)$ is given as

$$\rho_N(\Gamma_N;\, t) = \Xi^{-1} \exp\left[\sum_{i=1}^{N} \lambda(\mathbf{x}_i;\, t) - \sum_{\substack{i,j=1 \\ j \neq i}}^{N} \beta(\mathbf{r}_i)\, \phi(i, j)\right] \tag{2.18}$$

where Ξ is the normalization factor, and $\lambda(\mathbf{x}_i;t)$ and $\beta(\mathbf{r}_i;t)$ are Lagrange multiplier fields that have to be chosen such that the one-particle distribution function $F_1(\mathbf{x};t)$ and the potential energy density $u(\mathbf{r};t)$ are reproduced correctly. The quantity $\beta(\mathbf{r};t)$ is the multiplier field corresponding to the potential energy density and $k_B\beta(\mathbf{r};t)$ can be interpreted as the inverse of the local potential energy temperature (in what follows we will use the temperature scale for which $k_B=1$). In equilibrium the potential energy temperature equals the kinetic energy temperature, but out of equilibrium the two temperatures are not necessarily the same, which has a nontrivial effect on the bulk viscosity.(11) Assumption (2.18) yields the closure approximation for the two-particle reduced distribution function

$$F_2^{\mathrm{KVT}}(\mathbf{x}_1,\mathbf{x}_2;t)=F_1(\mathbf{x}_1;t)\,F_1(\mathbf{x}_2;t)\,g_2(\mathbf{r}_{12};t) \tag{2.19}$$

Through the constraints imposed on the Lagrange multipliers $\lambda(\mathbf{x};t)$ and $\beta(\mathbf{r};t)$ the pair correlation function g_2 depends functionally on the local number density $n(\mathbf{r};t)=\int d\mathbf{v}\,F_1(\mathbf{x};t)$ and the energy density $u(\mathbf{r};t)$. In the sequel we will assume that the change of variables $u(\cdot;t)\to\beta(\cdot;t)$ is possible in the correlation function g_2 and all other functionals of n (or F_1) and u.

3. ENTROPY DENSITY WITHIN KVT III

Keeping in mind the assumption (2.18) on an approximate statistical ensemble, we define now a nonequilibrium entropy-density functional for the system described by KVT III. The structure of the approximate ensemble (2.18) has a form very similar to a grand canonical ensemble appropriate for description of equilibrium nonuniform fluids (see, e.g., the review article by Evans(12)). Besides the velocity dependence of the distribution function, the only important difference is that the inverse temperature β in the ensemble (2.18) is nonuniform, whereas for equilibrium states the temperature is always constant throughout a system. Although this difference is important from the physical point of view, it does not influence greatly the formal structure of the theory, and a number of important expressions for equilibrium thermodynamic potentials can be easily adapted to the nonequilibrium situation. A brief derivation of formulas necessary to define a local entropy density in the framework of KVT III is given in Appendix A.

The most natural choice of the form of the local entropy density $s(1\,|\,F_1(t),\beta(t))$ (per unit volume) leads to

$$s(1\,|\,F_1(t),\beta(t))=s^{\mathrm{B}}(1\,|\,F_1(t))+s^{\mathrm{corr}}(1\,|\,n(t),\beta(t)) \tag{3.1}$$

The first term in expression (3.1) corresponds to Boltzmann's theory (ideal-gas contribution):

$$s^{\mathrm{B}}(1\,|\,F_1(t)) = -\int d\mathbf{v}_1\, F_1(\mathbf{x}_1;t)\{\ln[h^3 F_1(\mathbf{x}_1;t)]-1\} \tag{3.2}$$

The second term describes the effect of correlations. We define it as a Legendre transform of the nonequilibrium counterpart $\psi(1)$ of the nonideal (excess) part of the equilibrium Massieu-function local density (the function $-\beta^{-1}\psi$ is a counterpart of excess free energy density)

$$s^{\mathrm{corr}}(1\,|\,n,\beta) = \psi(1\,|\,n,\beta) + \beta(1)\,u(1\,|\,n,\beta) \tag{3.3}$$

The Massieu function ψ, as in an equilibrium theory, can be expressed as an integral of a one-particle direct correlation function c_1

$$\psi(1\,|\,n,\beta) = n(1)\int_0^1 d\alpha\, c_1(1\,|\,\alpha n,\beta) \tag{3.4}$$

As discussed in Appendix A, the one-particle correlation function c_1 obeys a hierarchy equation of the form

$$\begin{aligned} n(1)\,\partial c_1(1\,|\,n,\beta)/\partial\mathbf{r}_1 &\\ = \int d2[\Delta(12) - \beta(12)\,\phi_s'(12)]&\\ \times n(1)\,n(2)\,g_2(12\,|\,n,\beta) - u(1\,|\,n,\beta)\,\partial\beta(1)/\partial\mathbf{r}_1& \end{aligned} \tag{3.5}$$

where

$$\Delta(12) = [\delta(r_{12}-\sigma^+) - \delta(r_{12}-R^-) + \delta(r_{12}-R^+)]\hat{\mathbf{r}}_{12} \tag{3.6}$$

and

$$\beta(12) = [\beta(1)+\beta(2)]/2 \tag{3.7}$$

Further, c_1 has the properties

$$\left(\frac{\delta c_1(1)}{\delta n(2)}\right)_\beta = \left(\frac{\delta c_1(2)}{\delta n(1)}\right)_\beta \tag{3.8}$$

$$\left(\frac{\delta c_1(2)}{\delta\beta(1)}\right)_n = -\left(\frac{\delta u(1)}{\delta n(2)}\right)_\beta \tag{3.9}$$

From expression (3.4), property (3.9), and a very important identity

$$\int d(k+1)\, n(k+1) \int_0^1 d\alpha \frac{\delta A(1,..., k \mid \alpha n, \beta)}{\alpha\, \delta n(k+1)} = A(1,..., k \mid n, \beta) \quad (3.10)$$

valid for any functional $A(1,..., k \mid n, \beta)$ for which $A(1,..., k \mid n=0, \beta)=0$, and $k=0, 1,...,$ it follows immediately that

$$\int d2 \left(\frac{\delta\psi(2)}{\delta\beta(1)}\right)_n = -u(1) \quad (3.11)$$

Using the above identity and Eq. (3.3), one can easily find the following expressions for functional derivatives of the correlation part of the entropy s^{corr}:

$$\begin{aligned}\left(\frac{\delta s^{\text{corr}}(1)}{\delta n(2)}\right)_u = \left(\frac{\delta\psi(1)}{\delta n(2)}\right)_\beta &+ \int d3\, [1-\hat{P}(13)] \\ &\times \left(\frac{\delta\psi(1)}{\delta\beta(3)}\right)_n \left(\frac{\delta\beta(3)}{\delta n(2)}\right)_u \end{aligned} \quad (3.12)$$

and

$$\begin{aligned}\left(\frac{\delta s^{\text{corr}}(1)}{\delta u(2)}\right)_n = \beta(1)\, \delta(1-2) &+ \int d3\, [1-\hat{P}(13)] \\ &\times \left(\frac{\delta\psi(1)}{\delta\beta(3)}\right)_n \left(\frac{\delta\beta(3)}{\delta u(2)}\right)_n \end{aligned} \quad (3.13)$$

where the operator $\hat{P}(ij)$ permutes the variables i and j:

$$\hat{P}(ij))\, F(ij) = F(ji)$$

Note that the nonequilibrium entropy density s defined in this section resolves itself in an equilibrium state into the usual equilibrium entropy density.

4. LOCAL *H*-THEOREM

We will now go on to a derivation of a balance equation for the nonequilibrium entropy density. Our strategy is as follows: First we evaluate the time derivative of the entropy density with the help of the kinetic equations (2.4) and (2.5). The next and crucial step is to separate the expressions obtained in this way into a sum of an entropy-flow term and a positive-definite entropy production. We will use the invariance of the resulting entropy-balance equation under the Galilean transformation as an important criterion for correctness of the final result.

To separate entropy-flow terms from the entropy production, we will repeatedly apply in our expressions the following general identity:

$$\int dj\,[f(ij)-f(ji)] = -\frac{\partial}{\partial \mathbf{r}_i}\left[\int_0^1 d\lambda \int d\mathbf{r}\,\mathbf{r}f(\mathbf{r}_i+(1-\lambda)\mathbf{r}, \mathbf{r}_i-\lambda\mathbf{r})\right] \tag{4.1}$$

which is valid for any function f of the variables (ij) and allows us to transform an integral with an integrand antisymmetric under a permutation of its variables into the divergence of an appropriate current. In order to express our results in a compact form, in the remainder of this paper we will use the following shortened notation:

$$\hat{\mathscr{T}}(12)\,f(12) = \mathbf{r}_2 \int_0^1 d\lambda\, f(\mathbf{r}_1+(1-\lambda)\mathbf{r}_2, \mathbf{r}_1-\lambda\mathbf{r}_2) \tag{4.2}$$

First we will analyze the time derivative of the Boltzmann part of the entropy density. The kinetic equation (2.4) implies the continuity equation

$$\frac{\partial}{\partial t}n = -\frac{\partial}{\partial \mathbf{r}_1}(n\mathbf{w}) \tag{4.3}$$

where the mean velocity field $\mathbf{w}(1;t)$ is defined by

$$n(1;t)\,\mathbf{w}(1;t) = \int d\mathbf{v}_1\,\mathbf{v}_1 F_1(\mathbf{x}_1;t) \tag{4.4}$$

By applying the kinetic equation (2.4) with the closure (2.19) we calculate the time derivative of the Boltzmann part (3.2) of the entropy density. Taking into account identity (2.12) for the T and $\bar{T}$ operators, Eq. (2.17), and the definition (2.10) of the operator δL_{12}, we find

$$\begin{aligned}\frac{\partial}{\partial t}s^{\mathrm{B}} = {} & -\frac{\partial}{\partial \mathbf{r}_1}(\mathbf{w}s^{\mathrm{B}}+\mathbf{J}_s^{\mathrm{B}k}) \\ & -\int d\mathbf{v}_1 \int d\mathbf{x}_2\, F_2^{\mathrm{KVT}}(\mathbf{x}_1,\mathbf{x}_2)\, T(ij) \ln F_1(\mathbf{x}_1)\end{aligned} \tag{4.5}$$

where $\mathbf{J}_s^{\mathrm{B}k}$ is the kinematic Boltzmann entropy-current density:

$$\mathbf{J}_s^{\mathrm{B}k}(1;t) = -\int d\mathbf{v}_1\,[\mathbf{v}_1-\mathbf{w}_1(1;t)]\,F_1(\mathbf{x}_1;t)\ln[h^3F_1(\mathbf{x}_1;t)] \tag{4.6}$$

To transform the last term on the right-hand side (rhs) of Eq. (4.5), we use the identity (4.1). The antisymmetric part contributes to the entropy-flow term, and the symmetric part will be interpreted as the source term. We can rewrite Eq. (4.5) in the form

$$\frac{\partial}{\partial t} s^{\mathrm{B}} + \frac{\partial}{\partial \mathbf{r}_1} (\mathbf{w} s^{\mathrm{B}} + \mathbf{J}_s^{\mathrm{B}k} + \mathbf{J}_s^{\mathrm{B}p}) = \sigma^{\mathrm{B}} \tag{4.7}$$

where the potential part of the entropy-current density is given by

$$\begin{aligned} \mathbf{J}_s^{\mathrm{B}p}(1, t) = & -\frac{1}{2}\int d2\, \mathscr{T}(12) \\ & \times \int d\mathbf{v}_1 \int d\mathbf{v}_2\, F_2^{\mathrm{KVT}}(\mathbf{x}_1, \mathbf{x}_2)\, T(12) \ln F_1(\mathbf{x}_1) \end{aligned} \tag{4.8}$$

and the source term is of the form

$$\sigma_s^{\mathrm{B}}(1, t) = -\frac{1}{2}\int d\mathbf{v}_1 \int d\mathbf{x}_2\, F_2^{\mathrm{KVT}}(\mathbf{x}_1 \mathbf{x}_2)\, T(12) \ln[F_1(\mathbf{x}_1)\, F_1(\mathbf{x}_2)] \tag{4.9}$$

We now study the time derivative for the correlation part of the entropy density:

$$\begin{aligned} \frac{\partial}{\partial t} s^{\mathrm{corr}}(1) = & \int d2 \left(\frac{\delta s^{\mathrm{corr}}(1)}{\delta n(2)}\right)_u \frac{\partial}{\partial t} n(2) \\ & + \int d2 \left(\frac{\delta s^{\mathrm{corr}}(1)}{\delta u(2)}\right)_n \frac{\partial}{\partial t} u(2) \end{aligned} \tag{4.10}$$

Using the expressions (3.12) and (3.13) for the functional derivatives of s^{corr}, we can rewrite the time derivative as a sum of four terms

$$\frac{\partial}{\partial t} s^{\mathrm{corr}} = A + B + C + D \tag{4.11}$$

where

$$A(1) = \int d2 \left(\frac{\delta\psi(1)}{\delta n(2)}\right)_\beta \frac{\partial n(2)}{\partial t} \tag{4.12a}$$

$$B(1) = \int d2 \int d3\, [1 - \hat{P}(13)] \left(\frac{\delta\psi(1)}{\delta\beta(3)}\right)_n \left(\frac{\delta\beta(3)}{\delta n(2)}\right)_u \frac{\partial n(2)}{\partial t} \tag{4.12b}$$

$$C(1) = \beta(1) \frac{\partial u(1)}{\partial t} \tag{4.12c}$$

and

$$D(1) = \int d2 \int d3\, [1 - \hat{P}(13)] \left(\frac{\delta\psi(1)}{\delta\beta(3)}\right)_n \left(\frac{\delta\beta(3)}{\delta u(2)}\right)_n \frac{\partial u(2)}{\partial t} \tag{4.12d}$$

First we will transform the term A. Using the continuity equation (4.3), the expression (3.4) relating the function ψ to the one-particle direct correlation function c_1, and the symmetry property (3.8) of the functional derivatives of c_1, one readily finds

$$A(1) = -\frac{\partial}{\partial \mathbf{r}_1}(\psi(1)\,\mathbf{w}(1)) + \int d2\,\mathbf{w}(2)\,n(1)\int_0^1 d\alpha\left\{\frac{\delta}{\delta n(1)}\left[n(2)\frac{\partial}{\partial \mathbf{r}_2}c_1(2\,|\,\alpha n,\beta)\right]\right\}_\beta \tag{4.13}$$

The last term on the rhs of the above equation can be evaluated with the help of the hierarchy equation (3.5). By appropriately permuting the variables and applying the identity (3.10), we can conveniently write this term

$$\begin{aligned}
&\frac{1}{2}\int d2\,[1-\hat{P}(12)]\int d3\,[\mathbf{w}(2)-\mathbf{w}(3)][\varDelta(23)-\beta(23)\,\phi_s'(23)]\\
&\quad\times n(1)\int_0^1 d\alpha\,\alpha\left[\frac{\delta}{\delta n(1)}n(2)\,n(3)\,g_2(23\,|\,\alpha n,\beta)\right]_\beta\\
&\quad-\int d2\,[1-\hat{P}(12)]\,\mathbf{w}(2)\,n(1)\int_0^1 d\alpha\,\alpha^{-1}\left(\frac{\delta u(2)\,|\,\alpha n,\beta)}{\delta n(1)}\right)_\beta\frac{\partial\beta(2)}{\partial \mathbf{r}_2}\\
&\quad+\frac{1}{2}\int d2\,[\mathbf{w}(1)-\mathbf{w}(2)][\varDelta(12)-\beta(12)\,\phi_s'(12)]\,n(1)\,n(2)\,g_2(12\,|\,n,\beta)\\
&\quad-\mathbf{w}(1)\,u(1\,|\,n,\beta)\frac{\partial\beta(1)}{\partial \mathbf{r}_1}
\end{aligned}\tag{4.14}$$

The integrands of the first and the second terms of expression (4.14) are antisymmetric with respect to the permutation of the variables 1 and 2 and thus they contribute to the entropy flow. Using the standard technique, they can be transformed into minus the divergence of the respective currents $\mathbf{J}_{A1}$ and $\mathbf{J}_{A2}$. The expression for the current $\mathbf{J}_{A1}$ reads

$$\begin{aligned}
\mathbf{J}_{A1}(1) = {}&\frac{1}{2}\int d2\,\hat{\mathscr{T}}(12)\int d3\,[\mathbf{w}(2)-\mathbf{w}(3)][\varDelta(23)-\beta(23)\,\phi_s'(23)]\\
&\times n(1)\int_0^1 d\alpha\,\alpha\left[\frac{\delta}{\delta n(1)}n(2)\,n(3)\,g_2(23)\,|\,\alpha n,\beta)\right]_\beta
\end{aligned}\tag{4.15}$$

For the current $\mathbf{J}_{A2}$, using, in addition to (4.1), Eqs. (3.9) and (3.4), we get

$$\mathbf{J}_{A2}(1) = \int d2\,\hat{\mathscr{T}}(12)\left(\frac{\delta\psi(1)}{\delta\beta(2)}\right)_\beta\mathbf{w}(2)\cdot\frac{\partial\beta(2)}{\partial \mathbf{r}_2} \tag{4.16}$$

The third term of expression (4.14) has a symmetric integrand and contributes to the entropy source. It is convenient to represent this term as a sum of two contributions. The first contribution, which includes the operator $\varDelta$, is related to the entropy production at the potential discontinuities. Taking into account the definitions of the operators $\varDelta$ and T, it can be transformed into the following form:

$$\sigma_A^{\text{corr}}(1)=\frac{1}{2}\int d\mathbf{v}_1 \int d\mathbf{x}_2\, T(12)\, F_2^{\text{KVT}}(12) \tag{4.17}$$

The second contribution is related to the continuous part of the potential and it reads

$$R_0(1)= -\frac{1}{2}\int d\mathbf{v}_1 \int d\mathbf{x}_2\, \mathbf{v}_{12}\beta(12)\, \phi_s'(12)\, F_2^{\text{KVT}}(\mathbf{x}_1, \mathbf{x}_2) \tag{4.18}$$

As we will see, this contribution will be canceled in the final expression for the entropy-production density. Collecting the above results, we get the following expression:

$$A+\partial(\mathbf{w}\psi+\mathbf{J}_{A1}+\mathbf{J}_{A2})/\partial\mathbf{r}_1=\sigma_A+R_0-\mathbf{w}u\cdot\partial\beta/\partial\mathbf{r}_1 \tag{4.19}$$

Now we will make a similar transformation of the term C. By using the energy equation (2.5) with the closure (2.19), this term can be written as follows:

$$\begin{aligned} C(1)= {} & -\partial[\mathbf{w}(1)\, u(1)\, \beta(1)]/\partial\mathbf{r}_1+\mathbf{w}(1)\, u(1)\cdot\partial\beta(1)/\partial\mathbf{r}_1 \\ & +\frac{1}{4}\int d2\, [1-P(12)]\, \beta(1)\int d\mathbf{v}_1 \int d\mathbf{v}_2 \\ & \times[\phi(12)\, \bar{T}(12)+\mathbf{v}_{12}\phi_s'(12)]\, F_2^{\text{KVT}}(\mathbf{x}_1, \mathbf{x}_2) \\ & +\frac{1}{2}\int d\mathbf{v}_1 \int d\mathbf{x}_2\, \beta(12)\, \phi(12)\, \bar{T}(12)\, F_2^{\text{KVT}}(\mathbf{x}_1, \mathbf{x}_2) \\ & +\frac{1}{2}\int d\mathbf{v}_1 \int d\mathbf{x}_2\, \mathbf{v}_{12}\beta(12)\, \phi_s'(12)\, F_2^{\text{KVT}}(\mathbf{x}_1, \mathbf{x}_2) \end{aligned} \tag{4.20}$$

The third term on the rhs of (4.20) has an antisymmetric integrand and therefore constitutes the contribution to the entropy flux. It yields the negative of the divergence of the current $\mathbf{J}_C$ given by

$$\begin{aligned} \mathbf{J}_C(1)= {} & \frac{1}{4}\int d2\, \hat{\mathscr{T}}(12)\, \beta(1)\int d\mathbf{v}_1 \int d\mathbf{v}_2 \\ & \times[\phi(12)\, \bar{T}(12)+\mathbf{v}_{12}\phi_s'(12)]\, F_2^{\text{KVT}}(\mathbf{x}_1, \mathbf{x}_2) \end{aligned} \tag{4.21}$$

The fourth term in (4.20) yields the contribution to the entropy production. The discontinuity in the potential $\phi(ij)$ at $r_{ij}=R$ implies a corresponding discontinuity in g_2:

$$g_2(12)=\chi(12)\exp[-\beta(12)\,\phi(12)]$$

where the $\chi(12)$ is a continuous function. Taking this and Eq. (2.17) into account, we can transform the fourth term into the form

$$\sigma_C(1)=-\frac{1}{2}\int d\mathbf{v}_1\int d\mathbf{x}_2\,F_2(12)\,T(12)\ln g_2(12) \tag{4.22}$$

The last term in expression (4.20) is simply equal to $-R_0$. Collecting the above results, we get

$$C+\partial(\mathbf{w}\beta u+\mathbf{J}_C)/\partial\mathbf{r}_1=\sigma_C-R_0+\mathbf{w}u\cdot\partial\beta/\partial\mathbf{r}_1 \tag{4.23}$$

The terms B and D have integrands antisymmetric with respect to the permutation of variables and they constitute the entire contributions to the entropy flux. With the help of identity (4.1) they can be transformed directly into the divergence of the current. However, the resulting expression needs further transformation to get the total entropy current in a manifestly invariant form with respect to the Galilean transformations. Since the final expression is already very long, we relegate details of the calculations to Appendix B. The resulting expressions reads

$$B+D=-\partial(\mathbf{J}_{B+D}-\mathbf{J}_{A2})/\partial\mathbf{r}_1 \tag{4.24}$$

where

$$\begin{aligned}\mathbf{J}_{B+D}(1)=\int d2\,\hat{\mathscr{T}}(12)\left(\frac{\delta\psi(1)}{\delta\beta(2)}\right)_n&\\ \times\Bigg\{-\int d3\left[\left(\frac{\delta\beta(2)}{\delta n(3)}\right)_u n(3)+\left(\frac{\delta\beta(2)}{\delta u(3)}\right)_n u(3)\right]\frac{\partial\mathbf{w}(3)}{\partial\mathbf{r}_3}&\\ +\int d\mathbf{x}_3\int d\mathbf{x}_4\left(\frac{\delta\beta(2)}{\delta u(3)}\right)_n[\phi(34)\,\bar{T}(34)+\mathbf{v}_{34}\phi'_s(34)]\,F_2^{\mathrm{KVT}}(\mathbf{x}_3,\mathbf{x}_4)&\\ -\int d3\int d4\left(\frac{\delta\beta(2)}{\delta u(3)}\right)_n\left[\left(\frac{\delta u(3)}{\delta n(4)}\right)_\beta\frac{\partial n(4)}{\partial\mathbf{r}_4}\right.&\\ \left.+\left(\frac{\delta u(3)}{\delta\beta(4)}\right)_n\frac{\partial\beta(4)}{\partial\mathbf{r}_4}\right][\mathbf{w}(3)-\mathbf{w}(4))\Bigg\}&\end{aligned} \tag{4.25}$$

and $\mathbf{J}_{A2}$ is given by Eq. (4.16).

Let us now collect previously obtained results. Taking into account Eqs. (3.1), (3.3), (4.7), (4.11), (4.19), (4.23), and (4.24), we get the following balance equation for the entropy density:

$$\frac{\partial s}{\partial t} + \frac{\partial}{\partial \mathbf{r}_1} (\mathbf{w} s + \mathbf{J}_s) = \sigma \tag{4.26}$$

where the entropy-current density $\mathbf{J}_s$ is given by

$$\mathbf{J}_s = \mathbf{J}_s^{Bk} + \mathbf{J}_s^{\mathrm{B}p} + \mathbf{J}_{A1} + \mathbf{J}_C + \mathbf{J}_{B+D} \tag{4.27}$$

with respective terms $\mathbf{J}_s^{\mathrm{B}k}$, $\mathbf{J}_s^{\mathrm{B}p}$, $\mathbf{J}_{A1}$, $\mathbf{J}_C$, and $\mathbf{J}_{B+D}$ given by (4.6), (4.8), (4.15), (4.21), and (4.25). Note that all terms which survived in the expression (4.27) are invariant under the Galilean transformations. With the help of (4.9), (4.17), (4.22), and (2.19) one can write the entropy-production density σ in very compact form:

$$\sigma(1) = \frac{1}{2} \int d\mathbf{v}_1 \int d\mathbf{x}_2 \times [T_{12} F_2^{\mathrm{KVT}}(\mathbf{x}_1, \mathbf{x}_2) - F_2^{\mathrm{KVT}}(\mathbf{x}_1, \mathbf{x}_2)\, T(12) \ln F_2^{\mathrm{KVT}}(\mathbf{x}_1, \mathbf{x}_2)] \tag{4.28}$$

Entropy-production density (4.28) is a positive-definite quantity. To prove this, let us rewrite it as

$$\sigma(1) = \frac{1}{2} \int d\mathbf{v}_1 \int d\mathbf{x}_2\, \delta(r_{12} - R_l)\, |\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12}| \sum_{l=1}^{4} \theta_l(\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12}) \times \left[X_l(\mathbf{x}_1, \mathbf{x}_2) - Y_l(\mathbf{x}_1, \mathbf{x}_2) - Y_l(\mathbf{x}_1, \mathbf{x}_2) \ln \frac{X_l(\mathbf{x}_1, \mathbf{x}_2)}{Y_l(\mathbf{x}_1, \mathbf{x}_2)} \right] \tag{4.29}$$

where

$$X(\mathbf{x}_1, \mathbf{x}_2) = b_l(12)\, d_l^*(12)\, F_2^{\mathrm{KVT}}(\mathbf{x}_1, \mathbf{x}_2) \tag{4.30a}$$

and

$$Y(\mathbf{x}_1, \mathbf{x}_2) = d_l^\dagger(12)\, F_2^{\mathrm{KVT}}(\mathbf{x}_1, \mathbf{x}_2) \tag{4.30b}$$

[see Eqs. (2.13)–(2.14)]. Since $x - y - y \ln(x/y) \geqslant 0$ for $x > 0$ and $y > 0$, it follows immediately from (4.29) that

$$\sigma(\mathbf{r}; t) \geqslant 0 \tag{4.31}$$

for any $\mathbf{r}$ and t.

The balance equation (4.26), together with the inequality (4.31), serve us as a local formulation of the H-theorem for KVT III. By integrating the entropy density (3.1) and entropy-production density (4.28) over the volume of the fluid we recover the global entropy and entropy-production functionals introduced by Karkheck *et al.*(1) In the present notation, entropy production $\sigma(1)=0$ if and only if

$$T_l(12)\,F_1(\mathbf{x}_1)\,F_1(\mathbf{x}_2)\exp[-\beta(12)\,\phi(12)]=0 \tag{4.32}$$

for $l=1$, 2, 3, and 4. As was already discussed in I (see also ref. 13), condition (4.32) with $l=1$ is satisfied at the time t if and only if

$$F_1(\mathbf{x};t)=n(\mathbf{r};t)\left(\frac{m}{2\pi k_{\mathrm{B}}T(t)}\right)^{3/2}\exp-\frac{m[\mathbf{v}-\mathbf{w}(t)]^2}{2k_{\mathrm{B}}T(t)} \tag{4.33}$$

where the local density $n(\mathbf{r};t)$ is an arbitrary function, and the temperature $T(t)$ and the average velocity $\mathbf{w}(t)$ are uniform. Equation (4.32) with $l=2$, 3, 4 and the one-particle distribution function F_1 of the form (4.33) requires the inverse potential-temperature field β to be uniform and equal to $1/k_{\mathrm{B}}T$. At equilibrium the kinetic equation (2.4) with the closure (2.9) resolves itself into the first equilibrium BGY equation. Therefore, like the REE,(8) KVT III exactly describes the equilibrium state of uniform and nonuniform fluids.

5. DISCUSSION

In this paper we introduced a definition of an entropy density for a system described by KVT III and then derived a local entropy balance equation. We showed that it is possible to define a flux and a source term in such a way that the entropy-production density is a positive-definite quantity. All the quantities $s(\mathbf{r})$, $\mathbf{J}_s(\mathbf{r})$, and $\sigma(\mathbf{r})$ are local on a macroscopic scale, but on a microscopic scale they depend on the state of the system within the correlation range. The entropy, the entropy-current, and the entropy-production densities depend on the velocity distribution in such a way that only differences of particle velocities at different points are important. Therefore all these quantities are manifestly invariant with respect to the Galilean transformations.

Due to the nonlocality on a microscopic scale of the entropy, entropy-flux, and entropy-production densities, the definitions of these quantities are nonunique. More specifically, the entropy produced, say, at point $\mathbf{r}$ can be as well assigned to any other point within the range of the correlations. Such change can always be compensated by an appropriate change of the definition of the current. This nonuniqueness is of a similar sort as a nonuniqueness of the definitions of other quantities nonlocal on the microscopic scale, such as the potential energy density.

Equation (4.28) shows that within KVT III the entropy is produced by the instantaneous collisions at the hard core and at the edge of the potential well. Since the influence of a smooth part of the potential on the evolution of the system is treated in a mean-field manner, there is no entropy production due to this part of the interaction. For the same reason only the impulsive collisions on the potential-well edge leads to the exchange between potential and kinetic energy.

Karkheck *et al.*⁽⁴⁾ have described the transport properties of real fluids by modeling them as a fluid composed of particles with a hard core and a truncated Lennard-Jones tail. While KVT III seems to work fairly well for the shear viscosity and the heat conductivity when applied to such a model, Stell and his colleagues⁽¹⁴⁾ have found that it predicts an infinite bulk viscosity when the truncation radius R goes to infinity (or when there is no discontinuity in the Lennard-Jones tail in the first place). The simple explanation of this is as follows. In the absence of such a discontinuity the exchange rate between the kinetic and potential energies is infinitely slow. A change of the volume of a system without an exchange between the kinetic and potential energies, for the states close to equilibrium, leads to a difference between potential and kinetic temperatures. On the other hand, a difference between the temperatures causes a proportional pressure difference in comparison with the total equilibrium situation. For infinitely small exchange rate between kinetic and potential energy, even a very slow change of the volume leads to the occurrence of a finite excess pressure, which corresponds to the infinite bulk viscosity coefficient. To avoid this difficulty, one needs a more sophisticated theory, which describes the exchange between kinetic and potential energies that actually occurs even for smooth potentials.

APPENDIX A

In this Appendix we discuss briefly the definition of the correlation part of an entropy density associated with a nonequilibrium statistical ensemble (2.18). We start from the excess part of the Massieu function Ψ associated with (2.18):

$$\Psi = \ln \Xi - \int d1\, \lambda^*(1)\, n(1) - \Psi^{id} \tag{A.1}$$

where

$$\Xi = \sum_{N=0}^{\infty} \int d\Gamma_N \exp\left[\sum_{i=1}^{N} \lambda(\mathbf{x}_i; t) - \sum_{\substack{i,j=1\\ j\neq i}}^{N} \beta(i)\,\phi(ij)\right] \tag{A.2}$$

$$\lambda^*(1) = \int d\mathbf{v}_1\, \lambda(\mathbf{x}_1) \tag{A.3}$$

and

$$\Psi^{id} = -\int d1\, n(1) \ln[h^3 n(1) - 1] \tag{A.4}$$

is the ideal part of the Massieu function. In our expression $\lambda^*(1)$ plays a similar role to the quantity $[\mu - \Phi(1)]/k_B T$ in equilibrium theory, where μ is a chemical potential and $\Phi(1)$ is an external potential. Taking into account the definition (A.1), it is a simple exercise to show that the quantity c_1 defined by

$$c_1(1) = \left(\frac{\delta \Psi}{\delta n(1)}\right)_\beta \tag{A.5}$$

can be expressed as

$$c_1(1) = \ln n(1) - \lambda^*(1) \tag{A.6}$$

From (A.6) it follows that Eq. (3.5) is an analogue of the first BGY equation for equilibrium systems.

Due to (A.5) and the general identity (3.10), the function ψ defined by Eq. (3.4) is the density of the nonequilibrium Massieu function (A.1):

$$\int d1\, \psi(1) = \Psi \tag{A.7}$$

By differentiating Eq. (A.1), one also can easily demonstrate the identity

$$\left(\frac{\partial \Psi}{\partial \beta(1)}\right)_n = -u(1) \tag{A.8}$$

which is equivalent to (3.11). Identities (3.8) and (3.9) follow from (A.5), (A.8), and the general identity

$$\frac{\delta^2 A[\alpha, \beta]}{\delta\alpha(1)\, \delta\beta(2)} = \frac{\delta^2 A[\alpha, \beta]}{\delta\beta(2)\, \delta\alpha(1)} \tag{A.9}$$

valid for a sufficiently smooth functional $A[\alpha, \beta]$ of functions α and β.

APPENDIX B

In this Appendix we prove the identity (4.25) for the partial entropy current $\mathbf{J}_{B+D}$. It follows from (4.1), (4.12b), and (4.12*d*) that $B+D$ can be expressed in the form

$$B + D = -\partial \mathbf{J}'_{B+D}/\partial \mathbf{r}_1 \tag{B.1}$$

where

$$\mathbf{J}'_{B+D} = \int d2\, \hat{\mathscr{T}}(12) \left(\frac{\delta\psi(1)}{\delta\beta(2)}\right)_n \int d3 \times \left[\left(\frac{\delta\beta(2)}{\delta n(3)}\right)_u \frac{\partial n(3)}{\partial t} + \left(\frac{\delta\beta(2)}{\delta u(3)}\right)_n \frac{\partial u(3)}{\partial t}\right] \tag{B.2}$$

We can evaluate the rhs of the above expression by applying the energy equation (2.5) and the continuity equation (4.3):

$$\begin{aligned} J'_{B+D} = &-\int d2\, \hat{\mathscr{T}}(12) \left(\frac{\delta\psi(1)}{\delta\beta(2)}\right)_n \\ &\times \left\{ -\int d3 \left(\frac{\delta\beta(2)}{\delta u(3)}\right)_n \int d\mathbf{v}_3 \right. \\ &\times \int d\mathbf{x}_4\, [\phi(34)\, \bar{T}(34) + \mathbf{v}_{34} \phi'_s(34)]\, F_2^{\mathrm{KVT}}(\mathbf{x}_3, \mathbf{x}_4) \\ &+ \int d3 \left[\left(\frac{\delta\beta(2)}{\delta n(3)}\right)_u n(3) + \left(\frac{\delta\beta(2)}{\delta u(3)}\right)_n u(3)\right] \frac{\partial \mathbf{w}(3)}{\partial \mathbf{r}_3} \\ &\left. + \int d3 \left[\left(\frac{\delta\beta(2)}{\delta n(3)}\right)_u \frac{\partial n(3)}{\partial \mathbf{r}_3} + \left(\frac{\delta\beta(2)}{\delta u(3)}\right)_n \frac{\partial u(3)}{\partial \mathbf{r}_3}\right] \cdot \mathbf{w}(3) \right\} \end{aligned} \tag{B.3}$$

The first and the second terms in the curly brackets are invariant with respect to the Galilean transformations. The third term, which is not invariant, can be transformed with the help of the identity

$$\frac{\partial u(3 \mid n, \beta)}{\partial \mathbf{r}_3} = \int d4 \left[\left(\frac{\delta u(3)}{\delta n(4)}\right)_\beta \frac{\partial n(4)}{\partial \mathbf{r}_4} + \left(\frac{\delta u(3)}{\delta \beta(4)}\right)_n \frac{\partial \beta(4)}{\partial \mathbf{r}_4}\right] \tag{B.4}$$

which follows from the translational invariance of u. As result, we get

$$\begin{aligned} &\int d3 \left[\left(\frac{\delta\beta(2)}{\delta n(3)}\right)_u \frac{\partial n(3)}{\partial \mathbf{r}_3} + \int d4 \left(\frac{\delta\beta(2)}{\delta u(3)}\right)_n \left(\frac{\delta u(3)}{\delta n(4)}\right)_\beta \frac{\partial n(4)}{\partial \mathbf{r}_4}\right] \cdot \mathbf{w}(3) \\ &\quad + \int d3 \int d4 \left(\frac{\delta\beta(2)}{\delta u(3)}\right)_n \left(\frac{\delta u(3)}{\delta \beta(4)}\right)_n \frac{\partial \beta(4)}{\partial \mathbf{r}_4} \cdot \mathbf{w}(3) \end{aligned} \tag{B.5}$$

By appropriate permutation of the variables, using the chain-rule identity

$$\left(\frac{\delta A(1)}{\delta B(2)}\right)_C = -\int d3 \left(\frac{\delta A(1)}{\delta C(3)}\right)_B \left(\frac{\delta C(3)}{\delta B(2)}\right)_A$$

and

$$\int d3 \left(\frac{\delta A(1)}{\delta B(3)}\right)_C \left(\frac{\delta B(3)}{\delta A(2)}\right)_C = \delta(\mathbf{r}_1 - \mathbf{r}_2)$$

where A, B, and C are arbitrary functionals, we can transform (B.5) into the form

$$\int d3 \int d4 \left(\frac{\delta\beta(2)}{\delta u(3)}\right)_n \left[\left(\frac{\delta u(3)}{\delta n(4)}\right)_\beta \cdot \frac{\partial n(4)}{\partial \mathbf{r}_4} + \left(\frac{\delta u(3)}{\delta\beta(4)}\right)_n \frac{\partial\beta(4)}{\partial \mathbf{r}_4}\right] \cdot [\mathbf{w}(3) - \mathbf{w}(4)] + \mathbf{w}(2) \cdot \frac{\partial\beta(2)}{\partial \mathbf{r}_2} \tag{B.6}$$

Collecting Eqs. (B.1), (B.3), and (B.6) and taking into account definitions (4.16) and (4.24), we get Eq. (4.25).

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of the National Science Foundation. G. S. also acknowledges the support of NATO Research grant 419/82, which has facilitated valuable interaction with Prof. Henk van Beijeren in connection with this work. This is SUSB College of Engineering Report 527.

REFERENCES

1. J. Karkheck, H. van Beijeren, I. de Schepper, and G. Stell, *Phys. Rev. A* **32**:2517 (1985).
2. G. Stell, J. Karkheck, and H. van Beijeren, *J. Chem. Phys.* **79**:3166 (1983).
3. H. Wilbertz, J. P. J. Michels, and H. van Beijeren, *J. Stat. Phys.* **53**:1155 (1988).
4. J. Karkheck, G. Stell, and J. Xu, Transport in simple dense fluids, presented at the 10th Symposium of Thermophysical Properties, June 1988; *Int. J. Thermophys.*, to appear; J. Karkheck, G. Stell, and J. Xu, *J. Chem. Phys.* **89**:5829 (1988).
5. H. T. Davis, S. A. Rice, and J. V. Sengers, *J. Chem. Phys.* **35**:2210 (1961).
6. J. Karkheck and G. Stell, *J. Chem. Phys.* **75**:1475 (1981); *Phys. Rev. A* **25**:3302 (1982).
7. H. van Beijeren and M. H. Ernst, *Physica* **68**:473 (1973); **70**:225 (1973).
8. H. van Beijeren, *Phys. Rev. Lett.* **51**:1503 (1983).
9. J. Karkheck, *Kinam* **7A**:191 (1986).
10. M. Mareschal, J. Bławzdziewicz, and J. Piasecki, *Phys. Rev. Lett.* **52**:1169 (1984); J. Piasecki, *J. Stat. Phys.* **48**:1203 (1987).
11. H. van Beijeren, J. Karkheck, and J. V. Sengers, *Phys. Rev. A* **37**:2247 (1988).
12. R. Evans, *Adv. Phys.* **28**:143 (1979).
13. P. Résibois, *Phys. Rev. Lett.* **40**:1409 (1978); *J. Stat. Phys.* **19**:593 (1978).
14. G. Stell *et al.*, to be published.