LIMITING BEHAVIOR OF THE KINETIC THEORY FOR SYSTEMS WITH MULTISTEP INTERACTION

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The kinetic theory of mixtures with a multistep potential (MSP) is considered. A passage to the limit of the smooth continuous potential for the kinetic equation and the potential energy density balance equation is analyzed. When the "hard spheres + soft tail" form for the limiting potential is chosen, the kinetic equation reduces to that of the kinetic variational theory (KVT), while the limiting balance equation for the kinetic energy density differs from its KVT counterpart.

1. Introduction

Triple and higher-order collisions present a considerable difficulty for the development of the kinetic theory for dense systems with realistic potentials, e.g., of the Lennard-Jones type and, specifically, for treating a long-range interaction in explicit way. The significant progress has been achieved, therefore, for model systems based on the Enskog kinetic theory for hard spheres [1–4] which include the long-range interaction in some approximate way. The addition of a Fokker–Planck-type term to the Enskog collision integral [5] results in that the hard spheres move as Brownian particles between hard-core collisions. However, the shear viscosity and thermal conductivity coefficients of the model differ appreciably [6] from the molecular dynamic data.

Using the approach of maximizing the entropy with certain constraints, several kinetic mean-field theories (KMFT) for a system of particles interacting via a "hard-core + soft tail" potential were proposed [7–9]. They take the attraction into account through the mean-field collision integral and thermodynamic quantities. A mixture version was considered, and the theory in the Kac-tail limit was examined [10]. Though the proposed balance equation for the kinetic energy density is of non-typical form, the theory is considered successful up till now [11]. There also appear the semiphenomenological ways to treat the interparticle attraction through, e.g., the average cross-section of the momentum transfer used for viscosity [12].

The kinetic theory for MSP [13–17] generalizes the theory for a square well [18–20]. The both are characteristic in that the long-range attraction is included into an appropriate collision integral explicitly and in irreversible fashion. The balance equation for the interaction energy density is a necessary ingredient of these theories. It is worth noting that one can deduce the simplest version of KMFT, called KVT, by passing to the limit upon the potential, when the starting point is the MSP kinetic theory, the number of steps increases, and, simultaneously, separations between them decrease [14]. Thus, we get a way to verify KVT by the MSP theory. The question on the limiting behavior concerning the MSP kinetic equation alone was considered earlier [14], but for a one-component model and for such a closure relation [18] for the two-particle distribution function that the potential energy equation was neglected. It was revealed that the MSP kinetic equation transforms in the limit to the KVT-type one, while the question on the limiting behavior of the balance equations for kinetic and potential energy densities remained without attention.

We consider a mixture version of the MSP kinetic theory, when the closure relation used takes the potential energy density into consideration [19]. The passage to the limit is analyzed both on the kinetic level and in hydrodynamic equations. The limiting equation for the

kinetic energy density is found to differ from that proposed in KVT and to include contributions to the stress tensor and the heat flux from the soft tail of a limiting potential. In Section 2, we present the equations of the kinetic level, the closure, and the corresponding hydrodynamics [21]. In Section 3, the main ideas and results of KVT are outlined. The passage to the limit of a continuous potential for both the kinetic and hydrodynamic equations is considered in Section 4. In the last section, conclusions are made.

2. Kinetic Description and Hydrodynamic Equations

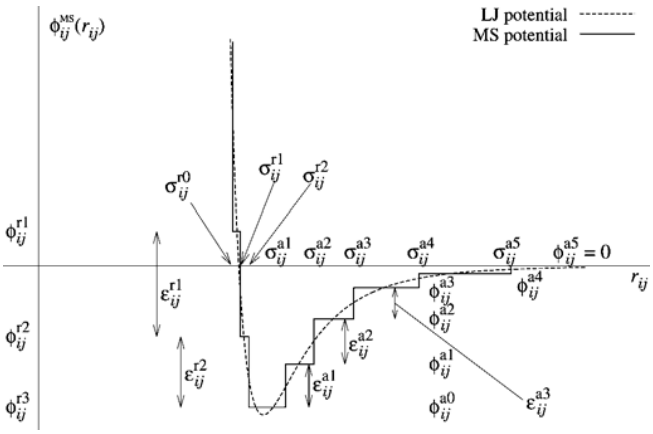
The contribution from a long-range interaction to the total energy density cannot be neglected at intermediate and high number densities. This is the reason for the kinetic equation for the one-particle distribution function to be complemented with an appropriate balance equation for the potential energy density [19, 20, 22, 23]. This circumstance changes qualitatively the scenario of the kinetic stage of evolution as compared with that of the hard-sphere system and must be included into the construction of kinetic theories for dense systems with a realistic smooth interaction [24, 25].

We consider an M-component system of classical particles interacting by pair central forces. The multistep potential $\phi_{ij}^{\rm MS}$ mimics the realistic one consisting of a hard core and a set of repulsive and attractive walls of finite heights. The geometry of MSP is determined by the following parameters [15,16,21]: σ_{ij}^0, $\sigma_{ij}^{{\rm r}l}$, σ_{ij}^{al} are allocations of the hard-core, repulsive, and attractive walls, $K_{ij}^{\rm r}$ and $K_{ij}^{\rm a}$ are numbers of the repulsive and attractive walls (Fig. 1). Parameters $\phi_{ij}^{{\rm r}l}$ and ϕ_{ij}^{al} denote values of MSP between walls, while $\epsilon_{ij}^{{\rm r}l} = \phi_{ij}^{{\rm r}l} - \phi_{ij}^{{\rm r},l+1}$, $\epsilon_{ij}^{al} = \phi_{ij}^{al} - \phi_{ij}^{{\rm a},l-1}$ characterize heights of the walls and are introduced in such a way that $\epsilon_{ij}^{{\rm r}l}$, $\epsilon_{ij}^{al} > 0$. The plateaux are numbered in the direction of increasing r_{ij}: from the hard core for the repulsive part and from the first attractive wall for the attractive part of MSP.

The one-particle distribution functions f_1^i are governed by the system of kinetic equations [21]

$$[\partial_t + \mathbf{v}_i \cdot \nabla]\, f_1^i(\mathbf{r}, \mathbf{v}_i, t) = \sum_{j=1}^{M} \Big\{ I_{ij}^{\rm E}[f_2^{ij}] + I_{ij}^{\rm MS}[f_2^{ij}] \Big\}, \quad (1)$$

where $\partial_t \equiv \frac{\partial}{\partial t}$, $\nabla \equiv \frac{\partial}{\partial \mathbf{r}}$, and f_2^{ij} are the two-particle distribution functions, the closure relations for which will be given below. The collision integrals $I_{ij}^{\rm E}$ and $I_{ij}^{\rm MS}$ describe pair processes at the hard core and the walls of



Model multistep potential $\phi_{ij}^{\rm MS}$, with $K_{ij}^{\rm r} = 2$, $K_{ij}^{\rm a} = 5$

finite height. Expression for the Enskog-type term, $I_{ij}^{\rm E}$, is conventional [4, 21] and not given here.

The contribution $I_{ij}^{\rm MS}$ can be presented in a compact form [21] with the aid of a type-of-step parameter q and a type of process p at the step: $q =$ 'r' for the repulsive steps and $q =$ 'a' for the attractive ones. There are three types of (ij)-processes at a step: *descending* $p = \oplus$, *ascending* $p = \ominus$, and *reflection* $p = \otimes$, therefore

$$I_{ij}^{\rm MS}[f_2^{ij}] = \sum_{q}^{\rm r,a} \sum_{l=1}^{K_{ij}^q} \sum_{p}^{\oplus,\ominus,\otimes} I_{ij}^{qlp}[f_2^{ij}]. \quad (2)$$

We ascribe formal numerical values to the parameters as follows:

$$q = \begin{pmatrix} {\rm r} \\ {\rm a} \end{pmatrix} = \begin{pmatrix} -1 \\ +1 \end{pmatrix}, \quad p = \begin{pmatrix} \oplus \\ \ominus \\ \otimes \end{pmatrix} = \begin{pmatrix} +1 \\ -1 \\ 0 \end{pmatrix}, \quad (3)$$

so that contributions to the $I_{ij}^{\rm MS}$ can be given as

$$I_{ij}^{ql\otimes}[f_2^{ij}] = (\sigma_{ij}^{ql})^2 \int {\rm d}\mathbf{v}_j {\rm d}\hat{\sigma}\, v_{ji\sigma}\, \theta(v_{ji\sigma})\, \theta(v_{ij}^{ql} - v_{ji\sigma}) \times$$
$$\times [f_2^{ij}(\mathbf{r}, \mathbf{v}_i', \mathbf{r} - q\boldsymbol{\sigma}_{ij}^{ql}, \mathbf{v}_j')^{-q} -$$
$$- f_2^{ij}(\mathbf{r}, \mathbf{v}_i, \mathbf{r} + q\boldsymbol{\sigma}_{ij}^{ql}, \mathbf{v}_j)^{-q}] \quad (4)$$

for the reflection process at step $\{q, l\}$ and

$$I_{ij}^{qlp}[f_2^{ij}] = (\sigma_{ij}^{ql})^2 \int {\rm d}\mathbf{v}_j {\rm d}\hat{\sigma}\, v_{ji\sigma}\, \theta(v_{ji\sigma} + \frac{p-1}{2} v_{ij}^{ql}) \times$$
$$\times [f_2^{ij}(\mathbf{r}, \mathbf{v}_i^{qlp}, \mathbf{r} + qp\boldsymbol{\sigma}_{ij}^{ql}, \mathbf{v}_j^{qlp})^{-qp} -$$
$$- f_2^{ij}(\mathbf{r}, \mathbf{v}_i, \mathbf{r} - qp\boldsymbol{\sigma}_{ij}^{ql}, \mathbf{v}_j)^{+qp}] \quad (5)$$

for the descending and ascending processes. Here, *numerical* values of p and q are used to determine the position of particle j for the function f_2^{ij}, the argument

of the θ function in Eq. (5), and to fix the right or left limiting values for f_2^{ij} in Eqs. (4), (5). Otherwise, q and p are *symbols* being used for designation.

Notations introduced for velocities of particles i and j mean: $\mathbf{v}_i$, $\mathbf{v}_j$ – just before a process; $\mathbf{v}_i'$, $\mathbf{v}_j'$ – just after a pair collision at the hard core or a reflection process at a step; $\mathbf{v}_i^{qlp}$, $\mathbf{v}_j^{qlp}$ – after processes $p = \oplus, \ominus$ at the step $\{q, l\}$; $\hat{\sigma}$ is a unit vector from the center of particle j to the center of particle i, $\boldsymbol{\sigma}_{ij}^0 = \sigma_{ij}^0 \hat{\sigma}$, $\boldsymbol{\sigma}_{ij}^{ql} = \sigma_{ij}^{ql} \hat{\sigma}$, $v_{ji\sigma} = (\mathbf{v}_j - \mathbf{v}_i) \cdot \hat{\sigma}$. The corresponding rules for the pair processes read

$$\mathbf{v}_i' = \mathbf{v}_i + 2M_{ji}\mathbf{v}_{ji} \cdot \hat{\sigma}\hat{\sigma}, \qquad \mathbf{v}_j' = \mathbf{v}_j - 2M_{ij}\mathbf{v}_{ji} \cdot \hat{\sigma}\hat{\sigma}, \quad (6)$$

$$\mathbf{v}_i^{qlp} = \mathbf{v}_i + M_{ji}[v_{ji\sigma} - \sqrt{v_{ji\sigma}^2 + p(v_{ij}^{ql})^2}]\,\hat{\sigma},$$
$$\mathbf{v}_j^{qlp} = \mathbf{v}_j - M_{ij}[v_{ji\sigma} - \sqrt{v_{ji\sigma}^2 + p(v_{ij}^{ql})^2}]\,\hat{\sigma}, \quad (7)$$

where $M_{ji} = m_j/(m_i + m_j)$, $v_{ij}^{ql} = (2\epsilon_{ij}^{ql}/\mu_{ij})^{1/2}$ is the step height in velocity units, $\mu_{ij} = m_i m_j/(m_i + m_j)$ is the reduced mass. The quantity f_2^{ij} is discontinuous in configurations, for which MSP is, and $f_2^{ij}(.)^{\pm}$ denotes the right $(+)$ or left $(-)$ limiting value.

Averages with f_1^i and f_2^{ij} will be designated as

$$\langle \psi_1 \rangle_{\mathbf{v}_i}^{1,i} \stackrel{\text{df}}{=} \int \mathrm{d}\mathbf{v}_i\, f_1^i\, \psi_1, \quad \langle \psi_2 \rangle_{\mathbf{v}_i x_j}^{2,ij} \stackrel{\text{df}}{=} \int \mathrm{d}\mathbf{v}_i \mathrm{d}x_j\, f_2^{ij}\, \psi_2,$$

where the subscripts indicate variables of integration.

The balance equation for the potential energy density

$$e^{\mathrm{p}}(\mathbf{r}, t) \stackrel{\text{df}}{=} \sum_{i,j=1}^{M} \langle \frac{1}{2}\phi_{ij}^{\mathrm{MS}}(r_{ij}) \rangle_{\mathbf{v}_i x_j}^{2,ij} \big|_{\mathbf{r}_i \to \mathbf{r}} \quad (8)$$

must be considered on the kinetic level of description together with the kinetic equations for f_1^i. Its heuristic derivation based on ideas of the numbers of direct and inverse collisions gives [21]

$$\partial_t e^{\mathrm{p}} + \nabla \cdot [\mathbf{V} e^{\mathrm{p}} + \mathbf{q}_{\mathrm{p}}] = s_{\mathrm{p}}, \quad (9)$$

where $\mathbf{V}(\mathbf{r}, t)$ is the hydrodynamic velocity defined below Eq. (17) below and

$$\mathbf{q}_{\mathrm{p}}(\mathbf{r}, t) = \sum_{i,j=1}^{M} \langle \frac{1}{2}\mathbf{c}_i \phi_{ij}^{\mathrm{MS}}(r_{ij}) \rangle_{\mathbf{v}_i x_j}^{2,ij} \big|_{\mathbf{r}_i \to \mathbf{r}}, \quad (10)$$

$$s_{\mathrm{p}}(\mathbf{r}, t) = -\sum_{i,j=1}^{M} \sum_{q}^{\mathrm{r,a}} \sum_{l=1}^{K_{ij}^q} \sum_{p}^{\oplus,\ominus} \frac{1}{2} p\, \epsilon_{ij}^{ql} (\sigma_{ij}^{ql})^2 \int \mathrm{d}\mathbf{v}_i \mathrm{d}\mathbf{v}_j \mathrm{d}\hat{\sigma} \times$$
$$\times\, v_{ji\sigma}\, \theta(v_{ji\sigma} + \frac{p-1}{2} v_{ij}^{ql}) f_2^{ij}(\mathbf{r}, \mathbf{v}_i, \mathbf{r} - qp\boldsymbol{\sigma}_{ij}^{ql}, \mathbf{v}_j)^{qp} \quad (11)$$

are the flux in the local reference system and the source which concern to the potential energy of interaction; and $\mathbf{c}_i \equiv \mathbf{v}_i - \mathbf{V}$ is the thermal velocity.

So far, Eq. (1) has been being considered as the first equation of the BBGKY hierarchy for MSP. The closure relation for the collision integrals I_{ij}^{E}, I_{ij}^{MS} and the source s_{p} is chosen as in Ref. [19], when correlations in the velocity space are neglected, i.e., f_2^{ij} is replaced with

$$\bar{f}_2^{ij}(x_i, x_j, t) \equiv f_i(x_i, t) f_j(x_j, t)\, g_2^{ij}(\mathbf{r}_i, \mathbf{r}_j, t), \quad (12)$$

and g_2^{ij} is a functional of number densities $n_k(\mathbf{r}, t)$ and the inverse potential quasitemperature $\beta^{\mathrm{p}}(\mathbf{r}, t)$

$$g_2^{ij}(\mathbf{r}_i, \mathbf{r}_j, t) = g_2^{ij}(\mathbf{r}_i, \mathbf{r}_j | \{n\}, \beta^{\mathrm{p}}), \quad (13)$$

so that g_2^{ij} has the same cluster expansion (n-vertex, f-bond) as in equilibrium. However, in the nonequilibrium case, $n_k(\mathbf{r}, t)$ replaces each n_k, and $\beta_{ij}^{\mathrm{p}}(\mathbf{r}_i, \mathbf{r}_j, t) = \frac{1}{2}[\beta^{\mathrm{p}}(\mathbf{r}_i, t) + \beta^{\mathrm{p}}(\mathbf{r}_j, t)]$ replaces $1/k_{\mathrm{B}}T$ at each bond. The quantity $\beta^{\mathrm{p}}(\mathbf{r}, t)$ is the Lagrange multiplier conjugated to the potential energy density [19, 23–25] and is treated in the theory using the balance equation for $e^{\mathrm{p}}(\mathbf{r}, t)$. The functional g_2^{ij} is discontinuous at each point of discontinuity of MSP and obeys the relation

$$g_2^{ij}(\mathbf{r}, \mathbf{r} \pm \boldsymbol{\sigma}_{ij}^{ql}, t)^{-qp} = \mathrm{e}^{p\beta_{ij}^{\mathrm{p}} \epsilon_{ij}^{ql}} g_2^{ij}(\mathbf{r}, \mathbf{r} \pm \boldsymbol{\sigma}_{ij}^{ql}, t)^{qp}. \quad (14)$$

Other closures are proposed for the case of a one-component system with the square-well potential using the *equilibrium* pair distribution function of the *uniform* system [18] or the pair distribution function of the *hard sphere* system in the state of nonuniform equilibrium [9].

The kinetic equation introduced can be used in the high-density region only, where the contributions from successive processes at two and more neighbouring steps may be neglected (the pair collision approximation for each step) [14, 15]. This approximation induces the restriction [15, 17]

$$\frac{\Delta\sigma}{\sigma_{\mathrm{m}}^0} \gg \frac{1}{4\sqrt{2}\,\pi\, n\, (\sigma_{\mathrm{m}}^0)^3\, g_2^{\mathrm{m}}(\sigma^0)^+}, \quad (15)$$

where $\Delta\sigma$ is the smallest separation between walls, $\sigma_{\mathrm{m}}^0 = \min\{\sigma_{ij}^0\}$, n is the total number density, and $g_2^{\mathrm{m}}(\sigma^0)^+ = \min\{g_2^{ij}(\sigma_{ij}^0)^+\}$ is the smallest contact value of g_2^{ij}'s.

On the hydrodynamic level, the system is described by balance equations for the densities of conserved quantities, namely the mass ρ, momentum $\mathbf{p}$, and energy e densities. Such equations for ρ, $\mathbf{p}$, and the *kinetic* energy density e^{k} only

$$\begin{bmatrix} \rho(\mathbf{r}, t) \\ \mathbf{p}(\mathbf{r}, t) \\ e^{\mathrm{k}}(\mathbf{r}, t) \end{bmatrix} \stackrel{\text{df}}{=} \sum_{i=1}^{M} \left\langle \begin{bmatrix} m_i \\ m_i \mathbf{v}_i \\ \frac{1}{2} m_i v_i^2 \end{bmatrix} \right\rangle_{\mathbf{v}_i}^{1,i} \quad (16)$$

can be derived from Eq. (1). In the case of M species, they were obtained in Ref. [21]:

$$\partial_t \begin{bmatrix} \rho \\ \mathbf{p} \\ e^{\rm k} \end{bmatrix} + \nabla\cdot \begin{bmatrix} \mathbf{V}\rho \\ \mathbf{V}\mathbf{p} + \mathsf{P} \\ \mathbf{V}e^{\rm k} + \mathsf{P}\cdot\mathbf{V} + \mathbf{q}_{\rm k} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ s_{\rm k} \end{bmatrix}, \tag{17}$$

where $\mathbf{V}(\mathbf{r},t) \stackrel{\rm df}{=} \mathbf{p}(\mathbf{r},t)/\rho(\mathbf{r},t)$ is the hydrodynamic velocity. The stress tensor P and the heat flux $\mathbf{q}_{\rm k}$ of the kinetic energy contain contributions of the kinetic type (k), from repulsion at the hard core (c) due to $I_i^{\rm E}$, and from processes at steps (MS):

$$\begin{bmatrix} \mathsf{P} \\ \mathbf{q}_{\rm k} \end{bmatrix} = \begin{bmatrix} \mathsf{P}^{\rm k} + \mathsf{P}^{\rm c} + \mathsf{P}^{\rm MS} \\ \mathbf{q}_{\rm k}^{\rm k} + \mathbf{q}_{\rm k}^{\rm c} + \mathbf{q}_{\rm k}^{\rm MS} \end{bmatrix},$$

where $\mathsf{P}^{\rm MS} = \mathsf{P}^{\otimes} + \mathsf{P}^{\oplus} + \mathsf{P}^{\ominus}$, $\mathbf{q}_{\rm k}^{\rm MS} = \mathbf{q}_{\rm k}^{\otimes} + \mathbf{q}_{\rm k}^{\oplus} + \mathbf{q}_{\rm k}^{\ominus}$. Here, we give only expressions for the contributions from the processes at steps [21]:

$$\begin{pmatrix} \mathsf{P} \\ \mathbf{q}_{\rm k} \end{pmatrix}^{\otimes} = \sum_{i,j=1}^{M} \sum_{q}^{\rm r,a} \sum_{l=1}^{K_{ij}^q} (-\frac{q}{2})(\sigma_{ij}^{ql})^3 \int {\rm d}\mathbf{v}_i {\rm d}\mathbf{v}_j {\rm d}\hat{\sigma}\, v_{ji\sigma} \times$$

$$\times\, \theta(v_{ji\sigma})\, \theta(v_{ij}^{ql} - v_{ji\sigma})\, \hat{\sigma} \int_0^1 {\rm d}\lambda \begin{pmatrix} m_i[\mathbf{c}_i' - \mathbf{c}_i] \\ \frac{1}{2} m_i[c_i'^2 - c_i^2] \end{pmatrix} \times$$

$$\times f_2^{ij}(\mathbf{r} - \lambda q \boldsymbol{\sigma}_{ij}^{ql}, \mathbf{v}_i, \mathbf{r} + [1-\lambda] q \boldsymbol{\sigma}_{ij}^{ql}, \mathbf{v}_j)^{-q}, \tag{18}$$

$$\begin{pmatrix} \mathsf{P} \\ \mathbf{q}_{\rm k} \end{pmatrix}^{\oplus+\ominus} = \sum_{i,j=1}^{M} \sum_{q}^{\rm r,a} \sum_{l=1}^{K_{ij}^q} \sum_{p}^{\oplus,\ominus} \frac{qp}{2} (\sigma_{ij}^{ql})^3 \int {\rm d}\mathbf{v}_i {\rm d}\mathbf{v}_j {\rm d}\hat{\sigma} \times$$

$$\times v_{ji\sigma}\, \theta(v_{ji\sigma} + \frac{p-1}{2} v_{ij}^{ql})\, \hat{\sigma} \int_0^1 {\rm d}\lambda \begin{pmatrix} m_i[\mathbf{c}_{il}^{qp} - \mathbf{c}_i] \\ \frac{1}{2} m_i[(c_{il}^{qp})^2 - c_i^2] \end{pmatrix} \times$$

$$\times f_2^{ij}(\mathbf{r} + \lambda q p \boldsymbol{\sigma}_{ij}^{ql}, \mathbf{v}_i, \mathbf{r} - [1-\lambda] q p \boldsymbol{\sigma}_{ij}^{ql}, \mathbf{v}_j)^{qp}. \tag{19}$$

The source $s_{\rm k}$ on the right-hand side of Eq. (17) for $e^{\rm k}$ is such that $s_{\rm k} = -s_{\rm p}$ identically, see Eq. (11). As a result, the balance equation for the total energy density $e = e^{\rm k} + e^{\rm p}$ has no source, so that the local energy conservation law is satisfied.

3. Kinetic Variational Theory

The main idea of KVT lies in the construction of a collision integral for the potential given as a sum of the hard-sphere repulsion and an arbitrary smooth tail

$$\phi_{ij}^{\rm hs+t}(r) = \phi_{ij}^{\rm hs}(r) + \phi_{ij}^{\rm t}(r), \tag{20}$$

when a form of the functional dependence of the N-particle distribution function is searched through maximizing the entropy subjected to certain constraints [8,9]. As a result, the pair correlations in the velocity space are neglected, and the dependence of g_2^{ij} on $\{n\}$ and $\beta^{\rm p}$ is determined by the type of a constraint.

In the approximation called KVT-III, the constraint consists in the requirement that the *local potential energy density* $e^{\rm p}(\mathbf{r},t)$ is recovered correctly by the searched N-particle distribution. The entropy maximization principle results in the function $g_2^{ij,{\rm hs+t}}$ for $\phi_{ij}^{\rm hs+t}$ in form (13). In addition to the contribution $I_{ij}^{\rm E}$ from $\phi_{ij}^{\rm hs}$, there is a term of mean-field type *linear* in $\phi_{ij}^{\rm t}$ [10]:

$$I_i^{\rm E+KVT} \equiv \sum_{j=1}^{M} \Big\{ I_{ij}^{\rm E}[f_1^i, f_1^j] + I_{ij}^{\rm KVT}[f_1^i, n_j] \Big\},$$

where $I_{ij}^{\rm KVT}$ is given by

$$I_{ij}^{\rm KVT}[f_1^i, n_j] = \frac{1}{m_i} \int\limits_{r_{12} > \sigma_{ij}^0} {\rm d}\mathbf{r}_2\, g_2^{ij,{\rm hs+t}}(\mathbf{r}_1, \mathbf{r}_2 | \{n\}, \beta^{\rm p}) \times$$

$$\times n_j(\mathbf{r}_2, t)[\nabla_1 \phi_{ij}^{\rm t}(r_{12})] \cdot \boldsymbol{\partial}_1 f_1^i(x_1, t). \tag{21}$$

The approximation accepted for g_2^{ij} is used in both $I_{ij}^{\rm KVT}$ and $I_{ij}^{\rm E}$.

For the collision integral $I_i^{\rm E+KVT}$, the authors of KVT gave a slightly unconventional balance equation for $e^{\rm k}$ in both one- [7] and many-component [10] cases:

$$\partial_t e^{\rm k} + \nabla\cdot\big[\mathbf{V}e^{\rm k} + \mathsf{P}^{\rm k+c}\cdot\mathbf{V} + \mathbf{q}_{\rm k}^{\rm k+c}\big] + \mathbf{V}\cdot\big(\nabla\cdot\mathsf{P}^{\rm t}\big) = \Delta_{e^{\rm k}}^{\rm t}, \tag{22}$$

where the contribution to the stress tensor from the $I_i^{\rm KVT}$ reads

$$\mathsf{P}^{\rm t}(\mathbf{r}_1, t) \stackrel{\rm df}{=} -\frac{1}{2} \sum_{i,j=1}^{M} \int {\rm d}\mathbf{s}\, \mathbf{s} \frac{\partial \phi_{ij}^{\rm t}(s)}{\partial \mathbf{s}} \times$$

$$\times \int_0^1 {\rm d}\lambda\, n_2^{ij,{\rm hs+t}}(\mathbf{r}_1 - \lambda\mathbf{s}, \mathbf{r}_1 + [1-\lambda]\mathbf{s}), \tag{23}$$

$n_2^{ij,{\rm hs+t}}(\mathbf{r}_1, \mathbf{r}_2) \equiv n_i(\mathbf{r}_1, t) n_j(\mathbf{r}_2, t) g_2^{ij,{\rm hs+t}}(\mathbf{r}_1, \mathbf{r}_2 | \{n\}, \beta^{\rm p})$. It is not hard to recover for a general case the remainder term $\Delta_{e^{\rm k}}^{\rm t}$ (given in Ref. [10] in the Kac-tail limit):

$$\Delta_{e^{\rm k}}^{\rm t}(\mathbf{r}_1, t) = \sum_{i,j=1}^{M} [\mathbf{V}_i - \mathbf{V}] \times$$

$$\times \int {\rm d}\mathbf{r}_{21}\, n_2^{ij,{\rm hs+t}}(\mathbf{r}_1, \mathbf{r}_2 | \{n\}, \beta^{\rm p}) \phi_{ij}^{\rm t\prime}(r_{12})\, \hat{r}_{21}, \tag{24}$$

where $\mathbf{V}_i \equiv \langle \mathbf{v}_i \rangle_{\mathbf{v}_i}^{1,i} / n_i$ is the average velocity of species i. The following distinctions of Eq. (22) should be pointed out: a) the contribution with $\mathsf{P}^{\rm t}$ is not of the standard

form $-\nabla\cdot(\mathsf{P}^{\rm t}\cdot\mathbf{V})$, as those with $\mathsf{P}^{\rm k}$ or $\mathsf{P}^{\rm c}$; b) there is no contribution $\mathbf{q}^{\rm t}_{\rm k}$ from $I_i^{\rm KVT}$ to the heat flux of the kinetic energy; and c) due to the difference $\mathbf{V}_i-\mathbf{V}$, the source $\Delta^{\rm t}_{e^{\rm k}}$ is of the diffusion type and therefore vanishes in the one-component case.

The balance equation for $e^{\rm p}$ of KVT was introduced in Ref. [10] only, where many-component system was considered, and simpler constraints which do not allow the appearance of $\beta^{\rm p}$ were used. It was shown in *the Kac-tail limit* that the total energy density obeys a correct balance equation *through second order in gradients*.

The indicated shortcomings require a more detailed analysis of this theory.

4. Passage to the Limit in the MSP Kinetic Theory

Starting from MSP, an arbitrary potential $\tilde{\phi}_{ij}(r)$ can be approximated better and better by increasing the number of steps and by a simultaneous decrease in separations between them [14]. This passage to the limit can be denoted as

$$\lim_{\substack{\{\epsilon^{ql}_{ij}\}\to 0\\ \{\Delta\sigma^{ql}_{ij}\}\to 0}}(\ldots)\equiv\lim_{\phi^{\rm MS}\to\tilde{\phi}}(\ldots). \tag{25}$$

Though the applicability condition (15) of the MSP kinetic theory is violated, we consider consequences of the passage, when the model potential (20) plays the role of the limiting potential $\tilde{\phi}_{ij}(r)$. In this case, $I_i^{\rm E}$ remains the same, while the contribution $I_i^{\rm MS}$ undergoes a change.

Transformations below resemble those applied to the derivation [26] of the Landau kinetic equation from the Boltzmann equation and use expansions into series in a small value of the momentum transferred in pair collisions.

4.1. The limit of the kinetic equation

Like in Ref. [14], we search for the limiting form of $I_{ij}^{\rm MS}$, Eqs. (2), (4), (5), when

$$f_1^i(\mathbf{r}_i,\mathbf{v}_{il}^{qp},t)\,f_1^j(\mathbf{r}_j,\mathbf{v}_{jl}^{qp},t)\,g_2^{ij}(\mathbf{r}_i,\mathbf{r}_j|\{n\},\beta^{\rm p}) \tag{26}$$

is expanded into a series near $\mathbf{v}_i$ and $\mathbf{v}_j$; here, $\bar{f}_2^{ij}$ includes closure (12), (13).

For small step heights, $\{\epsilon^{ql}_{ij}\}\to 0$, the square root in the pair collision rule (7) for processes $\oplus$ and $\ominus$ is expanded into a series and restricted to the linear order in ϵ^{ql}_{ij}:

$$\begin{bmatrix}\mathbf{v}_{il}^{qp}\\ \mathbf{v}_{jl}^{qp}\end{bmatrix}=\begin{bmatrix}\mathbf{v}_i\\ \mathbf{v}_j\end{bmatrix}+\begin{bmatrix}M_{ji}\\ M_{ij}\end{bmatrix}\times\frac{1}{2}p\frac{2\epsilon^{ql}_{ij}}{\mu_{ij}v_{ji\sigma}}\hat{\sigma}. \tag{27}$$

For the contributions $I_{ij}^{ql\oplus}$ or $I_{ij}^{ql\ominus}$, this means

$$\bar{f}_2^{ij}(\mathbf{r},\mathbf{v}_{il}^{qp},\mathbf{r}+qp\boldsymbol{\sigma}_{ij}^{ql},\mathbf{v}_{jl}^{qp})^{-qp}=\Big[1+p\frac{\epsilon^{ql}_{ij}}{v_{ji\sigma}}\hat{\sigma}\times$$
$$\times\Big(-\frac{\boldsymbol{\partial}_i}{m_i}+\frac{\boldsymbol{\partial}_j}{m_j}\Big)+\ldots\Big]\bar{f}_2^{ij}(\mathbf{r},\mathbf{v}_i,\mathbf{r}+qp\boldsymbol{\sigma}_{ij}^{ql},\mathbf{v}_j)^{-qp}, \tag{28}$$

where, e.g., $\boldsymbol{\partial}_i\equiv\partial/\partial\mathbf{v}_i$. The term $I_{ij}^{ql\otimes}$ describes the reflection at steps of a very small height. Due to the second θ function in $I_{ij}^{ql\otimes}$, the projection $v_{ji\sigma}$ has an upper bound $0\le v_{ji\sigma}\le(2\epsilon^{ql}_{ij}/\mu_{ij})^{1/2}$. Therefore, $\mathbf{v}_i',\mathbf{v}_j'$ are close to $\mathbf{v}_i,\mathbf{v}_j$, see Eq. (6):

$$\bar{f}_2^{ij}(\mathbf{r},\mathbf{v}_i',\mathbf{r}-q\boldsymbol{\sigma}_{ij}^{ql},\mathbf{v}_j')^{-q}=\Big[1+2\mu_{ij}v_{ji\sigma}\hat{\sigma}\times$$
$$\times\Big(-\frac{\boldsymbol{\partial}_i}{m_i}+\frac{\boldsymbol{\partial}_j}{m_j}\Big)+\ldots\Big]\bar{f}_2^{ij}(\mathbf{r},\mathbf{v}_i,\mathbf{r}-q\boldsymbol{\sigma}_{ij}^{ql},\mathbf{v}_j)^{-q}. \tag{29}$$

Inserting these expressions into the formulas for I_{ij}^{qlp}, it can be observed that the main contributions ~ 1 from processes $\ominus$ and $\otimes$ in the square brackets cancel with that from process $\oplus$.

The first-order term $\sim v_{ji\sigma}$ in $I_{ij}^{ql\otimes}$, Eq. (29), gives the function with a fixed upper bound being integrated over the interval with the size tending to zero. As a result, $I_{ij}^{ql\otimes}$ vanishes. The first-order terms $\sim\epsilon_{ij}^{ql}$ in Eq. (28) gives a non-zero contribution. We now consider expressions from $\oplus$ and $\ominus$, e.g., for a repulsive step:

$$\sum_{l=1}^{K_{ij}^{\rm r}}\epsilon_{ij}^{{\rm r}l}(\sigma_{ij}^{{\rm r}l})^2\int{\rm d}\hat{\sigma}\hat{\sigma}\times$$
$$\times\Big\{\theta(v_{ji\sigma})\Big(-\frac{\boldsymbol{\partial}_i}{m_i}+\frac{\boldsymbol{\partial}_j}{m_j}\Big)\bar{f}_2^{ij}(\mathbf{r},\mathbf{v}_i,\mathbf{r}-\boldsymbol{\sigma}_{ij}^{\rm rl},\mathbf{v}_j)^{+}-$$
$$-\theta(v_{ji\sigma}-v_{ij}^{\rm rl})\Big(-\frac{\boldsymbol{\partial}_i}{m_i}+\frac{\boldsymbol{\partial}_j}{m_j}\Big)\bar{f}_2^{ij}(\mathbf{r},\mathbf{v}_i,\mathbf{r}+\boldsymbol{\sigma}_{ij}^{\rm rl},\mathbf{v}_j)^{-}\Big\}. \tag{30}$$

Some remarks concerning the passage to the limit are as follows: i) by increasing the number of steps and decreasing the separations between them, the sum $\sum_{l=1}^{K_{ij}^q}$ is transformed into an integral with respect to the continuous relative distance R:

$$\sum_{l=1}^{K_{ij}^{\rm r}}\Delta\sigma_{ij}^{{\rm r};l,l+1}\frac{\epsilon_{ij}^{\rm rl}}{\Delta\sigma_{ij}^{{\rm r};l,l+1}}\quad\longrightarrow\quad\int\limits_{\tilde{\phi}_{ij}'<0}{\rm d}R\,\Big(-\frac{\partial\tilde{\phi}_{ij}}{\partial R}\Big), \tag{31}$$

where the region with $\tilde{\phi}'_{ij}(R) < 0$ corresponds to repulsive steps and that with $\tilde{\phi}'_{ij}(R) > 0$ corresponds to attractive ones; ii) $\int \mathrm{d}\hat{\sigma}$ changes to the integral over the orientations $\hat{R}$ of the relative distance vector $\mathbf{R}$; iii) for the continuous part of $\tilde{\phi}_{ij}$, the right and left limiting values of $\bar{f}_2^{ij}$ are equal to each other: $\bar{f}_2^{ij}(.)^+ = \bar{f}_2^{ij}(.)^-$.

In those terms of the expressions obtained where $\bar{f}_2^{ij}$ depends on $\mathbf{r} - \mathbf{R}$, the integration variable should be changed to $\hat{R}' = -\hat{R}$. Keeping in mind that $\frac{\partial\tilde{\phi}_{ij}(R)}{\partial R}\hat{R} = \frac{\partial\tilde{\phi}_{ij}(R)}{\partial \mathbf{R}}$ and taking the equality of the limiting values of $\bar{f}_2^{ij}$ into account, it can be deduced that I_i^{MS} transforms into

$$\sum_{j=1}^{M}\int \mathrm{d}\mathbf{v}_j \mathrm{d}\mathbf{R}\frac{\partial\tilde{\phi}_{ij}(R)}{\partial\mathbf{R}}\cdot\Big(-\frac{\boldsymbol{\partial}_i}{m_i}+\frac{\boldsymbol{\partial}_j}{m_j}\Big)\bar{f}_2^{ij}(\mathbf{r},\mathbf{v}_i,\mathbf{r}+\mathbf{R},\mathbf{v}_j). \tag{32}$$

The integration by parts shows that the term with $\boldsymbol{\partial}_j f_2^{ij}$ vanishes as $\bar{f}_2^{ij}\big|_{|\mathbf{v}_j|\to+\infty} \to 0$. We can integrate further with respect to $\mathbf{v}_j$ due to the absence of velocity correlations, Eq. (26), with the result

$$-\frac{1}{m_i}\sum_{j=1}^{M}\int \mathrm{d}\mathbf{R}\, g_2^{ij}(\mathbf{r},\mathbf{r}+\mathbf{R}|\{n\},\beta^{\mathrm{p}})\times$$

$$\times n_j(\mathbf{r}+\mathbf{R},t)\frac{\partial\tilde{\phi}_{ij}(R)}{\partial\mathbf{R}}\cdot\boldsymbol{\partial}_i f_1^i(\mathbf{r},\mathbf{v}_i). \tag{33}$$

This expression coincides with the collision integral (21) of the kinetic variational theory, when g_2^{ij} is allowed to depend on β^{p} (the version KVT-III, [8]). It is important to stress this dependence, as the corresponding system of limiting equations for f_1^i is unclosed, until an equation for $\beta^{\mathrm{p}}(\mathbf{r},t)$ is proposed. It should be derived from the limiting equation for e^{p} complementing the system of kinetic equations. The final expression (33) was obtained for the first time in Ref. [14] for a one-component case, but no analysis of the g_2^{ij} functional dependence was given.

It is worth noting that Eq. (32) corresponds to the integral term of the first equation of the BBGKY hierarchy for a mixture with continuous potential $\tilde{\phi}_{ij}$. In other words, we have shown that the pair collision operator of MSP takes, in the limit, the form of a differential operator of pair interaction for the appropriate smooth potential.

4.2. The limit of the equation for e^{p}

Equation (9) is not changed, but the quantities in it are. The quantities e^{p} and $\mathbf{q}_{\mathrm{p}}$ contain ϕ_{ij}^{MS} and, in accordance with Eqs. (8) and (10), go over into

$$\begin{bmatrix}\tilde{e}^{\mathrm{p}}\\ \tilde{\mathbf{q}}_{\mathrm{p}}\end{bmatrix} \stackrel{\mathrm{df}}{=} \sum_{i,j=1}^{M}\langle\frac{1}{2}\begin{bmatrix}1\\ \mathbf{c}_i\end{bmatrix}\tilde{\phi}_{ij}(r_{ij})\rangle_{\mathbf{v}_i x_j}^{2,ij}\big|_{\mathbf{r}_i\to\mathbf{r}}. \tag{34}$$

The source s_{p} depends on parameters of ϕ_{ij}^{MS} and describes the processes at steps. The contributions from $\oplus$ and $\ominus$ in Eq. (11) for s_{p} can be written explicitly as

$$\sum_{i,j=1}^{M}\sum_{q}^{\mathrm{r,a}}\sum_{l=1}^{K_{ij}^q}\frac{1}{2}\epsilon_{ij}^{ql}(\sigma_{ij}^{ql})^2\int \mathrm{d}\mathbf{v}_i\mathrm{d}\mathbf{v}_j\mathrm{d}\hat{\sigma}\;\mathbf{v}_{ji}\cdot\hat{\sigma}\times$$
$$\times\Big\{\theta(-v_{ji\sigma})\bar{f}_2^{ij}(\mathbf{r},\mathbf{v}_i,\mathbf{r}+q\boldsymbol{\sigma}_{ij}^{ql},\mathbf{v}_j)^q +$$
$$+\theta(v_{ji\sigma}-v_{ij}^{ql})\bar{f}_2^{ij}(\mathbf{r},\mathbf{v}_i,\mathbf{r}+q\boldsymbol{\sigma}_{ij}^{ql},\mathbf{v}_j)^{-q}\Big\}, \tag{35}$$

where the variable $\hat{\sigma}$ in the term with $p = \oplus$ has been changed to $\hat{\sigma}' = -\hat{\sigma}$.

Relation (14) for the left and right limiting values of g_2^{ij} at the discontinuity points of ϕ_{ij}^{MS} can be expanded into a series as $\{\epsilon_{ij}^{ql}\} \to 0$,

$$g_2^{ij}(\mathbf{r},\mathbf{r}+q\boldsymbol{\sigma}_{ij}^{ql},t)^{-q} = [1+\beta_{ij}^{\mathrm{p}}\epsilon_{ij}^{ql}+\ldots]g_2^{ij}(\mathbf{r},\mathbf{r}+q\boldsymbol{\sigma}_{ij}^{ql},t)^q, \tag{36}$$

and inserted into expression (35). But the latter already contains the factor ϵ_{ij}^{ql}. Therefore, only the main term in square brackets of Eq. (36) is retained. After changing to $\hat{\sigma}' = -\hat{\sigma}$ in the term with $q = -1$, constructions (31) can be built up with the same rules of transformation. The two θ functions in Eq. (35) cover almost the whole region of $v_{ji\sigma}$ with the exception of the interval of size $\sim(\epsilon_{ij}^{ql})^{1/2}$ which tends to zero in the limit. Replacing the sum with the integral over the relative distance, we get

$$\tilde{s}_{\mathrm{p}}(\mathbf{r},t) = \sum_{i,j=1}^{M}\langle\frac{1}{2}\mathbf{v}_{ji}\cdot\frac{\partial\tilde{\phi}_{ij}(r_{ij})}{\partial\mathbf{r}_{ji}}\rangle_{\mathbf{v}_i x_j}^{2,ij}\big|_{\mathbf{r}_i\to\mathbf{r}}. \tag{37}$$

This limiting expression coincides with its counterpart for a system with smooth interaction which can be deduced [2], by starting immediately from the second equation of the BBGKY hierarchy and the definition of $\tilde{e}^{\mathrm{p}}$.

4.3. The limit of equations for one-particle densities

At the passage to the limit, only the expressions for contributions P^{MS} and $\mathbf{q}_{\mathrm{k}}^{\mathrm{MS}}$ are changed. The source s_{k} changes in the same way as s_{p}, Eq. (37).

The contributions $\mathsf{P}^{\otimes}$ and $\mathbf{q}_{\mathrm{k}}^{\otimes}$ tend rapidly to zero, as 1) due to the product $\theta(v_{ji\sigma})\,\theta(v_{ij}^{ql}-v_{ji\sigma})$, the size of

the integration interval over $v_{ij\sigma}$ vanishes; 2) owing to $\theta(v_{ij}^{ql} - v_{ji\sigma})$, the factors $m_i(\mathbf{c}_i' - \mathbf{c}_i)$ and $\frac{1}{2}m_i[c_i'^2 - c_i^2]$ vanish, as the upper bounds of their absolute values are proportional to $(\epsilon_{ij}^{ql})^{1/2}$.

The contributions $\oplus$ and $\ominus$ to $\mathsf{P}^{\rm MS}$ and $\mathbf{q}_{\rm k}^{\rm MS}$ depend on the height of steps through the differences which, for small $\{\epsilon_{ij}^{ql}\}$, are equal to Eq. (27):

$$\left[\begin{array}{c} \mathbf{c}_{il}^{qp} - \mathbf{c}_i \\ (c_{il}^{qp})^2 - c_i^2 \end{array}\right] = -\left[\begin{array}{c} \frac{1}{2} \\ 1 \end{array}\right] pM_{ji}\frac{(v_{ij}^{ql})^2}{c_{ji\sigma}}\left[\begin{array}{c} \hat{\sigma} \\ \mathbf{c}_i\cdot\hat{\sigma} \end{array}\right].$$

Inserting these into Eq. (19) and going over to the continuous variable $\mathbf{R}$ as we have done above for $I_{ij}^{\rm MS}$ and $s_{\rm p}$ yield

$$\left[\begin{array}{c} \tilde{\mathsf{P}} \\ \tilde{\mathbf{q}}_{\rm k} \end{array}\right]^{\oplus+\ominus} = -\frac{1}{2}\sum_{i,j=1}^{M}\int \mathrm{d}\mathbf{v}_i\,\mathrm{d}\mathbf{v}_j \left[\begin{array}{c} 1 \\ \mathbf{c}_i \cdot \end{array}\right] \int \mathrm{d}\mathbf{r}_{ji}\,\hat{r}_{ji}\mathbf{r}_{ji} \times$$

$$\times\tilde{\phi}_{ij}'(r_{ij})\int_0^1 \mathrm{d}\lambda \bar{f}_2^{ij}(\mathbf{r} - \lambda\mathbf{r}_{ji}, \mathbf{v}_i, \mathbf{r} + [1-\lambda]\mathbf{r}_{ji}, \mathbf{v}_j). \quad (38)$$

The expression for $\tilde{\mathsf{P}}^{\oplus+\ominus}$ can be integrated over $\mathbf{v}_i$ and $\mathbf{v}_j$ and, in the case of the potential $\phi_{ij}^{\rm hs+t}$, coincides with the expression [7] for the contribution $\mathsf{P}^{\rm t}$ from the soft tail $\phi_{ij}^{\rm t}$, Eq. (23). However, the limiting heat flux of the kinetic energy $\tilde{\mathbf{q}}_{\rm k}^{\oplus+\ominus}$ does not have such a counterpart in KVT.

The limiting equation for $e^{\rm k}$ is of the same form as Eq. (17), in which $\mathsf{P}^{\rm MS}$, $\mathbf{q}^{\rm MS}$, and $s^{\rm k}$ must be replaced with $\tilde{\mathsf{P}}^{\oplus+\ominus}$, $\tilde{\mathbf{q}}^{\oplus+\ominus}$, and $\tilde{s}^{\rm k} = -\tilde{s}^{\rm p}$, Eq. (37). It does not have the shortcomings inherent in Eq. (22).

5. Conclusions

We have considered a passage to the limit of the potential of "hard spheres + arbitrary tail" for the kinetic theory for the MSP system. The limiting kinetic equation obtained coincides with that of the kinetic variational theory [7, 9], namely KVT-III [8]. It is found out that the contribution $I_i^{\rm MS}$ from the processes at steps transforms into the mean-field term of this theory. Beside the earlier consideration for a one-component fluid [13], the limiting form of the balance equation for the potential energy density is additionally obtained with the explicit expression for the corresponding source.

Contrary to the result for the kinetic equation, the limiting equation for the kinetic energy density differs from its KVT counterpart for both one- and many-component cases. It includes additional terms with contributions to the stress tensor and the heat flux from a smooth tail. The reason for this disagreement will be analyzed separately.

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ГРАНИЧНА ПОВЕДІНКА КІНЕТИЧНОЇ ТЕОРІЇ ДЛЯ СИСТЕМ ІЗ БАГАТОСХОДИНКОВИМ ПОТЕНЦІАЛОМ

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Р е з ю м е

Розглянуто кінетичну теорію сумішей з багатосходинковим потенціалом взаємодії. Проаналізовано граничний перехід до плавного неперервного потенціалу для кінетичного рівняння і рівняння балансу для густини потенціальної енергії. Коли граничний потенціал вибрано у формі "тверді кульки + плавний хвіст", кінетичне рівняння зводиться до рівняння кінетичної варіаційної теорії (КВТ), однак граничне рівняння балансу для густини кінетичної енергії відрізняється від відповідного рівняння КВТ.