Kinetic theory and H theorem for a dense square-well fluid

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By the method of maximization of entropy a consistent kinetic theory is derived for a square-well fluid. The existence of an H theorem is shown, and the equilibrium solutions are constructed.

Kinetic equations for dense classical fluids can be obtained by closure of the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy equations. One method for obtaining such closures is based on the maximization of entropy subject to constraints on microscopic phase functions, the choice of which influences the accuracy and complexity of the resulting kinetic equations.[1,2] For a fluid of hard-sphere particles this method yields the revised Enskog theory (RET), an irreversible kinetic equation first derived by van Beijeren and Ernst on the basis of diagrammatic methods.[3] On adding a smooth tail to the hard-core potential one obtains kinetic equations[2] that treat the hard-core collisions in an irreversible way, but approximate the tail dynamics by a reversible mean-field-type term. In contrast, on adding to the hard core a tail consisting of flat steps, one recovers fully irreversible kinetic equations, as will be demonstrated here for the simplest case of the square-well potential. Previously Davis, Rice, and Sengers (DRS) derived a kinetic equation for a fluid of square-well particles.[4] This DRS theory is closely analogous to the so-called standard Enskog theory (SET) for a dense hard-sphere fluid, originally derived by Enskog. Just as SET, the DRS theory yields explicit expressions for the transport coefficients. Yet it is not entirely satisfactory because, in general, energy conservation is not satisfied. Furthermore, in the presence of a time-independent external potential the stationary solutions for the DRS theory, just as for SET, do not coincide with the distribution functions known from equilibrium theory.[5] For hard spheres this deficiency of SET is avoided in RET, for which, in addition, Résibois obtained an H theorem.[6] Using the method of maximization of entropy, we derive here a new square-well theory, which exhibits energy conservation, satisfies an H theorem, and leads to the correct equilibrium solutions.

We consider identical particles of mass m with phases $x_i=(\mathbf{r}_i,\mathbf{v}_i)$, where $\mathbf{r}_i$ is the position and $\mathbf{v}_i$ the velocity of particle i, and abbreviate $(x_1,x_2,\ldots,x_N)$ by x^N. The particles are subjected to a time-independent external potential $\Phi(\mathbf{r}_i)$, which includes a wall potential. They interact through a square-well potential $\varphi(r_{ij})$, which is equal to ∞ for $r_{ij}<\sigma$, $-\epsilon=-mv_e^2/4$ for $\sigma\leq r_{ij}<R$ and 0 for $r_{ij}\geq R$, where $r_{ij}=|\mathbf{r}_{ij}|$ with $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$. Here v_e is the minimal relative velocity for two particles to escape from the well. The time evolution of the phase-space density $\rho(x^N;t)$ for an ensemble of such systems is determined by

$$\left[\frac{\partial}{\partial t}+\sum_{i=1}^{N}\left(\mathbf{v}_i\cdot\frac{\partial}{\partial\mathbf{r}_i}-\frac{1}{m}\frac{\partial\Phi(\mathbf{r}_i)}{\partial\mathbf{r}_i}\cdot\frac{\partial}{\partial\mathbf{v}_i}\right)-\sum_{\substack{ij=1\\ j>i}}^{N}\overline{T}_{ij}\right]\rho(x^N;t)=0\ , \tag{1}$$

similar to the pseudo-Liouville equation for hard-sphere fluids.[7] The binary collision operator $\overline{T}_{ij}$ for a pair i,j is most conveniently defined through its adjoint operator $T_{ij}=\overline{T}_{ij}^{\dagger}$, where

$$\int d\mathbf{v}_i\,d\mathbf{v}_j\,fT_{ij}g=\int d\mathbf{v}_i\,d\mathbf{v}_j\,g\overline{T}_{ij}f$$

for any two functions f and g of (x_i,x_j). The terms in $T_{ij}=\sum_{l=1}^{4}T_{ij}^{(l)}$ describe collisions between particles i and j: at the hard core ($l=1$), entering ($l=2$), or leaving ($l=3$) the well, and rebounding at the inside square-well edge ($l=4$). Explicitly,

$$T_{ij}^{(l)}=\lim_{t\to 0^+}S_t^0\delta(r_{ij}-R_l)\,|\mathbf{v}_{ij}\cdot\hat{\mathbf{r}}_{ij}|\Theta_l\,(\mathbf{v}_{ij}\cdot\hat{\mathbf{r}}_{ij})[b^{(l)}(\hat{\mathbf{r}}_{ij})-1]S_t^0 \tag{2}$$

where $R_1=\sigma$, $R_2=R_3=R_4=R$, $\mathbf{v}_{ij}=\mathbf{v}_i-\mathbf{v}_j$, $\hat{\mathbf{r}}_{ij}=\mathbf{r}_{ij}/r_{ij}$, $\Theta_1(y)=\Theta_2(y)=\Theta(-y)$, $\Theta_3(y)=\Theta(y-v_e)$, $\Theta_4(y)=\Theta(y)\times\Theta(v_e-y)$, with $\Theta(y)$ the unit step function. The operators $b^{(l)}(\hat{\boldsymbol{\sigma}})$ replace the relative velocity $\mathbf{v}_{ij}$ in operands by $\mathbf{v}_{ij}-2\hat{\boldsymbol{\sigma}}\mathbf{v}_{ij}\cdot\hat{\boldsymbol{\sigma}}$,

$$\mathbf{v}_{ij}-\hat{\boldsymbol{\sigma}}\{[(\mathbf{v}_{ij}\cdot\hat{\boldsymbol{\sigma}})^2+v_e^2]^{1/2}+\mathbf{v}_{ij}\cdot\hat{\boldsymbol{\sigma}}\}\ ,$$

and

$$\mathbf{v}_{ij}+\hat{\boldsymbol{\sigma}}\{[(\mathbf{v}_{ij}\cdot\hat{\boldsymbol{\sigma}})^2-v_e^2]^{1/2}-\mathbf{v}_{ij}\cdot\hat{\boldsymbol{\sigma}}\}$$

for $l=1,2,3$, respectively, leaving the center-of-mass velocity $(\mathbf{v}_i+\mathbf{v}_j)/2$ unchanged, while $b^{(4)}(\hat{\boldsymbol{\sigma}})=b^{(1)}(\hat{\boldsymbol{\sigma}})$. The free streaming operators S_t^0 are needed to determine how

$T_{ij}^{(l)}$ acts upon functions which are discontinuous at $r_{ij}=R_l$. We note that $T_{ij}^{(l)}h(\mathbf{r}_i,\mathbf{r}_j)=0$ for any function h continuous at $r_{ij}=R_l$ and independent of $\mathbf{v}_i$ and $\mathbf{v}_j$. The adjoints $\overline{T}^{(l)}$ of $T^{(l)}$ follow from Eq. (2), $[b^{(1)}(\hat{\sigma})]^{\dagger}=b^{(1)}(\hat{\sigma})$ and

$$[|\mathbf{v}\cdot\hat{\sigma}|\Theta_2(\mathbf{v}\cdot\hat{\sigma})b^{(2)}(\hat{\sigma})]^{\dagger}=|\mathbf{v}\cdot\hat{\sigma}|\Theta_3(-\mathbf{v}\cdot\hat{\sigma})b^{(3)}(-\hat{\sigma}) \ .$$

From Eqs. (1) and (2) it follows that the one particle distribution function (df)

$$f_1(x;t)=\left\langle\sum_i\delta(x-x_i)\right\rangle$$

and the local potential energy density

$$u(\mathbf{r};t)=\tfrac{1}{2}\left\langle\sum_{\substack{i,j\\ i\neq j}}\varphi(r_{ij})\delta(\mathbf{r}-\mathbf{r}_i)\right\rangle$$

satisfy, respectively,

$$\left[\frac{\partial}{\partial t}+\mathbf{v}_1\cdot\frac{\partial}{\partial\mathbf{r}_1}-\frac{1}{m}\frac{\partial\Phi(\mathbf{r}_1)}{\partial\mathbf{r}_1}\cdot\frac{\partial}{\partial\mathbf{v}_1}\right]f_1(x_1;t)=\int dx_2\,\overline{T}_{12}f_2(x_1,x_2;t) \ , \tag{3a}$$

$$\frac{\partial}{\partial t}u(\mathbf{r}_1;t)+\frac{1}{2}\frac{\partial}{\partial\mathbf{r}_1}\cdot\int d\mathbf{v}_1\int dx_2\,\mathbf{v}_1\phi(r_{12})f_2(x_1,x_2;t)$$
$$=\frac{\epsilon}{2}\int d\mathbf{v}_1\int dx_2|\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}|f_2(x_1,x_2;t)[\Theta(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}-v_e)\delta(r_{12}-R^-)-\Theta(-\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})\delta(r_{12}-R^+)] \ . \tag{3b}$$

Here $R^{\pm}$ indicates evaluation just outside (R^+) or inside (R^-) the square-well edge. The two-particle df $f_2(x,x';t)$ is

$$\left\langle\sum_{\substack{i,j\\ i\neq j}}\delta(x-x_i)\delta(x'-x_j)\right\rangle$$

and

$$\langle(\cdots)\rangle=\sum_{N=0}^{\infty}\int d^Nx\,\rho(x^N;t)(\cdots) \ .$$

To derive Eq. (3b), the operators $\mathbf{v}_i\cdot\partial/\partial\mathbf{r}_i$ in Eq. (1) are understood to be given by the limit of $S_t^0\mathbf{v}_i\cdot\partial/\partial\mathbf{r}_iS_t^0$ for $t\to 0^-$. Equations (3a) and (3b) can be closed if $\rho(x^N;t)$ is approximated by the ensemble $\rho_M(x^N;t)$ that maximizes the entropy under the constraints that at given t, f_1, and u, which are assumed to be known, are reproduced correctly by ρ_M.[1,2] The entropy S as a functional of $\rho(x^N)$ is

$$S(\rho)=-k_B\sum_{N=0}^{\infty}\int dx^N\rho(x^N)\ln[\rho(x^N)a^NN!] \ , \tag{4}$$

where $a=(h/m)^3$, k_B and h are the constants of Boltzmann and Planck, respectively, and

$$\rho_M(x^N;t)=(Za^NN!)^{-1}\exp\left[-\left(\sum_{i=1}^{N}\lambda(x_i;t)+\sum_{\substack{i,j=1\\ j>i}}^{N}\beta_{ij}\varphi(r_{ij})\right)\right] , \tag{5}$$

with

$$\beta_{ij}=[\beta(\mathbf{r}_i;t)+\beta(\mathbf{r}_j;t)]/2$$

and Z the normalization factor. The relations

$$f_1(x;t)=\left\langle\sum_i\delta(x-x_i)\right\rangle_M$$

and

$$u(\mathbf{r};t)=\tfrac{1}{2}\left\langle\sum_{\substack{i,j\\ i\neq j}}\phi(r_{ij})\delta(\mathbf{r}-\mathbf{r}_i)\right\rangle_M$$

($\langle\cdots\rangle_M$ denotes average with ρ_M) yield upon inversion the Lagrange multiplier fields $\lambda(x;t)$ and $\beta(\mathbf{r};t)$ as functionals of f_1 and u. We assume that ρ_M determines all the df's of the fluid, in particular f_2, which depends functionally on λ and β, and hence on u and f_1. Thus our new kinetic theory is closed. The time evolution of f_1 and u, Eqs. (3a) and (3b), determines that of λ and β and of ρ_M. We note that for $\epsilon\to 0$ our new theory reduces to the RET. We will use the following features: (1) In Eq. (5) the velocities of the particles are uncorrelated so that

$$f_2(x_1,x_2;t)=f_1(x_1;t)f_1(x_2;t)g(\mathbf{r}_1,\mathbf{r}_2;t) \ . \tag{6}$$

The $g(\mathbf{r}_1,\mathbf{r}_2;t)$ defined in (6) has the same explicit "n-vertex, f-bond" cluster expansion as its equilibrium counterpart, except that here n is local density $n(r_i)$ and β_{ij} replaces $(k_BT)^{-1}$ in each f bond. As a result our $f_1(x;t)$ can be handled just as explicitly as in the case of the RET or the DRS theory. (For example, transport coefficients can be as readily obtained.) (2) Discontinuities in the potential $\phi(r)$ produce jump discontinuities in $g(\mathbf{r}_1,\mathbf{r}_2;t)$ at $r_{12}=\sigma$ and R. For the latter,

$$g(\mathbf{r}_1,\mathbf{r}_1+R^+\hat{\mathbf{r}}_{21};t)=e^{-\beta_{12}\epsilon}g(\mathbf{r}_1,\mathbf{r}_1+R^-\hat{\mathbf{r}}_{21};t) \ . \tag{7}$$

In general, f_1, u, λ, and β depend continuously on their arguments. (3) We define the field $\alpha(\mathbf{r};t)$ by

$$\alpha(\mathbf{r}_1;t)=\ln\left\{\sum_{N=1}^{\infty}\int dx_2dx_3\cdots dx_N[Za^{N-1}(N-1)!]^{-1}\exp\left[-\left(\sum_{i=2}^{N}\lambda(x_i;t)+\sum_{\substack{i,j=1\\ j>i}}^{N}\beta_{ij}\varphi(r_{ij})\right)\right]\right\} , \tag{8}$$

so that $\lambda(x;t)=\alpha(\mathbf{r};t)-\ln[af_1(x;t)]$. The velocity dependence of λ at $\mathbf{r}$ is directly related to that of $\ln f_1$.

Next we prove the H theorem, i.e., the property that $\partial S(\rho_M(x^N;t))/\partial t\equiv dS(t)/dt\geq 0$. From Eqs. (4) and (5), and subsequently Eq. (8), it follows that

$$\frac{dS(t)}{dt}=k_b\sum_{N=0}^{\infty}\int dx^N\left[\sum_i \lambda(x_i;t)+\sum_{\substack{i,j\\ i<j}}\beta_{ij}\varphi(r_{ij})\right]\frac{\partial\rho_M(x^N;t)}{\partial t}$$

$$=k_B\int dx\,\{\alpha(\mathbf{r};t)-\ln[af_1(x;t)]\}\frac{\partial f_1(x;t)}{\partial t}+k_B\int d\mathbf{r}\,\beta(\mathbf{r};t)\partial u(\mathbf{r};t)/\partial t\ . \tag{9}$$

We consider the three terms on the right-hand side separately. For the first term we obtain

$$\int dx\,\alpha(\mathbf{r};t)\frac{\partial f_1(x;t)}{\partial t}=\tfrac{1}{2}\int dx_1\,dx_2 f_2(x_1,x_2;t)$$
$$\times\left[-\varphi(r_{12})\mathbf{v}_1\cdot\frac{\partial\beta(\mathbf{r}_1;t)}{\partial\mathbf{r}_1}+\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}[\delta(r_{12}-\sigma^+)+\delta(r_{12}-R^+)-\delta(r_{12}-R^-)]\right]\ . \tag{10}$$

This relation follows from Eq. (3a), applying partial integrations with respect to positions and velocities, using $T_{12}\alpha(\mathbf{r}_1;t)=0$ and the explicit forms of $\alpha(\mathbf{r}_1,t)$ [cf. Eq. (8)], $f_1(x;t)$, and $\varphi(r)$. The second term yields similarly

$$-\int dx\,\ln[af_1(x;t)]\frac{\partial f_1(x;t)}{\partial t}=\tfrac{1}{2}\sum_{l=1}^{4}S_l(t) \tag{11}$$

with

$$S_l(t)=-\int dx_1\,dx_2 f_2(x_1,x_2;t)\,T_{12}^{(l)}\ln[a^2f_1(x_1;t)f_1(x_2;t)]\ ,$$

so that, using Eq. (2),

$$S_l(t)=\int dx_1\,dx_2 f_2(x_1,x_2;t)|\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}|\delta(r_{12}-R_l^*)\Theta_l(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})\ln\frac{f_1(x_1;t)f_1(x_2;t)}{b^{(l)}(\hat{\mathbf{r}}_{12})f_1(x_1;t)f_1(x_2;t)} \tag{12}$$

where $R_l^*=\sigma^+$, R^+, R^-, and R^- for $l=1$, 2, 3, and 4, respectively. For the third term we use [cf. Eq. (3b)]

$$\int d\mathbf{r}\,\beta(\mathbf{r};t)\frac{\partial u(\mathbf{r};t)}{\partial t}=\tfrac{1}{2}\int dx_1\,dx_2 f_2(x_1,x_2;t)\left[\varphi(r_{12})\mathbf{v}_1\cdot\frac{\partial\beta(\mathbf{r}_1;t)}{\partial\mathbf{r}_1}+\beta_{12}\epsilon|\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}|\right.$$
$$\left.\times[\Theta(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}-v_e)\delta(r_{12}-R^-)-\Theta(-\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})\delta(r_{12}-R^+)]\right]\ . \tag{13}$$

Collecting results yields

$$\frac{dS(t)}{dt}=\tfrac{1}{2}k_B\int dx_1\,dx_2 f_2(x_1,x_2;t)\left[\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}[\delta(r_{12}-\sigma^+)+\delta(r_{12}-R^+)-\delta(r_{12}-R^-)]\right.$$
$$\left.+|\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}|\sum_{l=1}^{4}\delta(r_{12}-R_l^*)\Theta_l(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})\ln\frac{f_1(x_1;t)f_1(x_2;t)\exp(\beta_{12}E_l)}{b^{(l)}(\hat{\mathbf{r}}_{12})f_1(x_1;t)f_1(x_2;t)}\right]\ , \tag{14}$$

with $E_l=0$, $-\epsilon$, $+\epsilon$, and 0 for $l=1$, 2, 3, and 4, respectively. Next we use in Eq. (14) that $\ln y/z\geqslant 1-z/y$, with $y=f_1(x_1;t)f_1(x_2;t)\exp(\beta_{12}E_l)$ and $z=b^{(l)}(\hat{\mathbf{r}}_{12})f_1(x_1;t)f_1(x_2;t)$, where equality holds only when $y=z$, and that $f_2(x_1,x_2;t)z/y=\exp(-\beta_{12}E_l)b^{(l)}(\mathbf{r}_{12})f_2(x_1,x_2;t)$ as follows from Eq. (6). Thus,

$$\frac{dS(t)}{dt}\geqslant\tfrac{1}{2}k_B\int dx_1\,dx_2\left[\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}[\delta(r_{12}-\sigma^+)+\delta(r_{12}-R^+)-\delta(r_{12}-R^-)]+|\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}|\right.$$
$$\left.\times\sum_{l=1}^{4}\delta(r_{12}-R_l^*)\Theta_l(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})[1-e^{-\beta_{12}E_l}b^{(l)}(\hat{\mathbf{r}}_{12})]\right]f_2(x_1,x_2;t)\ . \tag{15}$$

We let the $b^{(l)}$ operators act to the left, use Eq. (7), and find straightforwardly that the right-hand side of the inequality vanishes identically. Hence $dS(t)/dt\geqslant 0$, which completes the proof of the H theorem.

Distribution functions $f_1^{(0)}(x;t)$, for which $dS/dt=0$, obey the relations

$$\delta(r_{12}-R_l)\Theta_l(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})[e^{\beta_{12}E_l}-b^{(l)}(\hat{\mathbf{r}}_{12})]f_1^{(0)}(x_1;t)f_1^{(0)}(x_2;t)=0\ , \tag{16}$$

for $l=1$, 2, 3, and 4, as follows from Eqs. (14) and (15). Résibois[6] has shown that Eq. (16) with $l=1$ is satisfied if and only if

$$f_1^{(0)}(x;t)=n(\mathbf{r};t)\left[\frac{m}{2\pi k_BT(t)}\right]^{3/2}\exp\left[\frac{-m[\mathbf{v}-\mathbf{V}(t)]^2}{2k_BT(t)}\right]\ , \tag{17}$$

where the (local) density $n(\mathbf{r};t)$ is arbitrary and the (uniform) temperature $T(t)$ and average velocity $\mathbf{V}(t)$ depend on time

only. The $f_1^{(0)}(x;t)$ in Eq. (17) and Eq. (16) with $l=2$, 3, and 4 require the field β to be uniform and equal to $\beta(t)=1/k_BT(t)$. Thus, the parameters n, T, $\mathbf{V}$ in Eq. (17) determine both f_1 and β, and therefore the ensemble $\rho_M^{(0)}$ for which $dS/dt=0$. For equilibrium solutions $n(\mathbf{r})$, $\beta=1/k_BT$ and $\mathbf{V}=\mathbf{0}$ do not depend on t. As a consequence, stationary distributions $f_1^{(0)}(x)$ have the local Maxwellian form given by Eq. (17) where $n(\mathbf{r})$ satisfies [cf. Eqs. (3a), (3b), and (7)],

$$\frac{\partial}{\partial \mathbf{r}_1}[\ln n(\mathbf{r}_1)+\beta\Phi(\mathbf{r}_1)]=\int d\mathbf{r}_2\hat{\mathbf{r}}_{12}[\delta(r_{12}-\sigma^+)+(1-e^{\beta\epsilon})\delta(_{12}-R^+)]n(\mathbf{r}_2)g(\mathbf{r}_1,\mathbf{r}_2)\ , \tag{18}$$

similar to the integral equation for $n(\mathbf{r})$ in the limiting case ($\epsilon=0$) of a hard sphere fluid.[5] Since Eq. (18) is equivalent to the condition that in equilibrium the chemical potential is uniform, $\rho_M^{(0)}$ is the usual grand canonical equilibrium ensemble. Finally, we want to remark that the absence of velocity correlations between the four types of collisions [cf. Eq. (2)], as implied by Eq. (6), is a condition expected to be realized at high densities where the mean free path between collisions is smaller than the width of the square well. This absence prevents the theory from reducing to the Boltzmann limit at low density. The derivation of hydrodynamic equations is presently under investigation, as is the application of the theory to neutron spectra in a like manner to that made with the RET.[8]

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