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Generalized Nernst-Einstein relations for nonlinear transport coefficients

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A hierarchy of generalized Nernst-Einstein relations is derived that gives relations among the higher-order transport coefficients that describe nonlinear mobility and non-Fickian diffusion. The results are valid for the case where the transported species is present in only trace concentration, but are otherwise general. In particular, the relations are independent of the density of the medium and of the form of the molecular interactions. Both a phenomenological derivation and a more rigorous one based on a linear kinetic equation are given. Some additional relations are also obtained for the special case of gaseous ions interacting according to the Maxwell model, which may be approximately valid for gaseous ions having more general interactions.

I. INTRODUCTION

It has long been recognized that there should be some connection between the ease with which a species can be pulled through a medium by an external force, and the ease with which the species can diffuse through the same medium under the influence of its own concentration gradient. When both the force and the gradient are small enough that the transport follows linear equations (e.g., Ohm's law when an electric field supplies the external force, and Fick's law of diffusion), then the connection is given by the so-called Nernst-Einstein relation

$$K = q_i D / k_B T \,, \qquad (1)$$

where K is the mobility of a species of charge q_i in an external electric field, and D is its Fickian diffusion coefficient. The equivalent of this equation was obtained by Nernst,[1] who was interested in solutions of electrolytes and who used the concept of osmotic pressure as the driving force. The name of Einstein later became attached to the relation through his work on Brownian motion,[2] in which he estimated K by means of the Stokes formula for viscous drag on a sphere. The relation was also derived independently for the special case of ions in gases by Townsend,[3] who took his starting point from Maxwell's fundamental paper[4] on kinetic theory.

The question addressed in this paper is whether relations analogous to Eq. (1) hold when the external force and the concentration gradient are no longer so small that the transport is linear in these quantities. That is, when the mobility becomes nonlinear and the diffusion becomes non-Fickian, a number of higher-order transport coefficients are required to describe the transport. Are there relations among these higher-order coefficients? A suggestion that such relations might exist came from some explicit calculations of a few higher-order transport coefficients by Whealton and Mason[5] for a special simple case. Examination of the expressions for the coefficients showed some obvious relations, but unfortunately it was not clear whether these relations were reflections of a general law or were only artifacts of the special case considered. This case consisted of ions moving through a dilute monatomic gas, with the ion-atom interaction given by the Maxwell model, in which the cross section varies inversely as the relative speed, so that the mean free time between collisions is constant.

We show, by two separate lines of argument, that a number of generalized Nernst-Einstein relations exist under rather general circumstances. These apply not only to the transport of species number or mass, but also to the transport of other quantities such as momentum or energy. The main restrictive assumption we make is that the species on which the external force acts, and whose transport we are following, is present in very much lower concentration than the species of the background medium through which it moves. (For simplicity we shall henceforth refer to the species followed as "ions.") This assumption not only simplifies the form of the transport equations, but more importantly, simplifies the nature of the ion velocity distribution function in an essential way, as will be seen later. Incidentally, the derivation of the original Nernst-Einstein relation of Eq. (1) does *not* require the use of this assumption. The relations we obtain are otherwise generally applicable—they apply to liquids as well as to gases, for instance.

We begin with a phenomenological discussion that serves to indicate the physical basis of the argument, without too many mathematical trappings. The results are restricted to mass transport only. For a more rigorous and general form of results, we turn to a second line of argument based on a kinetic equation for the ion velocity distribution function, which we solve by a moment-expansion method. The crucial feature of the kinetic equation is its linearity, which follows from the assumption of trace concentration of ions. The generalized Nernst-Einstein relations obtained in this way have a mathematical structure that is simple enought to encourage us to conjecture a form of relation valid to all orders of deviation from linear transport laws.

We also work out the special case of Maxwell-model gaseous ions considered by Whealton and Mason. A few further simple relations of the Nernst-Einstein type are then also valid. These special relations may be approximately valid for gaseous ions having more general interactions than those of the Maxwell model, but this conjecture must be tested either by experiment or by detailed calculations for particular interactions.

II. PHENOMENOLOGICAL ARGUMENTS

We begin with a brief derivation of the original Nernst-Einstein relation of Eq. (1), without assuming that the ions are present in trace quantity. We assume only that the external force (electric field strength) and the concentration gradient are so weak that the system can be considered to be close to equilibrium, and that the flux density of ions $\vec{J}_i$ is linear in these quantities,

$$\vec{J}_i = n_i K \vec{E} - D \vec{\nabla} n_i , \tag{2}$$

where n_i is the number density of ions. The medium is assumed to be isotropic, so that both K and D are scalars. Since Eq. (2) is supposed to be valid anywhere sufficiently close to equilibrium, we can pick any convenient special case in order to investigate a possible relation between K and D. We choose the steady state, $\vec{J}_i = 0$, and in particular we can choose a steady state of true equilibrium, in which a steady electric field produces a steady concentration gradient, and the diffusion down this gradient exactly balances the forced flow due to the field. At equilibrium the field causes a spatial distribution of ions that is given by a Boltzmann expression

$$n_i = n_i^0 \exp(q_i \vec{E} \cdot \vec{x} / k_B T) , \tag{3}$$

where $\vec{x}$ is the position vector and n_i^0 is a constant. (A positive rather than a negative sign occurs in the exponential because of the sign convention for $\vec{E}$.) From Eq. (3) we obtain a relation between $\vec{\nabla} n_i$ and $\vec{E}$ by differentiation,

$$\vec{\nabla} n_i = n_i (q_i / k_B T) \vec{E} . \tag{4}$$

Substituting this expression into Eq. (2) and setting $\vec{J}_i = 0$, we immediately obtain the Nernst-Einstein relation of Eq. (1).

The interesting feature of the preceding argument is that the flux expression of Eq. (2) refers to a system that deviates from equilibrium, but for the ion distribution we can use the equilibrium formula of Eq. (3). If we extend the flux equation to allow for a second-order deviation from equilibrium, we might therefore expect to have to take into account at least first-order deviations from Eq. (3). Deviations from Eq. (3) might arise for strong fields, because a strong field could locally increase the ion density enough to cause appreciable ion-ion interactions, for example. The explicit assumption of trace concentration of ions, plus the implicit assumption that the background medium of neutral molecules is unaffected by the field, avoids the difficulty and allows us to use Eq. (3) even when the field and the gradient are no longer weak.

To extend the range of validity of the linear flux law of Eq. (2), we add on terms with higher powers of $\vec{E}$ and higher derivatives of n_i. No terms like $(\vec{\nabla} n_i)^2$ occur, however, because of the assumption of trace ion concentration. It is convenient to write the resulting nonlinear flux equation in the form[5]

$$\vec{J}_i = n_i K \vec{E} - \overleftrightarrow{D}^{(2)} \cdot \vec{\nabla} n_i + \overleftrightarrow{Q}^{(3)} : \vec{\nabla} \vec{\nabla} n_i - \overleftrightarrow{R}^{(4)} : \vec{\nabla} \vec{\nabla} \vec{\nabla} n_i + \cdots , \tag{5}$$

and let the transport coefficients depend on $\vec{E}$. The mobility K is still a scalar, but the diffusion coefficient $\overleftrightarrow{D}^{(2)}$ is a second-order tensor, $\overleftrightarrow{Q}^{(3)}$ a third-order tensor, and $\overleftrightarrow{R}^{(4)}$ a fourth-order tensor. Various symmetries require that these tensors have only two, three, and five independent components, respectively.[5] Moreover, inversion symmetry requires that K, $\overleftrightarrow{D}^{(2)}$, and $\overleftrightarrow{R}^{(4)}$ be even functions of $\vec{E}$ and that $\overleftrightarrow{Q}^{(3)}$ be an odd function. We can therefore expand the transport coefficients conveniently as power series in E. Assuming for simplicity that the field is homogeneous, and indicating by superscripts the components parallel to the field ($\parallel$) and parallel to the density gradient ($\perp$), we obtain

$$K = K_0 + K_2 E^2 + K_4 E^4 + \cdots , \tag{6a}$$

$$\overleftrightarrow{D}^{(2)} = \overleftrightarrow{I}^{(2)} (D_0 + d_2^{\perp} E^2 + d_4^{\perp} E^4 + \cdots) + \vec{E}\vec{E} (d_2^{\parallel} + d_4^{\parallel} E^2 + \cdots) , \tag{6b}$$

$$\overleftrightarrow{Q}^{(3)} = \overleftrightarrow{I}^{(2)} \vec{E} (q_1^{\perp} + q_3^{\perp} E^2 + \cdots) + \vec{E}\overleftrightarrow{I}^{(2)} (q_1^{\parallel} + q_3^{\parallel} E^2 + \cdots) , \tag{6c}$$

$$\overleftrightarrow{R}^{(4)} = \overleftrightarrow{I}^{(2)} \overleftrightarrow{I}^{(2)} (R_0 + \cdots) , \tag{6d}$$

where $\overleftrightarrow{I}^{(2)}$ is the unit second-order tensor. The angle between $\vec{E}$ and $\vec{\nabla} n_i$ is arbitrary, despite the suggestion of the $(\perp)$ superscript. More explicitly, the gradient terms in Eq. (5) are

$$\overleftrightarrow{\mathrm{D}}^{(2)}\cdot\vec{\nabla}n_i = D_0\vec{\nabla}n_i + d_2^{\perp}E^2\vec{\nabla}n_i + d_2^{\parallel}\vec{\mathrm{E}}(\vec{\mathrm{E}}\cdot\vec{\nabla}n_i) + \cdots , \tag{7a}$$

$$\overleftrightarrow{\mathrm{Q}}^{(3)}:\vec{\nabla}\vec{\nabla}n_i = q_1^{\perp}(\vec{\mathrm{E}}\cdot\vec{\nabla})\vec{\nabla}n_i + q_1^{\parallel}\vec{\mathrm{E}}(\nabla^2 n_i) + \cdots, \tag{7b}$$

$$\overleftrightarrow{\mathrm{R}}^{(4)}\vdots\,\vec{\nabla}\vec{\nabla}\vec{\nabla}n_i = R_0(\vec{\nabla}\cdot\vec{\nabla})\vec{\nabla}n_i + \cdots . \tag{7c}$$

We now repeat the argument used to obtain the original Nernst-Einstein relation, using the condition of trace ion concentration to justify the Boltzmann expression for the spatial distribution of ions at equilibrium. One differentiation yields Eq. (4), and further differentiation yields

$$\vec{\nabla}\vec{\nabla}n_i = n_i(q_i/k_B T)^2\vec{\mathrm{E}}\vec{\mathrm{E}} , \tag{8a}$$

$$\vec{\nabla}\vec{\nabla}\vec{\nabla}n_i = n_i(q_i/k_B T)^3\vec{\mathrm{E}}\vec{\mathrm{E}}\vec{\mathrm{E}} ,\ \text{etc.} \tag{8b}$$

Substituting these expressions back into Eq. (7), setting $\vec{\mathrm{J}}_i = 0$ in Eq. (5), and equating the coefficients of different powers of E separately to zero, we obtain

$$K_0 - D_0(q_i/k_B T) = 0 , \tag{9a}$$

$$K_2 - (d_2^{\perp} + d_2^{\parallel})(q_i/k_B T) + (q_1^{\perp} + q_1^{\parallel})(q_i/k_B T)^2 - R_0(q_i/k_B T)^3 = 0 ,\ \text{etc.} \tag{9b}$$

Equation (9a) is the original Nernst-Einstein relation, and (9b) is the first higher-order relation. It is probably not worthwhile to go beyond (9b) because of the experimental difficulty of measuring the higher-order transport coefficients, but the procedure is clear.

III. KINETIC DERIVATION

In this section we obtain a set of generalized Nernst-Einstein relations by systematic solution of a linear kinetic equation for the ion distribution function $f(i)$ of the form

$$\left(\vec{\mathrm{c}}_i\cdot\frac{\partial}{\partial\vec{\mathrm{x}}} + \frac{q_i}{m_i}\vec{\mathrm{E}}\cdot\frac{\partial}{\partial\vec{\mathrm{c}}}\right)f(i) = B(i)f(i) , \tag{10}$$

where $\vec{\mathrm{c}}_i$ is the velocity of species i, and $B(i)$ is a linear collision operator. We assume that the system is in a steady state, so that no time derivatives appear. Our procedure is to convert Eq. (10) into a system of algebraic equations by forming moments over a set of basis functions. Although these equations cannot be solved explicitly without specifying the form of $B(i)$, it turns out that the elements of the inverse collision matrix corresponding to $B(i)$ can be algebraically eliminated to yield relations among transport coefficients. These relations are independent of the nature of $B(i)$, other than that it be linear, although the calculation of any particular transport coefficient requires specific knowledge of $B(i)$.

The moment method is mathematically equivalent to an expansion of $f(i)$ in terms of a set of basis functions, which are determined by the requirement that the leading term of the expansion be the equilibrium distribution function $f_0(i)$ of the kinetic equation. We use the condition of trace concentration of ions as the justification for taking $f_0(i)$ to be Maxwellian in the ion velocities,

$$f_0(i) \propto \exp(-m_i c_i^2/2k_B T) . \tag{11}$$

We expand $f(i)$ in terms of basis functions $\Phi_{nlm}(i)$,

$$f(i) = A^{n,l,m}\Phi_{nlm}(i) , \tag{12}$$

using the convention of summing over indices appearing once and only once as subscript and superscript, and choosing the leading term proportional to $f_0(i)$,

$$\Phi_{000}(i) \propto f_0(i) . \tag{13}$$

Final details on the form of the basis set depend on the symmetry properties of the collision operator. If the molecular interactions are isotropic, it is advantageous for the basis functions to contain an irreducible representation of the group of three-dimensional rotations. We therefore define

$$\Phi_{nlm}(i) \equiv (m_i/k_B T)^{(n+3)/2}\,\Phi_{nl}(\epsilon_i)Y_{lm}(\theta,\phi) , \tag{14}$$

with spherical harmonics Y_{lm} depending on the direction (θ, ϕ) of the ion velocity $\vec{\mathrm{c}}_i$, and

$$\epsilon_i \equiv m_i c_i^2/2k_B T . \tag{15}$$

The energy-dependent functions $\Phi_{nl}(\epsilon_i)$ include the condition of Eq. (13) and contain generalized Laguerre (Sonine) polynomials $L_s^r(\epsilon_i)$;

$$\Phi_{nl}(\epsilon_i) \equiv (-1)^{(n-l)/2}2^{(l+1)/2}\frac{(2l+1)^{1/2}}{2\pi} \times \frac{\epsilon_i^{l/2}e^{-\epsilon_i}}{(n+l+1)!!}L_{(n-l)/2}^{(l+1/2)}(\epsilon_i) . \tag{16}$$

The expansion coefficients $A^{n,l,m}$ of Eq. (12) are generalized moments of $f(i)$, as can be shown in the following way. We construct a set of dual basis functions $\Phi^{nlm}(i)$ by means of an orthonormality requirement

$$\int d^3c_i\,\Phi^{n'l'm'}(i)\,\Phi_{nlm}(i) = \delta_n^{n'}\delta_l^{l'}\delta_m^{m'} , \tag{17}$$

which yields

$$\Phi^{nlm}(i) = (k_B T/m_i)^{n/2}\,\Phi_l^n(\epsilon_i)Y_{lm}^*(\theta,\phi) , \tag{18}$$

with

$$\Phi_l^n(\epsilon_i) = (-1)^{(n-l)/2} 2^{(l+1)/2} \left(\frac{2\pi}{2l+1}\right)^{1/2} \times (n-l)!! \, \epsilon_i^{l/2} L_{(n-l)/2}^{(l+1/2)}(\epsilon_i). \quad (19)$$

Multiplying the expansion of Eq. (12) by these functions and integrating, we obtain

$$A^{n,l,m} = \int d^3c_i \, \Phi^{n,l,m}(i) f(i). \quad (20)$$

The next step is to represent the kinetic equation in matrix form by means of the basis functions, which yields

$$D_{n,l,m}^{n',l',m'}(i) A^{n,l,m} = B_n^{n'}(l') A^{n,l,m}, \quad (21)$$

where

$$D_{n,l,m}^{n',l',m'}(i) \equiv \int d^3c_i \, \Phi^{n'l'm'}(i) \vec{c}_i \, \Phi_{nlm}(i) \cdot \frac{\partial}{\partial \vec{x}} + \frac{q_i}{m_i} \vec{E} \cdot \int d^3c_i \, \Phi^{n'l'm'}(i) \frac{\partial}{\partial \vec{c}_i} \Phi_{nlm}(i), \quad (22)$$

$$\delta_l^{l'} \delta_m^{m'} B_n^{n'}(l') \equiv \int d^3c_i \, \Phi^{n'l'm'}(i) B(i) \Phi_{nlm}(i). \quad (23)$$

Equation (21) is an infinite set of linear algebraic equations for the generalized moments $A^{n,l,m}$, which can be solved in a formal sense provided any dependent equations are first removed. The dependent equations represent the so-called collisional invariants and correspond to zero eigenvalues of $B(i)$. In classical kinetic theory there are five collisional invariants, corresponding to conservation of mass, energy, and the three components of linear momentum in a binary collision,[6] so that the zero eigenvalue of the binary collision operator is fivefold degenerate. But in the present case the collision operator $B(i)$ focuses on the ions, and the only property of the ions that is always conserved in an interaction with the medium is the ion mass. The zero eigenvalue of $B(i)$ is thus nondegenerate; moreover, its corresponding eigenfunction is $f_0(i)$. We can therefore restrict the indices in Eq. (21) to $n, n' > 0$, and rewrite it in inhomogeneous form as

$$D_{n,l,m}^{n',l',m'} A^{n,l,m} - B_n^{n'}(l') A^{n,l',m'} = -D_{0,0,0}^{n',l',m'} n_i(\vec{x}), \quad n, n' > 0, \quad (24)$$

where we have used the fact that the lowest moment is the ion density,

$$A^{0,0,0} = n_i(\vec{x}). \quad (25)$$

The restricted collision matrix B of this inhomogeneous system of equations is seen from Eq. (23) to be diagonal in l, l' and m, m'; it also is regular and can in principle be inverted. Multiplying Eq. (24) by this inverse matrix, we obtain

$$(\delta_n^{n'} \delta_l^{l'} \delta_m^{m'} - S_{n,l,m}^{n',l',m'}) A^{n,l,m} = G^{n',l',m'}, \quad (26)$$

where

$$S_{n,l,m}^{n',l',m'} \equiv [B^{-1}(l')]_{\bar{n}}^{n'} D_{n,l,m}^{\bar{n},l',m'}(i), \quad (27)$$

$$G^{n',l',m'} \equiv [B^{-1}(l')]_{\bar{n}}^{n'} D_{0,0,0}^{\bar{n},l',m'}(i) n_i(\vec{x}). \quad (28)$$

A formal solution of Eq. (26) can be obtained by series expansion, which yields

$$A^{n',l',m'} = \sum_{k=0}^{\infty} [S^k]_{n,l,m}^{n',l',m'} G^{n,l,m}. \quad (29)$$

This is the unique series expansion of the generalized moments in terms of powers of the gradient operator and the electric field. Because the gradient and the field occur only linearly in D and because of the linear nature of B, the structure of Eq. (29) provides the kinetic justification for the more phenomenological Eqs. (5)–(7) of Sec. II.

To find explicit relations among transport coefficients, we need a definite procedure for generating the formal solution indicated by Eq. (29). The needed matrix elements of D, defined in Eq. (22), have been discussed previously,[7] and in the present case are

$$\begin{aligned} D_{n,l,m}^{n',l',m'}(i) A^{n,l,m} = {} & \frac{l'}{2l'+1} \frac{\langle l',m' | 1,M; l'-1,m\rangle}{\langle l',0 | 1,0; l'-1,0\rangle} \left\{ (n'+l'+1)\left[\frac{k_B T}{m_i}\left(\frac{\partial}{\partial x}\right)^M - \frac{q_i}{m_i} E^M\right] \times A^{n'-1,l'-1,m} + \left(\frac{\partial}{\partial x}\right)^M A^{n'+1,l'-1,m} \right\} \\ & + \frac{l'+1}{2l'+1} \frac{\langle l',m' | 1,M; l'+1,m\rangle}{\langle l',0 | 1,0; l'+1,0\rangle} \left\{ (n'-l')\left[\frac{k_B T}{m_i}\left(\frac{\partial}{\partial x}\right)^M - \frac{q_i}{m_i} E^M\right] \times A^{n'-1,l'+1,m} + \left(\frac{\partial}{\partial x}\right)^M A^{n'+1,l'+1,m} \right\}. \end{aligned} \quad (30)$$

In this expression all vectorial quantities are represented by their spherical components, denoted by a superscript M. That is, the spherical components of $\vec{E}$ are $\mp(E_x \pm iE_y)/2^{1/2}$ and E_z. The symbols enclosed in angular brackets represent conventional Clebsch-Gordan coefficients, and the summation convention is extended for them so that indices in bra vectors correspond to superscripts and indices in ket vectors to subscripts.

We now construct the formal solution (29) by a recurrence procedure. Starting with initial values of the generalized moments from Eq. (26) of the form

$$A_{(0)}^{n',l',m'} \equiv G^{n',l',m'} = [B^{-1}(1)]_1^{n'} \delta_1^{l'} \left[\frac{k_B T}{m_i} \left(\frac{\partial n_i}{\partial x} \right)^{m'} - \frac{q_i}{m_i} E^{m'} n_i(\vec{x}) \right], \quad (31)$$

we generate higher values by recursion,

$$A_{(k+1)}^{n',l',m'} = S_{n,l,m}^{n',l',m'} A_{(k)}^{n,l,m}. \quad (32)$$

This procedure generates the generalized moments as a series,

$$A^{n',l',m'} = \sum_{k=0}^{\infty} A_{(k)}^{n',l',m'}, \quad (33)$$

where the summation index k has the same meaning as in Eq. (29).

If the elements of the inverse (restricted) collision matrix are known, Eqs. (31)–(33) generate a complete series solution of the transport equation. The recursion procedure (32) does not pose any basic difficulty of principle, but in practice becomes complicated because of the necessity of generating the elements of the inverse collision matrix. Fortunately, we do not need to proceed to high-order results for the present purposes; the results of the first iterations are straightforward and are given in the Appendix. What is somewhat surprising is that the elements of the inverse collision matrix can be algebraically eliminated from the expressions for the transport coefficients, to produce a number of generalized Nernst-Einstein relations among transport coefficients. To exhibit these relations, we first define generalized transport coefficients as the expansion coefficients in the Taylor series represented by Eq. (33), which can be written symbolically as

$$A^{n',l'} = \sum_{\substack{k,q \\ q \le k}} \alpha_{q,k-q}^{n',l'} \left(\frac{q_i}{m_i} E \right)^q \left(-\frac{\partial}{\partial x} \right)^{k-q} n_i(\vec{x}). \quad (34)$$

The appearance of this symbolic expansion is deceptively simple—the transport coefficients α are really complicated tensorial quantities coupling the qth-order tensorial powers of $\vec{E}^q$ and the $(k-q)$th-order tensorial powers of the gradient operator to the generalized moments of order n' and rank l'. An explicit general representation of this feature of the α's is not necessary for the present purposes, however. Since only a few of the lower Nernst-Einstein relations are likely to be of interest, it should suffice to give expressions for the simple cases $l'=0, 1, 2$.

For $l'=0$, we have the scalar quantities,

$$A^{n',0,0} = \alpha_{0,2}^{n',0} \nabla^2 n_i - \alpha_{1,1}^{n',0} \frac{q_i}{m_i} \vec{E} \cdot \frac{\partial n_i}{\partial \vec{x}} + \alpha_{2,0}^{n',0} \left(\frac{q_i}{m_i} \right)^2 \vec{E} \cdot \vec{E} n_i(\vec{x}) + \cdots. \quad (35)$$

For $l'=1$, we have the spherical components of the vectorial quantities,

$$A^{n',1,m'} = \alpha_{1,0}^{n',1} \frac{q_i}{m_i} E^{m'} n_i(\vec{x}) - \alpha_{0,1}^{n',1} \left(\frac{\partial n_i}{\partial x} \right)^{m'} + \alpha_{3,0}^{n',1} \left(\frac{q_i}{m_i} \right)^3 E^{m'} \vec{E} \cdot \vec{E} n_i(\vec{x}) - \alpha_{2,1}^{n',1}(\perp) \left(\frac{q_i}{m_i} \right)^2 \vec{E} \cdot \vec{E} \left(\frac{\partial n_i}{\partial x} \right)^{m'}$$
$$- \alpha_{2,1}^{n',1}(\|) \left(\frac{q_i}{m_i} \right)^2 E^{m'} \vec{E} \cdot \frac{\partial n_i}{\partial \vec{x}} + \alpha_{1,2}^{n',1}(\perp) \frac{q_i}{m_i} \vec{E} \cdot \frac{\partial}{\partial \vec{x}} \left(\frac{\partial n_i}{\partial x} \right)^{m'} + \alpha_{1,2}^{n',1}(\|) \frac{q_i}{m_i} E^{m'} \nabla^2 n_i - \alpha_{0,3}^{n',1} \nabla^2 \left(\frac{\partial n_i}{\partial x} \right)^{m'} + \cdots. \quad (36)$$

Here the tensorial character of the coefficients α, mentioned above, makes it necessary to distinguish between components parallel to the electric field ($\|$) and parallel to the density gradient ($\perp$). Finally, for $l'=2$ we can write

$$A^{n',2,m'} = \frac{\langle 2,m' | 1,M; 1,m \rangle}{\langle 2,0 | 1,0; 1,0 \rangle} \left[\alpha_{0,2}^{n',2} \left(\frac{\partial}{\partial x} \right)^M \left(\frac{\partial n_i}{\partial x} \right)^m - \alpha_{1,1}^{n',2} \frac{q_i}{m_i} E^M \left(\frac{\partial n_i}{\partial x} \right)^m + \alpha_{2,0}^{n',2} \left(\frac{q_i}{m_i} \right)^2 E^M E^m n_i(\vec{x}) \right] + \cdots. \quad (37)$$

Explicit expressions for the generalized transport coefficients in terms of the elements of the inverse collision matrix are given in the Appendix. As already mentioned, the matrix elements can be algebraically eliminated to obtain relations among the transport coefficients; for $l'=0$, we find

$$0 = \alpha_{0,2}^{n',0} - \frac{k_B T}{m_i} \alpha_{1,1}^{n',0} + \left(\frac{k_B T}{m_i} \right)^2 \alpha_{2,0}^{n',0}. \quad (38)$$

For $l'=1$, we obtain the analogs of the Eqs. (9) obtained phenomenologically in Sec. II,

$$0=\alpha_{0,1}^{n',1}-\frac{k_BT}{m_i}\alpha_{1,0}^{n',1}, \tag{39a}$$

$$0=\alpha_{0,3}^{n',1}-\frac{k_BT}{m_i}[\alpha_{1,2}^{n',1}(\perp)+\alpha_{1,2}^{n',1}(\|)] +\left(\frac{k_BT}{m_i}\right)^2[\alpha_{2,1}^{n',1}(\perp)+\alpha_{2,1}^{n',1}(\|)]-\left(\frac{k_BT}{m_i}\right)^3\alpha_{3,0}^{n',1}, \tag{39b}$$

which differ from Eqs. (9) only by some obvious multiplicative factors of q_i/m_i and k_BT. Finally, for $l'=2$ we find

$$0=\alpha_{0,2}^{n',2}-\frac{k_BT}{m_i}\alpha_{1,1}^{n',2}+\left(\frac{k_BT}{m_i}\right)^2\alpha_{2,0}^{n',2}. \tag{40}$$

All these equations are of a generalized Nernst-Einstein type, and their structure is simple enough to suggest the following conjecture for a general relation:

$$0=\sum_{q=0}^{k}\alpha_{q,k-q}^{n',l'}\left(\frac{k_BT}{m_i}\right)^q. \tag{41}$$

This expression is symbolic in the same sense that Eq. (34) defining the α's is symbolic.

IV. MAXWELL MODEL

Whereas the relations deduced in Secs. II and III are independent of the molecular interaction, the restriction to the case of Maxwell-model interactions generates some further simple relations, which may also be approximately true for more general interactions. We limit the discussion of these relations to the case $n'=l'=1$, corresponding to the spherical components of the diffusion flux vector $\vec{J}_i$.

For the Maxwell model the collision matrix is diagonal in n, n'; we therefore can write

$$B_n^{n'}(l')=\delta_n^{n'}b(n',l'). \tag{42}$$

The inversion of this matrix is trivial, and from the general expressions in the Appendix we can immediately write down explicit expressions for the transport coefficients as defined by Eqs. (6),

$$K_0=-\frac{q_i}{m_i}\frac{1}{b(1,1)}, \tag{43a}$$

$$K_2=0, \tag{43b}$$

$$D_0=-\frac{k_BT}{m_i}\frac{1}{b(1,1)}, \tag{44a}$$

$$d_2^{\perp}=\frac{2}{3}\left(\frac{q_i}{m_i}\right)^2\frac{1}{[b(1,1)]^2}\left(\frac{1}{b(2,2)}-\frac{1}{b(2,0)}\right), \tag{44b}$$

$$d_2^{\|}=-2\left(\frac{q_i}{m_i}\right)^2\frac{1}{[b(1,1)]^2b(2,2)}, \tag{44c}$$

$$q_1^{\perp}=-\frac{2}{3}\frac{k_BT}{m_i}\frac{q_i}{m_i}\frac{1}{[b(1,1)]^2}\left(\frac{1}{b(2,2)}+\frac{2}{b(2,0)}\right), \tag{45a}$$

$$q_1^{\|}=-2\frac{k_BT}{m_i}\frac{q_i}{m_i}\frac{1}{[b(1,1)]^2b(2,2)}, \tag{45b}$$

$$R_0=-\frac{2}{3}\left(\frac{k_BT}{m_i}\right)^2\frac{1}{[b(1,1)]^2}\left(\frac{1}{b(2,0)}+\frac{2}{b(2,2)}\right). \tag{46}$$

Eliminating the matrix elements $b(n',l')$ among these expressions, we obtain a number of generalized Nernst-Einstein relations,

$$D_0=(k_BT/q_i)K_0, \tag{47}$$

$$q_1^{\|}=(k_BT/q_i)d_2^{\|}, \tag{48}$$

$$q_1^{\perp}=(k_BT/q_i)(2d_2^{\perp}+d_2^{\|}), \tag{49}$$

$$R_0=\tfrac{1}{2}(k_BT/q_i)(q_1^{\perp}+q_1^{\|})=(k_BT/q_i)^2(d_2^{\perp}+d_2^{\|}). \tag{50}$$

Clearly these relations are consistent with our general result—in particular, Eq. (47) is the original Nernst-Einstein relation, and our Eq. (9b) or Eq. (39b) is obtained by summing Eqs. (48)–(50) and setting $K_2=0$. These results are also consistent with the partial results obtained earlier by Whealton and Mason[5] for the Maxwell model.

V. DISCUSSION

The present results show that there is a whole hierarchy of relations among the nonlinear transport coefficients, analogous to the Nernst-Einstein relation between the linear coefficients. The main restriction in our derivation is that the transported species be present only in trace concentration.

Although the phenomenological derivation presented is straightforward, the more rigorous kinetic derivation appears rather roundabout. In particular, the way that the elements of the inverse collision matrix are eliminated at the end, so that the results are independent of the molecular interactions, appears almost fortuitous. We have sought a more direct derivation using projection operators rather than a matrix method, but without achieving the desired simplification. The trouble is that the interactions are contained in the inverse projected collision operators and do not drop out unless the inverse operators obey some special commutation relations. To prove these relations we have had to revert to a matrix representation, and the apparent simplicity is lost.

Finally, the present generalized Nernst-Einstein relations should be distinguished from some rather similar relations frequently used for gaseous ions at high electric fields, which are really extensions of the original linear relation given by Eq. (1).[8]

Only Fickian diffusion is considered, but the electric field may be so high that the components $D_\parallel$ and $D_\perp$ of $\overleftrightarrow{D}^{(2)}$ must be considered separately, and the form of Eq. (1) is largely preserved by defining special ion temperatures $T_\parallel$ and $T_\perp$,

$$D_\perp \approx \frac{k_B T_\perp}{q_i} K , \tag{51a}$$

$$D_\parallel \approx \frac{k_B T_\parallel}{q_i} K \left(1 + \frac{d \ln K}{d \ln (E/n_0)}\right), \tag{51b}$$

where n_0 is the number density of neutral particles, and

$$k_B T_\perp = k_B T + \zeta_\perp v_d^2 , \tag{52a}$$

$$k_B T_\parallel = k_B T + \zeta_\parallel v_d^2 . \tag{52b}$$

Here $v_d = KE$ is the ion drift speed, and $\zeta_\perp$ and $\zeta_\parallel$ are coefficients that depend primarily on the masses of the ions and the neutral molecules and weakly on their interaction. These relations were first obtained by Wannier[9] for the Maxwell model, for which they are exact, but they are often quite accurate for real ion-molecule systems.[10] Various refinements have been proposed for improving the accuracy of these useful relations, which need not concern us here. The essential difference between these and our results is that our results are exact relations among field-independent higher-order coefficients, whereas Eqs. (51) and (52) are approximate relations between field-dependent linear coefficients.

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APPENDIX

We use the abbreviation

$$\mathfrak{D}^m \equiv \frac{k_B T}{m_i}\left(\frac{\partial}{\partial x}\right)^m - \frac{q_i}{m_i} E^m , \tag{A1}$$

and have [cf. Eq. (31)]

$$A_{(0)}^{n',l',m'} = [B^{-1}(1)]_1^{n'} \delta_1^{l'} \mathfrak{D}^{m'} n_i . \tag{A2}$$

Application of the matrix S, Eq. (27), yields

$$A_{(1)}^{n',l',m'} = [B^{-1}(l')]_{\bar n}^{n'} D_{n,1,m}^{\bar n;l',m'}(i) \times [B^{-1}(1)]_1^n \mathfrak{D}^m n_i . \tag{A3}$$

Because of the particular structure of the differential matrix, Eq. (30), this expression is nonzero only for $l' = 0$ and 2. For $l' = 0$ we have

$$A_{(1)}^{n',0,0} = \beta_-^{n'}(0)\, \mathfrak{D}_m \mathfrak{D}^m n_i + \beta_+^{n'}(0) \frac{\partial}{\partial x^m} \mathfrak{D}^m n_i , \tag{A4}$$

where we have used the coupling property of the Clebsch-Gordan coefficients to generate the scalar product of two vectors,

$$\vec{a} \cdot \vec{b} = a^m b_m = \frac{\langle 0,0 | 1,M;1,m\rangle}{\langle 0,0|1,0;1,0\rangle} a^m b^M . \tag{A5}$$

The coefficients β are certain products of the inverse collision matrix and are listed at the end of this appendix.

Similarly, we obtain for $l' = 2$,

$$A_{(1)}^{n',2,m'} = \frac{2}{5} \frac{\langle 2,m' | 1,M;1,m\rangle}{\langle 2,0|1,0;1,0\rangle} \times \left[\beta_-^{n'}(2)\, \mathfrak{D}^M \mathfrak{D}^m n_i + \beta_+^{n'}(2) \left(\frac{\partial}{\partial x}\right)^M \mathfrak{D}^m n_i\right]. \tag{A6}$$

The second iteration again generates two contributions corresponding to $l' = 1$ and 3. For $l' = 3$ we have

$$A_{(2)}^{n',3,m'} = \frac{6}{35} \frac{\langle 3,m' | 1,M;2,m\rangle}{\langle 3,0|1,0;2,0\rangle} \frac{\langle 2,m | 1,\bar M;1,\bar m\rangle}{\langle 2,0|1,0;1,0\rangle} \times \left[\beta_{--}^{n'}(3,2)\mathfrak{D}^M \mathfrak{D}^{\bar M} \mathfrak{D}^{\bar m} n_i + \beta_{-+}^{n'}(3,2)\mathfrak{D}^M \left(\frac{\partial}{\partial x}\right)^{\bar M} \mathfrak{D}^{\bar m} n_i + \beta_{+-}^{n'}(3,2)\left(\frac{\partial}{\partial x}\right)^M \mathfrak{D}^{\bar M}\mathfrak{D}^{\bar m} n_i + \beta_{++}^{n'}(3,2)\left(\frac{\partial}{\partial x}\right)^M \left(\frac{\partial}{\partial x}\right)^{\bar M} \mathfrak{D}^{\bar m} n_i\right]. \tag{A7}$$

The second-order correction for $l' = 1$ consists of two terms:

$$A_{(2)}^{n',1,m'} = S_{n,2,m}^{n',1,m'} A_{(1)}^{n,2,m} + S_{n,0,0}^{n',1,m'} A_{(1)}^{n,0,0} . \tag{A8}$$

More explicitly we have

$$A_{(2)}^{n',1,m'}=\frac{4}{15}\frac{\langle 1,m'|1,M;2,m\rangle}{\langle 1,0|1,0;2,0\rangle}\frac{\langle 2,m|1,\bar{M};1,\bar{m}\rangle}{\langle 2,0|1,0;1,0\rangle}$$
$$\times\Big[\beta_{--}^{n'}(1,2)\mathfrak{D}^{M}\mathfrak{D}^{\bar{M}}\mathfrak{D}^{\bar{m}}n_i+\beta_{-+}^{n'}(1,2)\mathfrak{D}^{M}\left(\frac{\partial}{\partial x}\right)^{\bar{M}}\mathfrak{D}^{\bar{m}}n_i+\beta_{+-}^{n'}(1,2)\left(\frac{\partial}{\partial x}\right)^{M}\mathfrak{D}^{\bar{M}}\mathfrak{D}^{\bar{m}}n_i$$
$$+\beta_{++}^{n'}(1,2)\left(\frac{\partial}{\partial x}\right)^{M}\left(\frac{\partial}{\partial x}\right)^{\bar{M}}\mathfrak{D}^{\bar{m}}n_i\Big]$$
$$+\frac{1}{3}\Big[\beta_{--}^{n'}(1,0)\mathfrak{D}^{m'}\mathfrak{D}^{m}\mathfrak{D}_{m}n_i+\beta_{-+}^{n'}(1,0)\mathfrak{D}^{m'}\frac{\partial}{\partial x^{m}}\mathfrak{D}^{m}n_i+\beta_{+-}^{n'}(1,0)\left(\frac{\partial}{\partial x}\right)^{m'}\mathfrak{D}^{m}\mathfrak{D}_{m}n_i$$
$$+\beta_{++}^{n'}(1,0)\left(\frac{\partial}{\partial x}\right)^{m'}\frac{\partial}{\partial x^{m}}\mathfrak{D}^{m}n_i\Big]. \tag{A9}$$

We stop the iteration at this level and add a more detailed evaluation of Eq. (A9). The ratios of Clebsch-Gordan coefficients needed in the context of our iteration procedure are listed in Table I. By means of Table I, we can derive the relation,

$$\frac{\langle 1,m'|1,M;2,m\rangle}{\langle 1,0|1,0;2,0\rangle}\frac{\langle 2,m|1,\bar{M};1,\bar{m}\rangle}{\langle 2,0|1,0;1,0\rangle}a^{M}b^{\bar{M}}c^{\bar{m}}=-\tfrac{1}{2}a^{m'}\vec{b}\cdot\vec{c}+\tfrac{3}{4}b^{m'}\vec{a}\cdot\vec{c}+\tfrac{3}{4}c^{m'}\vec{a}\cdot\vec{b}, \tag{A10}$$

for the spherical components of the vectors $\vec{a}$, $\vec{b}$, and $\vec{c}$. Using instead the vector operators $\partial/\partial\vec{x}$ and $\vec{\mathfrak{D}}$ in the proper way, we obtain the following after some algebraic manipulations from Eq. (A9):

$$A_{(2)}^{n',1,m'}=\nabla^2\left(\frac{\partial n_i}{\partial x}\right)^{m'}\Bigg[\left(\frac{k_BT}{m_i}\right)^3\left[\tfrac{4}{15}\beta_{--}^{n'}(1,2)+\tfrac{1}{3}\beta_{--}^{n'}(1,0)\right]+\left(\frac{k_BT}{m_i}\right)^2\left[\tfrac{4}{15}\beta_{-+}^{n'}(1,2)+\tfrac{1}{3}\beta_{-+}^{n'}(1,0)+\tfrac{1}{3}\beta_{+-}^{n'}(1,0)\right.$$
$$\left.+\tfrac{4}{15}\beta_{+-}^{n'}(1,2)\right]+\frac{k_BT}{m_i}\left[\tfrac{4}{15}\beta_{++}^{n'}(1,2)+\tfrac{1}{3}\beta_{++}^{n'}(1,0)\right]\Bigg]+\frac{q_i}{m_i}E^{m'}\nabla^2 n_i$$
$$\times\Bigg[\left(\frac{k_BT}{m_i}\right)^2\left[\tfrac{4}{15}\beta_{--}^{n'}(1,2)+\tfrac{1}{3}\beta_{--}^{n'}(1,0)\right]+\frac{k_BT}{m_i}\left[\tfrac{1}{15}\beta_{-+}^{n'}(1,2)+\tfrac{2}{5}\beta_{+-}^{n'}(1,2)+\tfrac{1}{3}\beta_{-+}^{n'}(1,0)\right]+\tfrac{1}{5}\beta_{++}^{n'}(1,2)\Bigg]$$
$$-\frac{q_i}{m_i}E^{m}\frac{\partial}{\partial x^{m}}\left(\frac{\partial n_i}{\partial x}\right)^{m'}$$
$$\times\Bigg[\left(\frac{k_BT}{m_i}\right)^2\left[\tfrac{8}{15}\beta_{--}^{n'}(1,2)+\tfrac{2}{3}\beta_{--}^{n'}(1,0)\right]+\frac{k_BT}{m_i}\left[\tfrac{7}{15}\beta_{-+}^{n'}(1,2)+\tfrac{2}{15}\beta_{+-}^{n'}(1,2)+\tfrac{1}{3}\beta_{-+}^{n'}(1,0)+\tfrac{2}{3}\beta_{+-}^{n'}(1,0)\right.$$
$$\left.+\tfrac{1}{15}\beta_{++}^{n'}(1,2)+\tfrac{1}{3}\beta_{++}^{n'}(1,0)\right]\Bigg]+\left(\frac{q_i}{m_i}\right)^2E^{m}E_{m}\left(\frac{\partial n_i}{\partial x}\right)^{m'}$$
$$\times\Bigg[\frac{k_BT}{m_i}\left[\tfrac{4}{15}\beta_{--}^{n'}(1,2)+\tfrac{1}{3}\beta_{--}^{n'}(1,0)\right]+\tfrac{1}{5}\beta_{-+}^{n'}(1,2)-\tfrac{2}{15}\beta_{+-}^{n'}(1,2)+\tfrac{1}{3}\beta_{+-}^{n'}(1,0)\Bigg]+\left(\frac{q_i}{m_i}\right)^2E^{m'}E^{m}\frac{\partial n_i}{\partial x^{m}}$$
$$\times\Bigg[\frac{k_BT}{m_i}\left[\tfrac{8}{15}\beta_{--}^{n'}(1,2)+\tfrac{2}{3}\beta_{--}^{n'}(1,0)\right]+\tfrac{1}{15}\beta_{-+}^{n'}(1,2)+\tfrac{1}{3}\beta_{-+}^{n'}(1,0)+\tfrac{2}{5}\beta_{+-}^{n'}(1,2)\Bigg]$$
$$-\left(\frac{q_i}{m_i}\right)^3E^{m'}E^{m}E_{m}\left[\tfrac{4}{15}\beta_{--}^{n'}(1,2)+\tfrac{1}{3}\beta_{--}^{n'}(1,0)\right]. \tag{A11}$$

Comparing these results with Eqs. (35)–(37), we can make the following list of generalized transport coefficients:

$$\alpha_{0,2}^{n',0}=\left(\frac{k_BT}{m_i}\right)^2\beta_{-}^{n'}(0)+\frac{k_BT}{m_i}\beta_{+}^{n'}(0), \tag{A12}$$

$$\alpha_{1,1}^{n',0}=2\frac{k_BT}{m_i}\beta_{-}^{n'}(0)+\beta_{+}^{n'}(0), \tag{A13}$$

TABLE I. General values for the ratios of Clebsch-Gordan coefficients $\langle l', m' | 1, M; l, m'-M\rangle / \langle l', 0 | 1, 0; l, 0\rangle$.

M	$l = l' - 1$	$l = l' + 1$
-1	$\frac{1}{l'}\left(\frac{(l'-m')(l'-m'-1)}{2}\right)^{1/2}$	$-\frac{1}{l'+1}\left(\frac{(l'+m'+1)(l'+m'+2)}{2}\right)^{1/2}$
0	$\frac{1}{l'}(l'^2-m'^2)^{1/2}$	$\frac{1}{l'+1}[(l'+1)^2-m'^2]^{1/2}$
$+1$	$\frac{1}{l'}\left(\frac{(l'+m')(l'+m'-1)}{2}\right)^{1/2}$	$-\frac{1}{l'+1}\left(\frac{(l'-m'+1)(l'-m'+2)}{2}\right)^{1/2}$

$$\alpha_{2,0}^{n',0} = \beta_-^{n'}(0)\,, \tag{A14}$$

$$\alpha_{0,1}^{n',1} = -\frac{k_B T}{m_i}\overline{B}_1^{n'}(1)\,, \tag{A15}$$

$$\alpha_{1,0}^{n',1} = -\overline{B}_1^{n'}(1)\,, \tag{A16}$$

$$\alpha_{0,3}^{n',1} = -\left[\left(\frac{k_B T}{m_i}\right)^3 \left[\tfrac{4}{15}\beta_{--}^{n'}(1,2) + \tfrac{1}{3}\beta_{--}^{n'}(1,0)\right] + \left(\frac{k_B T}{m_i}\right)^2 \left[\tfrac{4}{15}\beta_{-+}^{n'}(1,2) + \tfrac{1}{3}\beta_{-+}^{n'}(1,0) + \tfrac{1}{3}\beta_{+-}^{n'}(1,0) + \tfrac{4}{15}\beta_{+-}(1,2)\right] + \frac{k_B T}{m_i}\left[\tfrac{4}{15}\beta_{++}^{n'}(1,2) + \tfrac{1}{3}\beta_{++}^{n'}(1,0)\right]\right], \tag{A17}$$

$$\alpha_{1,2}^{n',1}(\parallel) = -\left[\left(\frac{k_B T}{m_i}\right)^2 \left[\tfrac{4}{15}\beta_{--}^{n'}(1,2) + \tfrac{1}{3}\beta_{--}^{n'}(1,0)\right] + \frac{k_B T}{m_i}\left[\tfrac{1}{15}\beta_{-+}^{n'}(1,2) + \tfrac{2}{5}\beta_{+-}^{n'}(1,2) + \tfrac{1}{3}\beta_{-+}^{n'}(1,0)\right] + \tfrac{1}{5}\beta_{++}^{n'}(1,2)\right], \tag{A18}$$

$$\alpha_{1,2}^{n',1}(\perp) = -\left[\left(\frac{k_B T}{m_i}\right)^2 \left[\tfrac{8}{15}\beta_{--}^{n'}(1,2) + \tfrac{2}{3}\beta_{--}^{n'}(1,0)\right] + \frac{k_B T}{m_i}\left[\tfrac{7}{15}\beta_{-+}^{n'}(1,2) + \tfrac{2}{15}\beta_{+-}^{n'}(1,2) + \tfrac{1}{3}\beta_{-+}^{n'}(1,0) + \tfrac{2}{3}\beta_{+-}^{n'}(1,0)\right] + \tfrac{1}{15}\beta_{++}^{n'}(1,2) + \tfrac{1}{3}\beta_{++}^{n'}(1,0)\right], \tag{A19}$$

$$\alpha_{2,1}^{n',1}(\parallel) = -\left(\frac{k_B T}{m_i}\left[\tfrac{8}{15}\beta_{--}^{n'}(1,2) + \tfrac{2}{3}\beta_{--}^{n'}(1,0)\right] + \tfrac{1}{15}\beta_{-+}^{n'}(1,2) + \tfrac{1}{3}\beta_{-+}^{n'}(1,0) + \tfrac{2}{5}\beta_{+-}^{n'}(1,2)\right), \tag{A20}$$

$$\alpha_{2,1}^{n',1}(\perp) = -\left(\frac{k_B T}{m_i}\left[\tfrac{4}{15}\beta_{--}^{n'}(1,2) + \tfrac{1}{3}\beta_{--}^{n'}(1,0)\right] + \tfrac{1}{5}\beta_{-+}^{n'}(1,2) - \tfrac{2}{15}\beta_{+-}^{n'}(1,2) + \tfrac{1}{3}\beta_{+-}^{n'}(1,0)\right), \tag{A21}$$

$$\alpha_{3,0}^{n',1} = -\left[\tfrac{4}{15}\beta_{--}^{n'}(1,2) + \tfrac{1}{3}\beta_{--}^{n'}(1,0)\right], \tag{A22}$$

$$\alpha_{0,2}^{n',2} = \frac{2}{5}\left[\left(\frac{k_B T}{m_i}\right)^2 \beta_-^{n'}(2) + \frac{k_B T}{m_i}\beta_+^{n'}(2)\right], \tag{A23}$$

$$\alpha_{1,1}^{n',2} = \frac{2}{5}\left(2\frac{k_B T}{m_i}\beta_-^{n'}(2) + \beta_+^{n'}(2)\right), \tag{A24}$$

$$\alpha_{2,0}^{n',2} = \tfrac{2}{5}\beta_-^{n'}(2)\,. \tag{A25}$$

The coefficients β are the following products of inverse collision matrices, where we have abbreviated $[B^{-1}(l)]_n^{n'}$ as $\overline{B}_n^{n'}(l)$:

$$\beta_-^{n'}(2) = \sum_n \overline{B}_n^{n'}(2)(n+3)\overline{B}_1^{n-1}(1)\,,$$

$$\beta_+^{n'}(2) = \sum_n \overline{B}_n^{n'}(2)\overline{B}_1^{n+1}(1)\,,$$

$$\beta_-^{n'}(0) = \sum_n \overline{B}_n^{n'}(0)\,n\overline{B}_1^{n-1}(1)\,,$$

$$\beta_+^{n'}(0) = \sum_n \overline{B}_n^{n'}(0)\overline{B}_1^{n+1}(1)\,,$$

$$\beta_{--}^{n'}(3,2) = \sum_{n,\overline{n}} \overline{B}_{\overline{n}}^{n'}(3)(\overline{n}+4)\overline{B}_n^{\overline{n}-1}(2)(n+3)\overline{B}_1^{n-1}(1)\,,$$

$$\beta_{-+}^{n'}(3,2) = \sum_{n,\overline{n}} \overline{B}_{\overline{n}}^{n'}(3)(\overline{n}+4)\overline{B}_n^{\overline{n}-1}(2)\overline{B}_1^{n+1}(1)\,,$$

$$\beta_{+-}^{n'}(3,2) = \sum_{n,\overline{n}} \overline{B}_{\overline{n}}^{n'}(3)\overline{B}_n^{\overline{n}+1}(2)(n+3)\overline{B}_1^{n-1}(1)\,,$$

$$\beta_{++}^{n'}(3,2) = \sum_{n,\overline{n}} \overline{B}_{\overline{n}}^{n'}(3)\overline{B}_n^{\overline{n}+1}(2)\overline{B}_1^{n+1}(1)\,,$$

$$\beta_{--}^{n'}(1,2) = \sum_{n,\overline{n}} \overline{B}_{\overline{n}}^{n'}(1)(\overline{n}-1)\overline{B}_n^{\overline{n}-1}(2)(n+3)\overline{B}_1^{n-1}(1)\,,$$

$$\beta_{-+}^{n'}(1,2) = \sum_{n,\overline{n}} \overline{B}_{\overline{n}}^{n'}(1)(\overline{n}-1)\overline{B}_n^{\overline{n}-1}(2)\overline{B}_1^{n+1}(1)\,,$$

$$\beta_{+-}^{n'}(1,2)=\sum_{n,\bar{n}}\bar{B}_{\bar{n}}^{n'}(1)\,\bar{B}_{n}^{\bar{n}+1}(2)(n+3)\,\bar{B}_{1}^{n-1}(1)\,,$$

$$\beta_{++}^{n'}(1,2)=\sum_{n,\bar{n}}\bar{B}_{\bar{n}}^{n'}(1)\,\bar{B}_{n}^{\bar{n}+1}(2)\,\bar{B}_{1}^{n+1}(1)\,,$$

$$\beta_{--}^{n'}(1,0)=\sum_{n,\bar{n}}\bar{B}_{\bar{n}}^{n'}(1)(\bar{n}+2)\,\bar{B}_{n}^{\bar{n}-1}(0)\,n\bar{B}_{1}^{n-1}(1)\,,$$

$$\beta_{-+}^{n'}(1,0)=\sum_{n,\bar{n}}\bar{B}_{\bar{n}}^{n'}(1)(\bar{n}+2)\,\bar{B}_{n}^{\bar{n}-1}(0)\,\bar{B}_{1}^{n+1}(1)\,,$$

$$\beta_{+-}^{n'}(1,0)=\sum_{n,\bar{n}}\bar{B}_{\bar{n}}^{n'}(1)\,\bar{B}_{n}^{\bar{n}+1}(0)\,n\bar{B}_{1}^{n-1}(1)\,,$$

$$\beta_{++}^{n'}(1,0)=\sum_{n,\bar{n}}\bar{B}_{\bar{n}}^{n'}(1)\,\bar{B}_{n}^{\bar{n}+1}(0)\,\bar{B}_{1}^{n+1}(1)\,.$$

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