Kinetic variational theory for mixtures: Kac-tail limit

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A kinetic-variational theory recently derived for a pure fluid on the basis of maximization of entropy is given for mixtures. Explicit results are found for particles interacting via hard cores and Kac tails (i.e., weak long-range attraction).

In a previous article[1] we described the derivation of a mean-field type of kinetic equation for the one-particle distribution function for a one-component fluid whose particles interact through a pair potential consisting of a hard-sphere core plus a smooth attractive tail. In a separate investigation[2] we studied the thermodynamic and transport properties embedded in that equation. In this letter we extend the theory to a mixture of L species for the limiting case of the Kac-tail attractive potential.[3]

In Ref. 1 it is shown how, through maximization of entropy subject to certain constraints, a closed one-particle kinetic-variational equation and, at the same time, an entropy functional can be obtained which together engender an H theorem. The generalization of those results for mixtures turns out to be straightforward so that details are omitted here. The set of kinetic-variational equations for L species is, $i=1,\ldots,L$,

$$\left[\frac{\partial}{\partial t}+\vec{v}_1\cdot\vec{\nabla}_1\right]f_i(\vec{r}_1,\vec{v}_1,t)=C^{\mathrm{RET}}(f,f)+\frac{1}{m_i}\sum_{j=1}^{L}\int_{r_{12}>\sigma_{ij}}d\vec{r}_2 n_j(\vec{r}_2,t)g_{ij}^{HS}(\vec{r}_1,\vec{r}_2\,|\,\{n_k\})\times\vec{\nabla}_1\phi_{ij}^{\mathrm{tail}}(r_{12})\cdot\frac{\partial}{\partial\vec{v}_1}f_i(\vec{r}_1,\vec{v}_1,t)\;. \tag{1}$$

Notation is explained in Ref. 2. The shape of the attractive tail, $\phi_{ij}^{\mathrm{tail}}$, is continuous but otherwise arbitrary. The collision term, C^{RET}, has exactly the form of that which appears in the revised Enskog theory, introduced by van Beijeren and Ernst,[4]

$$C^{\mathrm{RET}}(f,f)=\sum_{j=1}^{L}\sigma_{ij}^2\int d\vec{v}_2\int d\hat{\sigma}\,\hat{\sigma}\cdot\vec{g}\,\Theta(\hat{\sigma}\cdot\vec{g})[g_{ij}^{HS}(\vec{r}_1,\vec{r}_1+\sigma_{ij}\hat{\sigma}\,|\,\{n_k\})f_i(\vec{r}_1,\vec{v}\,'_1,t)f_j(\vec{r}_1+\sigma_{ij}\hat{\sigma},\vec{v}\,'_2,t)-g_{ij}^{HS}(\vec{r}_1,\vec{r}_1-\sigma_{ij}\hat{\sigma}\,|\,\{n_k\})f_i(\vec{r}_1,\vec{v}_1,t)f_j(\vec{r}_1-\sigma_{ij}\hat{\sigma},\vec{v}_2,t)]\;. \tag{2}$$

Here σ_{ij} need not equal $\frac{1}{2}(\sigma_i+\sigma_j)$. The entropy functional is obtained as

$$S=k\ln\Phi(t)-k\sum_{i=1}^{L}\int d\vec{r}\,d\vec{v}\,f_i(\vec{r},\vec{v},t)\ln f_i(\vec{r},\vec{v},t)+k\sum_{i=1}^{L}\int d\vec{r}\,n_i(\vec{r},t)\ln a_i(\vec{r},t)\;. \tag{3}$$

The a_i is a function of f_i and depends only upon $\vec{r},t$; the $n_i=\int d\vec{v}\,f_i(\vec{r},\vec{v},t)$. The tail strength is not manifested explicitly in S, which reduces to S^{HS} at equilibrium. $\Phi(t)$, a normalization factor that plays a role analogous to the partition function in equilibrium theory, depends only upon the hard-core part of the potential. It is straightforward to show that $(\partial/\partial t)S \geq 0$ via (1) + (2), equality holding[1] when $f_i = f_i^0 = R_i(\vec{r},t)V_i(\vec{v},t)$. This is a stronger condition than f_i being a local Maxwellian f_i^{LM}, which is the corresponding result in the Boltzmann theory.[5] Unlike the case in the Boltzmann theory, here $(\partial/\partial t)S = 0$ is not sufficient to make the collision integral C^{RET} zero.[1]

The Kac limit[3] can be effected by taking $\sigma_{ij} \rightarrow 0$ in the mean-field term, which takes the form

$$\frac{1}{m_i} \sum_{j=1}^{L} \gamma^4 \int d\vec{r}_2 n_j(\vec{r}_2,t)\hat{r}_{12} V_{ij}'(\gamma r_{12}) \cdot \frac{\partial}{\partial \vec{v}_1} f_i(\vec{r}_1,\vec{v}_1,t) \; . \tag{4}$$

This mean-field term embodies naturally the "external" potential fields assumed in Ref. 6. We use $\phi_{ij}^{\mathrm{tail}} = \gamma^3 V_{ij}(\gamma r)$ in the usual Kac limit, $\gamma \rightarrow 0$. The limiting kinetic equation (1) + (4), when $L=1$, is of the Enskog-Vlasov type[7] which has been used to study condensation phenomena.

The conservation laws for n_i,

$$\vec{u} = \frac{1}{\rho} \sum_{i=1}^{L} \int d\vec{v}\, m_i \vec{v} f_i \; ,$$

and

$$T = \frac{1}{\frac{3}{2}nk} \sum_{i=1}^{L} \int d\vec{v} \tfrac{1}{2} m_i (\vec{v} - \vec{u})^2 f_i \; ,$$

where

$$\rho = \sum_{i=1}^{L} n_i m_i \equiv \sum_{i=1}^{L} \rho_i$$

and

$$n = \sum_{i=1}^{L} n_i \; ,$$

are found by taking the zeroth, first, and second velocity moments of (1) + (2) + (4) and they take the form

$$\frac{\partial}{\partial t} n_i + \vec{\nabla}_1 \cdot n_i \vec{u}_i = 0 \; , \tag{5a}$$

with

$$\vec{u}_i = \frac{1}{n_i} \int d\vec{v}\, \vec{v} f_i \; ,$$

$$\rho \frac{d}{dt} \vec{u} + \vec{\nabla}_1 \cdot \overleftrightarrow{P} = 0 \; , \tag{5b}$$

where the momentum flux has three terms[2]: $\overleftrightarrow{P} = \overleftrightarrow{P}^s + \overleftrightarrow{P}^c + \overleftrightarrow{P}^t$ and

$$\overleftrightarrow{P}^s(\vec{r}_1,t) = \sum_{i=1}^{L} \int d\vec{v}\, m_i (\vec{v} - \vec{u})(\vec{v} - \vec{u}) f_i \; , \tag{6a}$$

$$\begin{aligned} \overleftrightarrow{P}^c(\vec{r}_1,t) = \tfrac{1}{2} \sum_{i,j=1}^{L} m_i \sigma_{ij}^3 \int d\vec{v}_1 d\vec{v}_2 \int d\hat{\sigma}\, \hat{\sigma} \cdot \vec{g}\, \Theta(\hat{\sigma} \cdot \vec{g}) \hat{\sigma} (\vec{v}_1' - \vec{v}_1) \\ \times \int_0^1 d\lambda\, f_i(\vec{r}_1 + \lambda \sigma_{ij} \hat{\sigma}, \vec{v}_1, t) f_j(\vec{r}_1 + \lambda \sigma_{ij} \hat{\sigma} - \sigma_{ij} \hat{\sigma}, \vec{v}_2, t) \\ \times g_{ij}^{HS}(\vec{r}_1 + \lambda \sigma_{ij} \hat{\sigma}, \vec{r}_1 + \lambda \sigma_{ij} \hat{\sigma} - \sigma_{ij} \hat{\sigma} \mid \{ n_k \}) \; , \end{aligned} \tag{6b}$$

$$\overleftrightarrow{P}^t(\vec{r}_1,t) = -\tfrac{1}{2} \sum_{i,j=1}^{L} \gamma^4 \int_0^1 d\lambda \int d\vec{s}\, \hat{s} \vec{s}\, V_{ij}'(\gamma s) n_i(\lambda \vec{s} - \vec{s} + \vec{r}_1, t) n_j(\lambda \vec{s} + \vec{r}_1, t) \; , \tag{6c}$$

and

$$\frac{\partial}{\partial t}\,\tfrac{3}{2}nkT+\vec{\nabla}_1\cdot\tfrac{3}{2}nkT\vec{u}+\vec{\nabla}_1\cdot\vec{J}_q^T+\vec{P}^{s+c}:\nabla_1\vec{u}=\gamma^4\sum_{i,j=1}^{L}(\vec{u}_i-\vec{u})\cdot\int d\vec{s}\,\hat{s}V'_{ij}(\gamma s)n_i(\vec{r}_1,t)n_j(\vec{r}_1+\vec{s},t)\;. \tag{5c.1}$$

The temperature component of the heat flux is $\vec{J}_q^T=\vec{J}_q^s+\vec{J}_q^c$, where

$$\vec{J}_q^s(\vec{r}_1,t)=\sum_{i=1}^{L}\int d\vec{v}\;\tfrac{1}{2}m_i(\vec{v}-\vec{u})^2(\vec{v}-\vec{u})f_i\;, \tag{7a}$$

$$\vec{J}_q^c(\vec{r}_1,t)=\tfrac{1}{2}\sum_{i,j=1}^{L}m_i\sigma_{ij}^3\int d\vec{v}_1d\vec{v}_2\int d\hat{\sigma}\,\hat{\sigma}\cdot\vec{g}\,\Theta(\hat{\sigma}\cdot\vec{g})\hat{\sigma}(\vec{v}_1'-\vec{v}_1)\cdot\left[\frac{\vec{v}_1'+\vec{v}_1}{2}-\vec{u}\right]$$
$$\times\int_0^1 d\lambda\, f_i(\vec{r}_1+\lambda\sigma_{ij}\hat{\sigma},\vec{v}_1,t)f_j(\vec{r}_1+\lambda\sigma_{ij}\hat{\sigma}-\sigma_{ij}\hat{\sigma},\vec{v}_2,t)$$
$$\times g_{ij}^{HS}(\vec{r}_1+\lambda\sigma_{ij}\hat{\sigma},\vec{r}_1+\lambda\sigma_{ij}\hat{\sigma}-\sigma_{ij}\hat{\sigma}\,|\,\{n_k\})\;. \tag{7b}$$

The heat flux also has a component from the potential, $\vec{J}_q^t$. This term can be gleaned from the equation, analogous to (5c.1), for the potential energy density:

$$U(\vec{r}_1,t)=\tfrac{1}{2}\sum_{i,j=1}^{L}n_i(\vec{r}_1,t)\int d\vec{r}_2\phi_{ij}^{\rm tail}(r_{12})n_j(\vec{r}_2,t)$$

(Ref. 8). Through second order in gradients [tantamount to using Fourier's law in (5c.1), for example] obtain

$$\frac{\partial}{\partial t}U+\vec{\nabla}_1\cdot\vec{u}U=-2\sum_{i,j=1}^{L}a_{ij}n_j\vec{\nabla}_1\cdot n_i\vec{u}_i+U\vec{\nabla}\cdot\vec{u}+\vec{u}\cdot\vec{\nabla}U\;, \tag{5c.2}$$

where $2a_{ij}=\int d\vec{r}\,V_{ij}(r)$ and all field variables are evaluated at $\vec{r}_1,t$. Add (5c.1), expressed to the same order, to (5c.2), use (6c) to express $\vec{P}^t$ through linear order and obtain

$$\frac{\partial}{\partial t}e+\vec{\nabla}_1\cdot\vec{u}e+\vec{\nabla}_1\cdot\vec{J}_q^{s+c+t}+\vec{P}^{s+c+t}:\nabla_1\vec{u}=0\;. \tag{5c}$$

Here $e=\tfrac{3}{2}nkT+U$, $\vec{J}_q^{s+c+t}=\vec{J}_q^s+\vec{J}_q^c+\vec{J}_q^t$,

$$\vec{J}_q^t=2\sum_{i,j=1}^{L}a_{ij}n_j\frac{\vec{J}_{m_i}}{m_i}\;, \tag{7c}$$

and

$$\vec{J}_{m_i}=\int d\vec{v}\,m_i(\vec{v}-\vec{u})f_i \tag{8}$$

is the mass-diffusion flux of the ith species.

Explicit expressions for the transport coefficients are obtained by expanding (7a)—(7c), (6a)—(6c), and (8) to linear order in gradients through solving (1) + (2) + (4) in the form $f_i\simeq f_i^{(0)}[1+\Phi_i]$, where $\Phi=O(\nabla)$, via the Chapman-Enskog development.[5] This has already been done for (1) + (2) without the mean-field term,[4,9] inclusion of which in the linear regime merely requires superposition of specific contributions. We obtain the linearized integral equation for Φ_i:

$$\sum_{j=1}^{L} \sigma_{ij}^2 y_{ij} f_i^{(0)} \int d\vec{v}_2 f_j^{(0)} \int d\hat{\sigma}\,\hat{\sigma}\cdot\vec{g}\,\theta(\hat{\sigma}\cdot\vec{g})[\Phi_j(\vec{v}_2')+\Phi_i(\vec{v}_1')-\Phi_j(\vec{v}_2)-\Phi_i(\vec{v}_1)]$$

$$=f_i^{(0)}\left\{(\vec{v}_1-\vec{u})\cdot\left[\frac{n}{n_i}\vec{d}_i+\nabla\ln T\left[\mathscr{C}_i^2-\frac{5}{2}\right]\left[1+\frac{8\pi}{5}\sum_{j=1}^{L}\sigma_{ij}^3 y_{ij} n_j\frac{\mu_{ij}}{m_{ij}}\right]\right]\right.$$

$$+2\vec{\mathscr{C}}_i^{\circ}\vec{\mathscr{C}}_i:\nabla\vec{u}\left[1+\frac{8\pi}{15}\sum_{j=1}^{L}\sigma_{ij}^3 y_{ij} n_j\frac{\mu_{ij}}{m_i}\right]$$

$$\left.+\frac{2}{3}\left[\mathscr{C}_i^2-\frac{3}{2}\right]\vec{\nabla}\cdot\vec{u}\left[1-\frac{P^{HS}}{nkT}+\frac{4\pi}{3}\sum_{j=1}^{L}\sigma_{ij}^3 y_{ij} n_j\frac{\mu_{ij}}{m_i}\right]\right\}. \qquad (9)$$

The y_{ij} is the contact value of g_{ij}^{eq}, $\vec{\mathscr{C}}_i=\sqrt{m_i/2kT}(\vec{v}_1-\vec{u})$, $m_{ij}=m_i+m_j$, $\mu_{ij}=m_i m_j/m_{ij}$, and $\vec{\mathscr{C}}_i^{\circ}\vec{\mathscr{C}}_i=\vec{\mathscr{C}}_i\vec{\mathscr{C}}_i-\frac{1}{3}\mathscr{C}_i^2\overleftrightarrow{I}$, $\overleftrightarrow{I}$ being the unit dyadic. The presence of the tail is manifested only in $\vec{d}_i$ which has the form

$$\vec{d}_i=\vec{d}_i^{HS}+\vec{d}_i^{t}, \qquad (10)$$

where

$$\vec{d}_i^{HS}=\frac{n_i}{n}\left[\beta(\nabla\mu_i^{HS})_T-\beta\frac{m_i}{\rho}\nabla P^{HS}+\nabla\ln T\left[1+\frac{4\pi}{3}\sum_{j=1}^{L}\sigma_{ij}^3 y_{ij} n_j\frac{m_i}{m_{ij}}\right]\right]$$

has the property

$$\sum_{i=1}^{L}\vec{d}_i^{HS}=0,$$

and

$$\vec{d}_i^{t}=\frac{n_i}{n}\beta\left[2\sum_{j=1}^{L}a_{ij}\nabla n_j-\frac{m_i}{\rho}\nabla P^t\right]$$

also has the property $\sum_{i=1}^{L}\vec{d}_i^{t}=0$. Here $\beta=1/kT$. Also,

$$P^{HS}=kT\left[n+\frac{2\pi}{3}\sum_{i,j=1}^{L}\sigma_{ij}^3 y_{ij} n_i n_j\right]$$

and

$$P^t=\sum_{i,j=1}^{L}a_{ij}n_i n_j$$

follow from (6a)–(6c), respectively. An alternate route to equivalent thermodynamics[2] follows through e. The chemical potential

$$\mu_i(T,\{n_j\})=\mu_i^{HS}+\mu_i^t,$$

where

$$\mu_i^t=2\sum_{j=1}^{L}a_{ij}n_j$$

so that the isothermal, isobaric driving force $(\vec{d}_i)_{P,T}$ takes the form

$$(\vec{d}_i)_{P,T} = \frac{n_i}{n}\beta(\nabla\mu_i)_{T,P} \tag{11}$$

which is the form expected on the basis of phenomenological irreversible thermodynamics.[10] The expansion of Φ_i is assumed[5]:

$$\Phi_i = -\vec{A}_i\cdot\vec{\nabla}\ln T - \overleftrightarrow{B}_i:\nabla\vec{u} + H_i\vec{\nabla}\cdot\vec{u} - \sum_{l=1}^{L}\vec{D}_{il}\cdot\vec{d}_l \tag{12}$$

and it is straightforward to show using Eqs. (6)–(9) and Eq. (12) that

$$-\frac{n}{n_i m_i}\vec{J}_{m_i} = n^2\vec{\nabla}\ln T\cdot\{\vec{A},\vec{D}_i\} + n^2\sum_{l=1}^{L}\vec{d}_l\cdot\{\vec{D}_l,\vec{D}_i\}\ , \tag{13a}$$

$$\vec{J}'_q = -n^2kT\{\vec{A},\vec{A}\}\cdot\vec{\nabla}\ln T - \tfrac{4}{3}\sum_{i,j}\sigma_{ij}^4 y_{ij} n_i n_j \frac{(2\pi\mu_{ij}k^3T)^{1/2}}{m_{ij}}\nabla T - n^2kT\sum_{l=1}^{L}\vec{d}_l\cdot\{\vec{D}_l,\vec{A}\}\ , \tag{13b}$$

$$\overleftrightarrow{P} = (P^{HS}+P^t)\overleftrightarrow{I} - n^2kT\nabla\vec{u}:\{\overleftrightarrow{B},\overleftrightarrow{B}\} - \tfrac{8}{15}\sum_{i,j=1}^{L}\sigma_{ij}^4 y_{ij} n_i n_j\sqrt{2\pi\mu_{ij}kT}\,\overleftrightarrow{e}^{\circ}$$
$$-n^2kT\{H,H\}\vec{\nabla}\cdot\vec{u}\overleftrightarrow{I} - \tfrac{4}{9}\sum_{i,j=1}^{L}\sigma_{ij}^4 y_{ij} n_i n_j\sqrt{2\pi\mu_{ij}kT}\,\vec{\nabla}\cdot\vec{u}\overleftrightarrow{I}\ . \tag{13c}$$

The bracket notation of Ref. 5 has been used here with $\overleftrightarrow{e}^{\circ} \equiv \frac{1}{2}[\nabla\vec{u} + (\nabla\vec{u})^T] - \frac{1}{3}\vec{\nabla}\cdot\vec{u}\overleftrightarrow{I}$. Also,

$$\vec{J}'_q = \vec{J}_q^{\,s+c+t} - kT\sum_{i=1}^{L}\frac{\vec{J}_{m_i}}{m_i}\left[\tfrac{5}{2} + 2\sum_{j=1}^{L}n_j\left[\frac{2\pi}{3}\sigma_{ij}^3 y_{ij}\frac{m_i}{m_{ij}} + \frac{a_{ij}}{kT}\right]\right].$$

The "irreversible" part of the entropy production[1] has the form

$$\sigma_c^{(1)-} = -\frac{1}{T}\vec{J}'_q\cdot\vec{\nabla}\ln T - k\sum_{i=1}^{L}\frac{n}{n_i m_i}\vec{J}_{m_i}\cdot\vec{d}_i - \frac{1}{T}\overleftrightarrow{\Pi}:\nabla\vec{u}\ , \tag{14}$$

or, equivalently,

$$T\sigma_c^{(1)-} = -\left[\vec{J}_q^{\,s+c+t} - \sum_{i=1}^{L}\frac{\partial e}{\partial\rho_i}\vec{J}_{m_i}\right]\cdot\vec{\nabla}\ln T - \sum_{i=1}^{L}\frac{\vec{J}_{m_i}}{m_i}\cdot(\vec{\nabla}\mu_i)_T - \overleftrightarrow{\Pi}:\nabla\vec{u}\ ,$$

where $\overleftrightarrow{\Pi} = \overleftrightarrow{P} - (P^{HS}+P^t)\overleftrightarrow{I}$, and from (14) we identify fluxes conjugate[1,10] to the independent forces $-\nabla\ln T$, $-\vec{d}_i$ $(i=1,\ldots,L-1)$, and $-\nabla\vec{u}$ as

$$\vec{\mathscr{J}}_q = \vec{J}'_q\ ,$$

$$\vec{\mathscr{J}}_{m_i} = kT\left[\frac{n}{n_i m_i}\vec{J}_{m_i} - \frac{n}{n_L m_L}\vec{J}_{m_L}\right],$$

$$\vec{\mathscr{J}}_P = \overleftrightarrow{\Pi}\ ,$$

respectively. Since $\{\vec{A},\vec{D}_i\} = \{\vec{D}_i,\vec{A}\}$ and $\{\vec{D}_l,\vec{D}_i\} = \{\vec{D}_i,\vec{D}_l\}$ the kinetic coefficients which relate these fluxes to those forces satisfy the Onsager reciprocal relations.[10,11] In fact, these kinetic coefficients do not exhibit a dependence on the tail strength and so are identical to those of the RET.[1,4] Thus these kinetic coefficients bear discrepancies in form and in numerical values analogous to those well known for the one-component case. We emphasize that these kinetic coefficients represent an approximate realization for the hard-sphere reference quantities which appear in other treatments of the dynamics of the "van der Waals" fluid.[6,12]

It follows that the transport coefficients which bear dependence upon derivatives of thermodynamic functions—mass diffusion, thermal diffusion,[13] and barodiffusion[13] coefficients—can be the only ones to exhibit explicit dependence on the tail strength. We restrict our attention to the multicomponent binary-isothermal, isobaric mass-diffusion coefficients $\mathscr{D}_{ij}$ defined[14] from

$$\vec{J}_{m_i} = -\sum_{j=1}^{L-1}\mathscr{D}_{ij}(\nabla\rho_j)_{T,P}\ . \tag{15}$$

In (15) and the following, use is made of $\sum_{i=1}^{L} \vec{d}_i = 0$ to eliminate $\vec{d}_L$. Combining (11) and (12) with

$$\vec{D}_{il}(\vec{v}_1 - \vec{u}) = (\vec{v}_1 - \vec{u}) \sum_{r=0}^{\infty} d_r^{(il)} S_{3/2}^{(r)}(\mathscr{C}_i^2) ,$$

(13a), and (15) we obtain the expression

$$\mathscr{D}_{ij} = \frac{n_i}{m_j} \sum_{l=1}^{L-1} d_0^{(il)} \frac{n_l}{n} \left[\left[\frac{\partial \mu_l}{\partial n_j} \right]_{Tn_{k \neq j}} - \left[\frac{\partial \mu_l}{\partial n_L} \right]_{Tn_{k \neq L}} \frac{\partial P / \partial n_j}{\partial P / \partial n_L} \right] , \tag{16}$$

where $P(T, \{ n_j \}) = P^{HS} + P^t$. The $d_0^{(il)}$ is found by substituting the above expression for $\vec{D}_{il}$ and (12) into (9). In terms of the Helmholtz free energy per volume a_v, $\mathscr{D}_{ij}$ takes the form

$$\mathscr{D}_{ij} = \frac{n_i}{m_j} \sum_{l=1}^{L-1} d_0^{(il)} \frac{n_l}{n} \left[\frac{\partial P}{\partial n_L} \right]^{-1} \sum_{r=1}^{L} n_r \left[\frac{\partial^2 a_v}{\partial n_j \partial n_l} \frac{\partial^2 a_v}{\partial n_r \partial n_L} - \frac{\partial^2 a_v}{\partial n_l \partial n_L} \frac{\partial^2 a_v}{\partial n_r \partial n_j} \right] .$$

For $L = 2$ this yields

$$\mathscr{D}_{21} = \frac{n_1 n_2^2}{n m_1} d_0^{(21)} \left[\frac{\partial P}{\partial n_2} \right]^{-1} \left[\frac{\partial^2 a_v}{\partial n_1^2} \frac{\partial^2 a_v}{\partial n_2^2} - \left[\frac{\partial^2 a_v}{\partial n_1 \partial n_2} \right]^2 \right] ,$$

so that $\mathscr{D}_{21}$ vanishes on the critical line[15] and over the spinodal surface,[16] which is the limit surface of material stability. Similar behavior does not occur if the standard Enskog theory[17] (SET) form for the collision integral is used in (1), as was shown already for the case of a binary phase separation.[18]

A companion equation to (5a)–(5c), for the entropy density s follows from (5a)–(5c) and the Gibb's relation, assumed[10] to be valid in the form

$$T \frac{ds_m}{dt} = \frac{d\mu}{dt} + P \frac{d}{dt} \frac{1}{\rho} - \sum_{i=1}^{L} \frac{\mu_i}{m_i} \frac{dc_i}{dt} \tag{17}$$

in the regime of linear irreversible thermodynamics. Here $s_m = s/\rho$ = entropy per mass, $\mu = e/\rho$, $c_i = \rho_i/\rho$. The entropy equation reads

$$\frac{\partial}{\partial t} s + \nabla \cdot (s \vec{u} + \vec{J}_s) = \sigma , \tag{18}$$

where $\sigma = \sigma_c^{(1)-}$ as in Eq. (14) and

$$\vec{J}_s = \frac{1}{T} \left[\vec{J}_q^{s+c+t} - \sum_{i=1}^{L} \frac{\mu_i}{m_i} \vec{J}_{m_i} \right] .$$

This result can also be obtained[19] via Boltzmann theory for mixtures. However, combining (1), (2), and (3) for the special case $L = 1$ leads to the result,[1] to first-order expansion of f in gradients [denoted by superscript (1)],

$$\frac{\partial}{\partial t} s^{(1)} + \vec{\nabla} \cdot (s^{(1)} \vec{u} + \vec{J}_s^{(1)} + \vec{J}^{(1)}) = \sigma_c^{(1)-} + \sigma' . \tag{19}$$

The $\vec{J}_s^{(1)}$ does not contain[1] the collisional heat flux as does $\vec{J}_s$ and neither the

$$\vec{J}^{(1)} = (2\pi/3) d^3 k\, n^2 y(d) \vec{u}$$

(d = hard-sphere diameter) nor

$$\sigma' = \tfrac{2}{3} \pi d^3 k\, n^2 y(d) \left[b_0 \overleftrightarrow{e} {:} \nabla \vec{u} - \frac{5}{2} \frac{k}{m} a_1 \frac{(\nabla T)^2}{T} \right]$$

[which is ≥ 0 since the Sonine coefficients (Ref. 5) $b_0 > 0$, $a_1 < 0$] contain the ingredients necessary to ensure consistency of (19) with (18). The $\vec{J}^{(1)}$ and σ' arise from nonlocality of the collision, as exhibited by (2), and vanish as $\sigma_{ij} \rightarrow 0$ is effected in the arguments of f_j in the integrand of (2). In this same limit, the collisional contributions to the fluxes vanish and so the form (18) is recovered. Since nonlocality of collision is a general characteristic of collision dynamics (the Boltzmann equation is a special case[1,20]) the result (19) suggests that (17) is inappropriate in general in the linear regime. Based on this result we conclude that (18) is likewise an inappropriate starting point to study entropy fluctuations[6,21] except in the dilute-gas limit.

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