Linearized kinetic-variational theory and short-time kinetic theory

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We discuss the linearization of the kinetic-variational theory (KVT) II equation for mixtures around absolute equilibrium for a family of pair potentials with hard core and soft tail. In the case of a continuous soft tail, the linear equation reduces to that of Sung and Dahler [J. Chem. Phys. **80**, 3025 (1984)], which in turn generalizes to mixtures, the short-time result of Lebowitz, Percus, and Sykes [Phys. Rev. **188**, 487 (1969)] that had subsequently been obtained by others using different means. Our equation also represents a generalization of the linearized revised Enskog theory to potentials with attractive tails. Hence, at this level of theory the application of the fundamental technique in the kinetic-variational approach, maximization of entropy subject to constraints, is equivalent to the approaches used by others. However, this technique appears to be more amenable to the production of more general theories. Analysis of the structure of the KVT II theory reveals the necessity of relaxation mechanisms for fluid equilibration that are absent in the various linear theories. These include a mechanism for mixing kinetic and potential energies and a temperature associated with the relaxation of the fluid structure. Various options for these are described and compared. A consistent set of mechanisms provided by a more general class of kinetic-variational theories (KVT III) is discussed. These should serve as a useful guide in improving the alternative approaches that are equivalent to linearized KVT II.

I. INTRODUCTION

In this paper we discuss some properties exhibited by the kinetic-variational theory (KVT) II defined in Ref. 1, and we relate that theory to others obtained by quite different means. The kinetic equation associated with KVT II is a member of a sequence of kinetic equations that are derived[1] through a principle of entropy maximization subject to given constraints.[2] These equations describe the dynamics of particles interacting through a potential consisting of a short-ranged repulsive hard-sphere core $\phi^c(r)$ and a longer-ranged soft (but not necessarily continuous) tail $\phi^t(r)$. The sequence of equations is generated by imposing different constraints which yield diverse closures of the exact "first hierarchy" equation.[2] This relates $f_1(x_1,t)$, the one-particle distribution function, to $f_2(x_1,x_2,t)$, the two-particle distribution function [here $x=(\mathbf{r},\mathbf{v})$]. With

$$f_2(x_1,x_2,t)=f_1(x_1,t)f_1(x_2,t)G(x_1,x_2,t) \ , \qquad (1)$$

defining G, the KVT I closure is given by[3]

$$G(x_1,x_2,t)=g_2^{\mathrm{HS}}(\mathbf{r}_1,\mathbf{r}_2|n) \ , \qquad (2)$$

where $g_2^{\mathrm{HS}}(\mathbf{r}_1,\mathbf{r}_2|n)$ denotes the pair correlation function of a nonuniform hard-sphere fluid at equilibrium. When this closure is introduced in Eq. (2) of Ref. 3 we get the KVT I equation. This has been thoroughly investigated[4] and generalized to mixtures.[5] In Ref. 5 it was shown that the KVT I is internally consistent only with soft potentials that are weak and long ranged (*Kac* potentials).

If one imposes a constraint associated with total potential energy in the maximization procedure[1] one obtains a $G(x_1,x_2,t)$ such that

$$G(x_1,x_2,t)=g_2(\mathbf{r}_1,\mathbf{r}_2;\beta(t)|n) \ , \qquad (3)$$

where the $\beta(t)$ is a Lagrange multiplier conjugate to potential energy.

In Eq. (3) the g_2 depends on the full potential rather than just the hard-sphere part. This closure yields the KVT II theory. The extension to mixtures of this result is straightforward and the detailed derivation and study of the transport coefficients associated with it appear elsewhere.[6] Here we limit ourselves to the derivation of the linearized version of KVT II for mixtures. This work extends to mixtures previous work of Karkheck[7] for the linearized one-component KVT II, which was found to coincide with the short-time Lebowitz-Percus-Sykes (LPS) equation[8] derived from linear-response theory. Moreover, this linearized KVT II produced an equation which is identical in structure to the linearized revised Enskog theory[9] (RET) which in turn is identical to a kinetic equation for hard-sphere dynamics that was derived by alternative many-body methods.[10] Furthermore, it can be shown[11] that KVT II can also be associated with the same subset of graphs that van Beijeren used[12] to obtain the RET from a formally exact theory. We show below that the linearized KVT II for mixtures is identical to an equation of Sung and Dahler[13] (SD) that was obtained by using the Mori-Zwanzig formalism. Thus the short-time LPS and SD theories, which were originally derived by different means, can be obtained thorough a maximum-entropy formalism with subsequent linearization. The structure of the kinetic-variational (KV) approach is such that it provides new insight into several limitations of these theories.[14]

The KVT II does not exhibit local energy conservation, as has been shown in Ref. 1. Therefore the linear version also bears this shortcoming, which appears to restrict the theory to describing relaxation processes in which kinetic-potential energy exchange is not a significant factor. This shortcoming prevents consistent introduction of a local spatially varying temperature field, which is a requisite for general relaxation processes, such as transport considered by SD,[13] but is not essential for correctly describing the restricted class of short-time phenomena considered by LPS.[8] The KV approach provides an avenue to eliminate this shortcoming that is discussed in Sec. III.

II. LINEARIZATION OF THE EQUATION

For a potential of the form

$$\begin{aligned} \phi_{ij} &= \infty, \quad r \le \sigma_{ij} \\ \phi_{ij} &= \phi_{ij}^t, \quad r > \sigma_{ij} \end{aligned} \tag{4}$$

where ϕ_{ij} is the potential between a molecule of species i and a molecule of species j, the KVT II kinetic equations for the one-particle distribution functions of an S-species mixture can be written as

$$\begin{aligned} \left[\frac{\partial}{\partial t}+\mathbf{v}_1\cdot\frac{\partial}{\partial \mathbf{r}_1}\right] f_i(\mathbf{r}_1,\mathbf{v}_1,t) = {} & \frac{1}{m_i}\sum_{j=1}^{S}\int d\mathbf{r}_2 n_j(\mathbf{r}_2,t) g_{ij}(\mathbf{r}_1,\mathbf{r}_2;\beta(t)|\{n_k\})\frac{\partial}{\partial \mathbf{r}_1}\phi_{ij}^t(r_{12})\cdot\frac{\partial}{\partial \mathbf{v}_1} f_i(\mathbf{r}_1,\mathbf{v}_1,t) \\ & + \sum_{j=1}^{S}\sigma_{ij}^2\int d\mathbf{v}_2\int d\hat{\boldsymbol{\epsilon}}(\hat{\boldsymbol{\epsilon}}\cdot\mathbf{g})\Theta(\hat{\boldsymbol{\epsilon}}\cdot\mathbf{g})[g_{ij}(\mathbf{r}_1,\mathbf{r}_1+\sigma_{ij}\hat{\boldsymbol{\epsilon}};\beta(t)|\{n_k\})f_i(\mathbf{r}_1,\mathbf{v}_1',t)f_j(\mathbf{r}_1+\sigma_{ij}\hat{\boldsymbol{\epsilon}},\mathbf{v}_2',t) \\ & \qquad - g_{ij}(\mathbf{r}_1,\mathbf{r}_1-\sigma_{ij}\hat{\boldsymbol{\epsilon}};\beta(t)|\{n_k\})f_i(\mathbf{r}_1,\mathbf{v}_1,t) \\ & \qquad \times f_j(\mathbf{r}_1-\sigma_{ij}\hat{\boldsymbol{\epsilon}},\mathbf{v}_2,t)], \end{aligned} \tag{5}$$

where $\mathbf{g}=\mathbf{v}_2-\mathbf{v}_1$, m_i is the particle mass of species i, Θ is the Heaviside function, and g_{ij} is the full nonhomogeneous pair distribution function defined formally by the cluster expansion[15]

$$g_{ij}(\mathbf{r}_1,\mathbf{r}_2;\beta(t)|\{n_k\}) = e^{-\beta(t)\phi_{ij}(r_{12})}\left[1+\sum_{l=1}^{S}\int d\mathbf{r}_l n_l(\mathbf{r}_l,t)V_{ijl}(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_l)+\cdots\right]. \tag{6}$$

The n_l is the local density of species l.

In form, Eq. (5) is sufficient to reproduce the LPS and SD theories. However, the mean-field term does not yield collisional transfer of kinetic and potential energy, which is needed to relax $\beta(t)$. This difficulty does not appear explicitly in the LPS or SD theories because they treat β as a purely thermodynamic quantity for which no fluctuation mechanism is provided. As already noted, this is not generally valid, and will be discussed further in Sec. III.

To provide a relaxation mechanism for $\beta(t)$, one has several options. Time smoothing over a small but finite time interval appears to be one of them; this would add a considerable amount of technical complexity to the theory, however. The introduction of a discontinuity in the potential tail (for example, by truncating the tail) represents another. This mimics the effect of time smoothing but is far simpler, and is of interest in its own right in connection with square-well, truncated Lennard-Jones, and other model potentials with discontinuities in the "soft" potential tail. Therefore, instead of Eq. (4), we consider the potential

$$\begin{aligned} \phi_{ij} &= \infty, \quad r \le \sigma_{ij} \\ &= \phi_{ij}^t(r)\Theta(R_{ij}\sigma_{ij}-r), \quad r > \sigma_{ij} \end{aligned} \tag{7}$$

with $\phi_{ij}^t(r)$ smooth and

$$\phi_{ij}^t(R_{ij}\sigma_{ij}) = -\varepsilon_{ij},$$

such that $\varepsilon_{ij}\to 0$ as $R_{ij}\to\infty$. The correlation function

$$g_{ij}(\mathbf{r}_1,\mathbf{r}_2;\beta(t)|\{n_k\})$$

is still given by Eq. (6) with $\phi_{ij}(r_{12})$ defined by Eq. (7). The kinetic equation for this potential is

$$
\begin{aligned}
(\partial_t+\mathbf{v}_1\cdot\nabla_1)f_i(\mathbf{r}_1,\mathbf{v}_1,t)
&=\frac{1}{m_i}\sum_{j=1}^{S}\frac{\partial}{\partial\mathbf{v}_1}f_i(\mathbf{r}_1,\mathbf{v}_1,t)\int dx_2\Theta(R_{ij}\sigma_{ij}-r_{12})\nabla_1\phi_{ij}^t(r_{12})f_j(x_2,t)g_{ij}(\mathbf{r}_1,\mathbf{r}_2;\beta(t)|\{n_k\})\\
&+\sum_{j=1}^{S}\sigma_{ij}^2\int d\mathbf{v}_2\int d\hat{\epsilon}(\hat{\epsilon}\cdot\mathbf{g})\Theta(\hat{\epsilon}\cdot\mathbf{g})[g_{ij}(\mathbf{r}_1,\mathbf{r}_1+\sigma_{ij}\hat{\epsilon};\beta(t)|\{n_k\})f_i(\mathbf{r}_1,\mathbf{v}_1',t)f_j(\mathbf{r}_1+\sigma_{ij}\hat{\epsilon},\mathbf{v}_2',t)\\
&\qquad -g_{ij}(\mathbf{r}_1,\mathbf{r}_1-\sigma_{ij}\hat{\epsilon};\beta(t)|\{n_k\})f_i(\mathbf{r}_1,\mathbf{v}_1,t)f_j(\mathbf{r}_1-\sigma_{ij}\hat{\epsilon},\mathbf{v}_2,t)]\\
&+\sum_{j=1}^{S}R_{ij}^2\sigma_{ij}^2\int d\mathbf{v}_2\int d\hat{\epsilon}(\hat{\epsilon}\cdot\mathbf{g})\Theta(\hat{\epsilon}\cdot\mathbf{g})[f_i(\mathbf{r}_1,\mathbf{v}_1^+,t)f_j(\mathbf{r}_1+R_{ij}\sigma_{ij}\hat{\epsilon},\mathbf{v}_2^+,t)g_{ij}(\mathbf{r}_1,\mathbf{r}_1+R_{ij}^-\sigma_{ij}\hat{\epsilon};\beta(t)|\{n_k\})\\
&\qquad -f_i(\mathbf{r}_1,\mathbf{v}_1,t)f_j(\mathbf{r}_1-R_{ij}\sigma_{ij}\hat{\epsilon},\mathbf{v}_2,t)g_{ij}(\mathbf{r}_1,\mathbf{r}_1-R_{ij}^+\sigma_{ij}\hat{\epsilon};\beta(t)|\{n_k\})\\
&\qquad +\Theta(\hat{\epsilon}\cdot\mathbf{g}-(2\varepsilon_{ij}/\mu_{ij})^{1/2})\\
&\qquad \times[f_i(\mathbf{r}_1,\mathbf{v}_1^-,t)f_j(\mathbf{r}_1-R_{ij}\sigma_{ij}\hat{\epsilon},\mathbf{v}_2^-,t)g_{ij}(\mathbf{r}_1,\mathbf{r}_1-R_{ij}^+\sigma_{ij}\hat{\epsilon};\beta(t)|\{n_k\})\\
&\qquad -f_i(\mathbf{r}_1,\mathbf{v}_1,t)f_j(\mathbf{r}_1+R_{ij}\sigma_{ij}\hat{\epsilon},\mathbf{v}_2,t)g_{ij}(\mathbf{r}_1,\mathbf{r}_1+R_{ij}^-\sigma_{ij}\hat{\epsilon};\beta(t)|\{n_k\})]\\
&\qquad +\Theta((2\varepsilon_{ij}/\mu_{ij})^{1/2}-\hat{\epsilon}\cdot\mathbf{g})\\
&\qquad \times[f_i(\mathbf{r}_1,\mathbf{v}_1',t)f_j(\mathbf{r}_1-R_{ij}\sigma_{ij}\hat{\epsilon},\mathbf{v}_2',t)g_{ij}(\mathbf{r}_1,\mathbf{r}_1-R_{ij}^-\sigma_{ij}\hat{\epsilon};\beta(t)|\{n_k\})\\
&\qquad -f_i(\mathbf{r}_1,\mathbf{v}_1,t)f_j(\mathbf{r}_1+R_{ij}\sigma_{ij}\hat{\epsilon},\mathbf{v}_2,t)g_{ij}(\mathbf{r}_1,\mathbf{r}_1+R_{ij}^-\sigma_{ij}\hat{\epsilon};\beta(t)|\{n_k\})]] , \qquad (8)
\end{aligned}
$$

where the first term in the right-hand side (rhs) is a mean-field term for the smooth part of the potential, the second term gives the hard-core collision, and the last three terms represent the square-well-like collisions[16] at the discontinuity. To round out the theory, we must include an equation for the time evolution of the potential energy, which in essence yields the time evolution of $\beta(t)$. Taken together, these equations support an H theorem which shows that f_i and $\beta(t)$ relax to the canonical equilibrium forms. The potential-energy equation itself is not needed in what follows, however.

Linearization is performed around absolute equilibrium,

$$f_i=n_{0i}h_i(\mathbf{v})+\eta_i \; , \qquad (9a)$$

$$\beta(t)=\beta_0+\delta\beta(t) \; , \qquad (9b)$$

where $n_{0i}h_i(\mathbf{v})$ is the absolute equilibrium Maxwellian distribution function and η_i is a small fluctuation. The identification $\beta_0=1/kT_0=\text{const}$, where T_0 is the equilibrium temperature appearing in h_i, follows from the leading-order term in the expansion of the square-well-like collision integrals. The fluctuation $\delta\beta$, governed by the fluctuation of total potential energy, vanishes in the thermodynamic limit. So the nonfluctuation of $\beta(t)$ exhibited by the LPS and SD theories arises naturally here due to collisions at the tail discontinuity.

Since

$$\mathbf{v}_1'-\mathbf{v}_1=2M_{ji}(\mathbf{g}\cdot\hat{\epsilon})\hat{\epsilon} \qquad (10a)$$

and

$$\mathbf{v}_1^{\mp}-\mathbf{v}_1=M_{ij}\{(\hat{\epsilon}\cdot\mathbf{g})-[(\mathbf{g}\cdot\hat{\epsilon})^2\pm(2\varepsilon_{ij}/\mu_{ij})]^{1/2}\}\hat{\epsilon} \; , \qquad (10b)$$

where $M_{ji}=m_j/m_i+m_j$ and $\mu_{ij}=m_iM_{ji}$, it follows that

$$h_i(\mathbf{v}_1^{\mp})h_j(\mathbf{v}_2^{\mp})=e^{\mp\beta\varepsilon_{ij}}h_i(\mathbf{v}_1)h_j(\mathbf{v}_2) \; . \qquad (11)$$

Upon integration over the velocity in Eq. (9a) we obtain

$$n_i(\mathbf{r}_1,t)=n_{0i}+\delta n_i=n_{0i}+\int d\mathbf{v}\,\eta_i \; , \qquad (12)$$

whereupon, to linear order, we get

$$\Delta g_{ij}=g_{ij}-g_{ij}^{\text{eq}}=\sum_{L=1}^{S}\int dx'\eta_L(x',t)\left.\frac{\delta g_{ij}(\mathbf{r}_1,\mathbf{r}_2,t)}{\delta n_L(\mathbf{r}',t)}\right|_{\{n_{0L}\}} , \qquad (13)$$

from which we can show that

$$\Delta g_{ij}(\mathbf{r}_1,\mathbf{r}_1\pm R_{ij}^-\sigma_{ij}\hat{\epsilon},t)=e^{\beta\varepsilon_{ij}}\Delta g_{ij}(\mathbf{r}_1,\mathbf{r}_1\pm R_{ij}^+\sigma_{ij}\hat{\epsilon},t) \; . \qquad (14)$$

Combining Eqs. (8), (9), and (11)–(14), we arrive at the linearized equation

$$
\begin{aligned}
&(\partial_t+\mathbf{v}_1\cdot\nabla_1)\eta_i(\mathbf{r}_1,\mathbf{v}_1,t)\\
&\quad=-\beta h_i(\mathbf{v}_1)\mathbf{v}_1\cdot\sum_{J=1}^{S}n_{0i}n_{0j}\int dx_2\Theta(R_{ij}\sigma_{ij}-r_{12})\nabla_1\phi_{ij}^t h_j(\mathbf{v}_2)\Delta g_{ij}\\
&\qquad+\sum_{J=1}^{S}n_{0i}n_{0j}\sigma_{ij}^2 h_i(\mathbf{v}_1)\\
&\qquad\times\int d\mathbf{v}_2 h_j(\mathbf{v}_2)\int d\mathbf{r}_2\int d\hat{\boldsymbol\epsilon}(\hat{\boldsymbol\epsilon}\cdot\mathbf{g})\Delta g_{ij}(\mathbf{r}_1,\mathbf{r}_2,t)\\
&\qquad\qquad\times[\delta(\mathbf{r}_2-\mathbf{r}_1-\sigma_{ij}\hat{\boldsymbol\epsilon})+R_{ij}^2\delta(\mathbf{r}_2-\mathbf{r}_1-R_{ij}^+\sigma_{ij}\hat{\boldsymbol\epsilon})-R_{ij}^2\delta(\mathbf{r}_2-\mathbf{r}_1-R_{ij}^-\sigma_{ij}\hat{\boldsymbol\epsilon})]\\
&\qquad-\beta\sum_{J=1}^{S}\int dx_2\Theta(R_{ij}\sigma_{ij}-r_{12})\mathbf{v}_1\cdot\nabla_1\phi_{ij}^t n_{0i}h_i(\mathbf{v}_1)\eta_j(x_2,t)g_{ij}^{\mathrm{eq}}(r_{12})\\
&\qquad+\sum_{J=1}^{S}\sigma_{ij}^2\int d\mathbf{v}_2\int d\hat{\boldsymbol\epsilon}(\hat{\boldsymbol\epsilon}\cdot\mathbf{g})\Theta(\hat{\boldsymbol\epsilon}\cdot\mathbf{g})\\
&\qquad\qquad\times[g_{ij}^{\mathrm{eq}}(\sigma_{ij}^+)[n_{0i}h_i(\mathbf{v}_1')\eta_j(\mathbf{r}_1+\sigma_{ij}\hat{\boldsymbol\epsilon},\mathbf{v}_2',t)+n_{0j}h_j(\mathbf{v}_2')\eta_i(\mathbf{r}_1,\mathbf{v}_1',t)\\
&\qquad\qquad\qquad-n_{0i}h_i(\mathbf{v}_1)\eta_j(\mathbf{r}_1-\sigma_{ij}\hat{\boldsymbol\epsilon},\mathbf{v}_2,t)-n_{0j}h_j(\mathbf{v}_2)\eta_i(\mathbf{r}_1,\mathbf{v}_1,t)]\\
&\qquad\qquad+R_{ij}^2 g_{ij}(R^-\sigma_{ij})\{n_{0i}h_i(\mathbf{v}_1^+)\eta_j(\mathbf{r}_1+R_{ij}\sigma_{ij}\hat{\boldsymbol\epsilon},\mathbf{v}_2^+,t)+n_{0j}h_j(\mathbf{v}_2^+)\eta_i(\mathbf{r}_1,\mathbf{v}_1^+,t)\\
&\qquad\qquad\qquad-e^{-\beta\varepsilon_{ij}}n_{0i}h_i(\mathbf{v}_1)\eta_j(\mathbf{r}_1-R_{ij}\sigma_{ij}\hat{\boldsymbol\epsilon},\mathbf{v}_2,t)-e^{-\beta\varepsilon_{ij}}n_{0j}h_j(\mathbf{v}_2)\eta_i(\mathbf{r}_1,\mathbf{v}_1,t)\\
&\qquad\qquad\qquad+\Theta(\hat{\boldsymbol\epsilon}\cdot\mathbf{g}-(2\varepsilon_{ij}/\mu_{ij})^{1/2})\\
&\qquad\qquad\qquad\quad\times[e^{-\beta\varepsilon_{ij}}n_{0i}h_i(\mathbf{v}_1^-)\eta_j(\mathbf{r}_1-R_{ij}\sigma_{ij}\hat{\boldsymbol\epsilon},\mathbf{v}_2^-,t)+e^{-\beta\varepsilon_{ij}}n_{0j}h_j(\mathbf{v}_2^-)\eta_i(\mathbf{r}_1,\mathbf{v}_1^-,t)\\
&\qquad\qquad\qquad\qquad-n_{0i}h_i(\mathbf{v}_1)\eta_j(\mathbf{r}_1+R_{ij}\sigma_{ij}\hat{\boldsymbol\epsilon},\mathbf{v}_2,t)-n_{0j}h_j(\mathbf{v}_2)\eta_i(\mathbf{r}_1,\mathbf{v}_1,t)]\\
&\qquad\qquad\qquad+\Theta((2\varepsilon_{ij}/\mu_{ij})^{1/2}-\hat{\boldsymbol\epsilon}\cdot\mathbf{g})\\
&\qquad\qquad\qquad\quad\times[n_{0i}h_i(\mathbf{v}_1')\eta_j(\mathbf{r}_1-R_{ij}\sigma_{ij}\hat{\boldsymbol\epsilon},\mathbf{v}_2',t)+n_{0j}h_j(\mathbf{v}_2')\eta_i(\mathbf{r}_1,\mathbf{v}_1',t)\\
&\qquad\qquad\qquad\qquad-n_{0i}h_i(\mathbf{v}_1)\eta_j(\mathbf{r}_1+R_{ij}\sigma_{ij}\hat{\boldsymbol\epsilon},\mathbf{v}_2,t)-n_{0j}h_j(\mathbf{v}_2)\eta_i(\mathbf{r}_1,\mathbf{v}_1,t)]\}]\ .
\end{aligned}\tag{15}
$$

The first two terms on the rhs can be combined to yield

$$
n_{0i}h_i(\mathbf{v}_1)\mathbf{v}_1\cdot\sum_{L=1}^{S}\int dx_2\eta_L(x_2,t)(\nabla_1 C_{iL}(r_{12})-g_{iL}^{\mathrm{eq}}\nabla_1 f_{iL}^M)\ ,\tag{16}
$$

where $C_{iL}(r)$ is the homogeneous direct correlation function of the system and some properties of the Mayer function $f_{12}^M=e^{-\beta\phi(r_{12})}-1$ have been used.

Combining Eq. (16) with the third term in the rhs of Eq. (15) we finally arrive at

$$
\begin{aligned}
&(\partial_t+\mathbf{v}_1\cdot\nabla_1)\eta_i(\mathbf{r}_1,\mathbf{v}_1,t)\\
&\quad=n_{0i}h_i(\mathbf{v}_1)\mathbf{v}_1\cdot\nabla_1\sum_{L=1}^{S}\int dx_2\eta_L(x_2,t)[C_{iL}(r_{12})+g_{iL}^{\mathrm{eq}}(\sigma_{iL})\Theta(\sigma_{iL}^+-r_{12})+(1-e^{\beta\varepsilon_{iL}})g_{iL}^{\mathrm{eq}}(R_{iL}^+\sigma_{iL})\Theta(R_{iL}^+\sigma_{iL}-r_{12})]\\
&\qquad+\sum_{J=1}^{S}\sigma_{ij}^2\int d\mathbf{v}_2\int d\hat{\boldsymbol\epsilon}(\hat{\boldsymbol\epsilon}\cdot\mathbf{g})\Theta(\hat{\boldsymbol\epsilon}\cdot\mathbf{g})\\
&\qquad\qquad\times[g_{ij}^{\mathrm{eq}}(\sigma_{ij}^+)[n_{0i}h_i(\mathbf{v}_1')\eta_j(\mathbf{r}_1+\sigma_{ij}\hat{\boldsymbol\epsilon},\mathbf{v}_2',t)+n_{0j}h_j(\mathbf{v}_2')\eta_i(\mathbf{r}_1,\mathbf{v}_1',t)-n_{0i}h_i(\mathbf{v}_1)\eta_j(\mathbf{r}_1-\sigma_{ij}\hat{\boldsymbol\epsilon},\mathbf{v}_2,t)\\
&\qquad\qquad\qquad-n_{0j}h_j(\mathbf{v}_2)\eta_i(\mathbf{r}_1,\mathbf{v}_1,t)]\\
&\qquad\qquad+R_{ij}^2 g_{ij}(R_{ij}^-\sigma_{ij})\{n_{0i}h_i(\mathbf{v}_1^+)\eta_j(\mathbf{r}_1+R_{ij}\sigma_{ij}\hat{\boldsymbol\epsilon},\mathbf{v}_2^+,t)+n_{0j}h_j(\mathbf{v}_2^+)\eta_i(\mathbf{r}_1,\mathbf{v}_1^+,t)\\
&\qquad\qquad\qquad-e^{-\beta\varepsilon_{ij}}n_{0i}h_i(\mathbf{v}_1)\eta_j(\mathbf{r}_1-R_{ij}\sigma_{ij}\hat{\boldsymbol\epsilon},\mathbf{v}_2,t)-e^{-\beta\varepsilon_{ij}}n_{0j}h_j(\mathbf{v}_2)\eta_i(\mathbf{r}_1,\mathbf{v}_1,t)\\
&\qquad\qquad\qquad+\Theta(\hat{\boldsymbol\epsilon}\cdot\mathbf{g}-(2\varepsilon_{ij}/\mu_{ij})^{1/2})\\
&\qquad\qquad\qquad\quad\times[e^{-\beta\varepsilon_{ij}}n_{0i}h_i(\mathbf{v}_1^-)\eta_j(\mathbf{r}_1-R_{ij}\sigma_{ij}\hat{\boldsymbol\epsilon},\mathbf{v}_2^-,t)+e^{-\beta\varepsilon_{ij}}n_{0j}h_j(\mathbf{v}_2^-)\eta_i(\mathbf{r}_1,\mathbf{v}_1^-,t)\\
&\qquad\qquad\qquad\qquad-n_{0i}h_i(\mathbf{v}_1)\eta_j(\mathbf{r}_1+R_{ij}\sigma_{ij}\hat{\boldsymbol\epsilon},\mathbf{v}_2,t)-n_{0j}h_j(\mathbf{v}_2)\eta_i(\mathbf{r}_1,\mathbf{v}_1,t)]\\
&\qquad\qquad\qquad+\Theta((2\varepsilon_{ij}/\mu_{ij})^{1/2}-\hat{\boldsymbol\epsilon}\cdot\mathbf{g})\\
&\qquad\qquad\qquad\quad\times[n_{0i}h_i(\mathbf{v}_1')\eta_j(\mathbf{r}_1-R_{ij}\sigma_{ij}\hat{\boldsymbol\epsilon},\mathbf{v}_2',t)+n_{0j}h_j(\mathbf{v}_2')\eta_i(\mathbf{r}_1,\mathbf{v}_1',t)\\
&\qquad\qquad\qquad\qquad-n_{0i}h_i(\mathbf{v}_1)\eta_j(\mathbf{r}_1+R_{ij}\sigma_{ij}\hat{\boldsymbol\epsilon},\mathbf{v}_2,t)-n_{0j}h_j(\mathbf{v}_2)\eta_i(\mathbf{r}_1,\mathbf{v}_1,t)]\}]\ ,
\end{aligned}\tag{17}
$$

which generalizes the LPS and SD equations. To recover these equations we observe that for short-ranged ϕ_{ij}^t, $\varepsilon_{ij} \to 0$ strongly as $R_{ij} \to \infty$ so that the step contributions vanish in that limit. Therefore we get

$$(\partial_t + \mathbf{v}_1 \cdot \nabla_1)\eta_i(\mathbf{r}_1, \mathbf{v}_1, t) = \sum_{J=1}^{S} \sigma_{ij}^2 g_{ij}^{\text{eq}}(\sigma_{ij}^+) \times \int d\mathbf{v}_2 \int d\hat{\epsilon}(\hat{\epsilon}\cdot\mathbf{g})\Theta(\hat{\epsilon}\cdot\mathbf{g})[n_{0i}h_i(\mathbf{v}_1')\eta_j(\mathbf{r}_1 + \sigma_{ij}\hat{\epsilon}, \mathbf{v}_2', t) + n_{0j}h_j(\mathbf{v}_2')\eta_i(r_1, \mathbf{v}_1', t) - n_{0i}h_i(\mathbf{v}_1)\eta_j(\mathbf{r}_1 - \sigma_{ij}\hat{\epsilon}, \mathbf{v}_2, t) - n_{0j}h_j(\mathbf{v}_2)\eta_i(\mathbf{r}_1, \mathbf{v}_1, t)] + n_{0i}h_i(\mathbf{v}_1)\mathbf{v}_1\cdot\nabla_1 \sum_{L=1}^{S} \int dx_2 \eta_L(x_2, t)[C_{iL}(r_{12}) - g_{iL}^{\text{eq}}(\sigma_{iL}^+)\Theta(\sigma_{iL}^+ - r_{12})] \ . \tag{18}$$

Equation (18) can be Fourier transformed to give

$$(\partial_t + i\mathbf{k}\cdot\mathbf{v}_1)\chi_i = \sum_{J=1}^{S} \sigma_{ij}^2 g_{ij}^{\text{eq}}(\sigma_{ij}^+) \times \int d\mathbf{v}_2 \int d\hat{\epsilon}(\hat{\epsilon}\cdot\mathbf{g})\Theta(\hat{\epsilon}\cdot\mathbf{g}) \times [n_{0j}h_j'\chi_i(\mathbf{k}, \mathbf{v}_1', t) - n_{0j}h_j\chi_i(\mathbf{k}, \mathbf{v}_1, t) + n_{0i}h_i' e^{i\mathbf{k}\cdot\sigma_{ij}\hat{\epsilon}}\chi_j(\mathbf{k}, \mathbf{v}_2', t) - n_{0i}h_i e^{-i\mathbf{k}\cdot\sigma_{ij}\hat{\epsilon}}\chi_j(\mathbf{k}, \mathbf{v}_2, t)] + in_{0i}h_i(\mathbf{v}_1)\mathbf{v}_1\cdot\mathbf{k} \sum_{L=1}^{S} \left[\tilde{C}_{iL}(\mathbf{k}) + \frac{4\pi\sigma_{iL}^3}{k} j_1(k\sigma_{iL}) g_{iL}^{\text{eq}}(\sigma_{iL}^+)\right] \int \chi_L(\mathbf{k}, \mathbf{v}_L, t) d\mathbf{v}_L \ , \tag{19}$$

where $j_1(x)$ is a spherical Bessel function, and

$$\chi_i(\mathbf{k}, \mathbf{v}, t) = \int d\mathbf{r}\, e^{-i\mathbf{k}\cdot\mathbf{r}}\eta_i(\mathbf{r}, \mathbf{v}, t) \ .$$

This is the SD equation, which reduces to the LPS equation in the case of a single species.

III. DISCUSSION

Equation (19) is an extension of RET (Ref. 9) to mixtures of particles interacting with potentials which possess a repulsive core and a continuous tail. Equations of this type have been used for a description of the short-time behavior of space- and time-dependent fluctuations.[17] We have shown that these linearized kinetic equations can be obtained from the nonlinear KVT II theory. The full realm of validity or utility of (19) is not known. However, several features are already clear.

(i) When applied to initial-value problems associated with one-particle fluctuations about absolute equilibrium, Eq. (19) produces correct predictions[7] for short-time behavior, just as does the LPS equation,[8] e.g., sum rules through third derivative of $F(\mathbf{k}, t)$, the intermediate scattering function. This holds also for Eq. (17), and such results do not change when local energy conservation (KVT III) is included.[18]

(ii) For long times, and in particular for transport applications, there is no doubt that (19) is not exact, since it leaves out velocity correlations which build up in time. It is well known these have a significant numerical effect on the diffusion coefficient and shear viscosity of the hard-sphere fluid. These velocity correlations are suppressed in the LPS and SD theories by neglect of the memory terms; in KVT II the neglect of velocity correlation stems from its absence in Eq. (3). [In the corresponding kinetic reference theory (KRT II), one replaces[1,19] the effect of this missing correlation by that in a hard-sphere system at the same temperature and density. This effect is known quite accurately for hard spheres through computer simulations.]

(iii) Although the introduction of a discontinuity in $\phi_{ij}(r)$ provides a mechanism for potential-kinetic energy transfer in our approximation, there is still no mechanism for generating a well-defined temperature field $\beta(\mathbf{r}, t)$ in KVT II and its linearization or in theories equivalent to these. The need for such a quantity is supported by the presence, in general, of a fluctuating temperature $T(\mathbf{r}, t)$ manifested in (9a). This situation is somewhat analogous to the condition of the original standard Enskog theory (SET) with regard to density-field dependence. The density field $n(\mathbf{r}, t)$ is manifested in f_1, viz.,

$$n(\mathbf{r}, t) = \int f_1(\mathbf{r}, \mathbf{v}, t) d\mathbf{v} \ . \tag{20a}$$

The SET approximant to $G(x_1, x_2, t)$ is the radial distribution function for a *uniform* hard-sphere system at equilibrium evaluated at the number density $n = n(\mathbf{R}, t)$ where

$$\mathbf{R} = \frac{\mathbf{r}_1 + \mathbf{r}_2}{2} \tag{20b}$$

is the midpoint between centers of spheres in contact. This recipe yields a linearized theory that is not equivalent to the LPS equation and is somewhat inferior to it.[14] Moreover, its generalization to mixtures is not unique and whatever choice is made yields a theory that is inconsistent with the Onsager reciprocal relations, as first shown by Barajas *et al.*[20]

For interparticle potentials other than pure hard spheres, local thermodynamic quantities such as pressure depend upon local temperature in a nontrivial manner, and deviations from these local quantities bear dependence upon the gradients of local temperature. An early attempt to introduce such a local temperature was made in the theory of Davis, Rice, and Sengers,[21] who extended the Enskog ansatz for density field to the temperature field, treating $G(x_1,x_2,t)$ again as the equilibrium function but for a fluid of square-well particles at density $n(\mathbf{R},t)$ and temperature $T(\mathbf{R},t)$, with $\mathbf{R}$ the midpoint and T defined by

$$3n(\mathbf{r},t)kT(\mathbf{r},t)=\int m(\mathbf{v}-\mathbf{u})^2 f_1(\mathbf{r},\mathbf{v},t)d\mathbf{v} \;, \qquad (21a)$$

where $\mathbf{u}(\mathbf{r},t)=\int \mathbf{v} f_1 d\mathbf{v}/n(\mathbf{r},t)$, and

$$\beta(\mathbf{r},t)=1/kT(\mathbf{r},t) \;. \qquad (21b)$$

Problems associated with this approach have been discussed in Refs. 16 and 22. Again, it cannot be uniquely generalized to the case of mixtures.

(iv) In the KVT III, in which[1] the global energy constraint is replaced by a local energy constraint and an equation for the time evolution of the potential-energy density is conjoined to that for f_1, a potential-energy temperature field is introduced in a more satisfactory way that amounts to replacement of the $\beta(t)$, in Eq. (3), by $\beta(\mathbf{r},t)$ and, in (6), by

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

[This $\beta(\mathbf{r},t)$ is in general no longer the reciprocal of $kT(\mathbf{r},t)$ given by (21a), as discussed in some detail in Ref. 22, where it was shown that numerical distinction between these quantities has direct effect on the value of the bulk viscosity.] In the resulting theory,[7,16] one still requires an additional mechanism to assure mixing of potential and kinetic energies, and velocity correlation is still missing in Eq. (3). But the satisfaction of local energy conservation nevertheless removes an important limitation found in KVT II, and it will be of great interest to understand how different from (19) the linearized KVT III equations are found to be, and how the LPS and SD approaches must be modified to yield the linearized KVT III equations.[7]

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