Chain relations of reduced distribution functions and their associated correlation functions

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For a closed system, the integration (trace in the quantum case) over one particle of a reduced distribution function is related to the reduced distribution function of one lower order. The particular details of this ''chain'' relation depend sensitively on the detailed manner in which the reduced distribution functions are defined, specifically their normalization. Correlation functions are defined in terms of reduced distribution functions, which fixes the normalization of the correlation functions and, provided they exist, their associated chain relations. Chain relations for the correlation functions are shown to exist for normalizations of generic type but not for normalizations of specific type. The normalization requirement is shown, in general, to prevent the direct association of correlation functions with physical clusters, which is commonly assumed in the literature. These relations are illustrated for an ideal gas of monomers and dimers. The effect of taking the thermodynamic limit on the chain relations for this system is discussed. This illustrates how the thermodynamic limit generally destroys the chain relations. © *1998 American Institute of Physics.* [S0021-9606(98)51302-5]

I. INTRODUCTION

An important approach for evaluating properties of N-particle systems both in equilibrium and nonequilibrium situations is to use reduced density operators or their classical analogs, reduced distribution functions.[1–10] For a closed system, reduced distribution functions are defined with reference to the total (N-particle) distribution function $\rho_{1\cdots N}^{(N)}$, and explicitly involve fewer numbers of particles. But necessarily, they must reflect the physical properties of the total system of N particles.

For simplicity of mathematical notation a quantum terminology for density operators is used throughout this paper (with Boltzmann statistics always being assumed), but all results are immediately transferrable into (or interpretable as) a classical terminology of distribution functions with the replacement of $\rho^{(n)}\rightarrow f^{(n)}$ and $\mathrm{Tr}_{1\cdots n}\rightarrow\int\cdots\int d\mathbf{r}_1\cdots d\mathbf{p}_n$. In referring to these quantities, no distinction is made between quantum and classical quantities, and the classical and quantum languages are used interchangeably.

There are two basic ways for defining reduced distribution functions, namely, the generic type of reduced distribution functions and the specific type. The generic reduced distribution functions are usually defined as

$$\rho_{1\cdots n}^{(n)}=\frac{N!}{(N-n)!}\mathrm{Tr}_{n+1\cdots N}\rho_{1\cdots N}^{(N)}. \tag{1}$$

If the N-particle distribution function is normalized to 1, the n-particle distribution function is normalized according to

$$\mathrm{Tr}_{1\cdots n}\rho_{1\cdots n}^{(n)}=\frac{N!}{(N-n)!} \tag{2}$$

and is proportional to the probability of having an *arbitrary* set of n particles at a particular set of phase space points. This normalization has the advantage that for a homogeneous system (in a finite volume V) the one-particle reduced density operator $\rho_1^{(1)}$ is associated with the density N/V of the gas and the two-particle reduced density operator $\rho_{12}^{(2)}$ to the (generic) probability of finding two particles at a pair of points.

In contrast, the specific reduced distribution functions are usually defined by

$$\wp_{1\cdots n}^{(n)}=\mathrm{Tr}_{n+1\cdots N}\rho_{1\cdots N}^{(N)}, \tag{3}$$

thus having normalization

$$\mathrm{Tr}_{1\cdots n}\wp_{1\cdots n}^{(n)}=1. \tag{4}$$

These functions give the probability of having a *particular* set of n particles at a particular set of phase space points. Various factors may be added to the above definitions, but if treated properly, these factors do not change the general nature of the normalization.

After choosing a particular normalization convention for the reduced distribution functions, a series of equations between lower order and higher order reduced distribution functions can be obtained, called here ''chain relations.'' These relations between the reduced distribution functions and some of their properties are summarized in this paper. While some of the properties are well known, other properties appear to be not well known or new.

It is standard practice to expand the reduced distribution functions in terms of correlation functions. The normalization of the correlation functions is then fixed by the normalization chosen for the reduced distribution function. For example, the two-particle generic reduced density operator can be broken down into a product of one-particle reduced density operators and the correlation operator $c_{12}^{(2)}$, defined by

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$$\rho_{12}^{(2)}=\rho_1^{(1)}\rho_2^{(1)}+c_{12}^{(2)}. \tag{5}$$

It follows that the generic correlation operator has normalization

$$\mathrm{Tr}_{12}c_{12}^{(2)}=-N. \tag{6}$$

These formal aspects of the reduced density and correlation operators are treated in detail in this work.

For a particular system, $\rho^{(N)}$ is modeled by taking the physical characteristics of the system into consideration. Reduced density and correlation operators may then be derived from this $\rho^{(N)}$. This paper also emphasizes how the correlation functions are associated with different physical interpretations when different normalizations are used for their definition. The authors believe that these, at times subtle, differences are not commonly appreciated, yet their understanding is of particular importance, for example, when extending dilute gas kinetic theory to denser systems, with and/or without the presence of bound states.

A system illustrating this is a gas in which individual molecules (monomers) can combine to form bound pairs (dimers), where it appears natural to associate correlations with the *physical* presence of bound pairs. This is especially the case in kinetic theory where the chemical formation and destruction of dimers is to be described. Such formulations have been advanced in particular by Olmsted and Curtiss,[11] Lowry and Snider,[12] McLennan,[13] Eu,[14] Klimontovich and Kremp,[15] Hoffman *et al.*,[16] and Evans and co-workers.[17] The treatment by Lowry and Snider assumes a form for the N-particle density operator of a finite system consisting of monomers and dimers. Based on the form chosen for $\rho^{(N)}$, they derive exact expressions for the (generic) reduced density operators. In applications to real physical systems, the number of particles N is usually large so factors like $N-n$ are approximated by N. Formally this is usually done while carrying out the thermodynamic limit, $N, V\rightarrow\infty$ with $N/V=\text{const}$. In the thermodynamic limit, the analog of the Lowry–Snider two-particle reduced density operator, with the normalization of Eq. (2) is

$$\rho_{12}^{(2)}=\rho_1^{(1)}\rho_2^{(1)}+\rho_{b12}, \tag{7}$$

where ρ_{b12} is the bound pair density operator, see Sec. IV for a detailed discussion. This structure of reduced density operators has also been assumed by others.[11,13,15] By analogy with the structure of Eq. (5) for the two-particle reduced density operator and the normalization, Eq. (6), of the correlation operator, it appears to follow that the bound pair density operator corresponds to the correlation operator and thus must be normalized according to

$$\mathrm{Tr}_{12}\rho_{b12}=-N. \tag{8}$$

Since ρ_{b12} describes the probability of having a two-particle bound state, the negative normalization of Eq. (8) will appear as a negative probability and thus a physically inconsistent result. It also raises the question of how, or why, information regarding the total number of particles in the system is obtained from the density operator for the bound states. See Sec. IV for an elaboration of this illustration of the properties of the chain relations.

The thermodynamic limit is useful for simplifying formulas but leads to inconsistencies of the type seen in Eq. (8) with the formally exact normalizations and chain relations. These inconsistencies between the chain relations and the thermodynamic limit become particularly troublesome in moderately dense gas kinetic theory where dynamic processes are usually described in terms of a combination of reduced distribution functions of different orders. Since macroscopic quantities are evaluated at the thermodynamic level, which implies the use of the thermodynamic limit, consistent chain relations are required to ensure that all physical quantities are treated properly. A consistent incorporation of both the chain relation and the thermodynamic limit in dense gas kinetic theory does not appear to exist. Actually, the chain relations are not utilized in most kinetic theory treatments, see Sec. V. for comments on Cohen's formalism for dense gas kinetic theory.

The main purpose of this paper is to make connections between various normalizations of the reduced distribution functions that have appeared in the literature and to contrast their properties, such as the chain relations and to study the effects of taking the thermodynamic limit. This paper is divided into six sections. Section II is devoted to various generic distribution functions. The discussion starts with the commonly used decomposition of reduced distribution functions in terms of correlation functions. Chain relations among these correlation functions are known and reviewed. Variants of this chain relation due to different generic normalizations are illustrated in detail. Specific distribution functions are briefly discussed in Sec. III. Chain relations are especially simple for these distribution functions. Some of the relations of Secs. II and III are illustrated in Sec. IV, where an explicit form for the N-body distribution function of an ideal gas system consisting of monomers and dimers is assumed. It is seen that care is needed when interpreting the correlation operators for this system. In particular, the apparent interpretation of a second-order correlation function as describing the physical binding of two particles is in general not true. It is also observed that the correlation operators have a simpler structure for the generic reduced distribution functions than those for the specific reduced distribution functions. Section V uses Cohen's formalism of the cluster expansion to further illustrate the problems that may arise in regard to the chain relations when the thermodynamic limit is taken. The paper ends with a discussion.

II. GENERIC REDUCED DENSITY OPERATORS

In classic treatments of equilibrium statistical mechanics, see, e.g., Refs. 1–8, and in (apparently all) modern equilibrium studies, reduced density operators for systems in thermal equilibrium are normalized according to Eq. (2). Note that this normalization is inconsistent for $n=N$ and is to be applied only for $n<N$. Due to its simple physical interpretation, this normalization has been commonly used in

the literature for both equilibrium and nonequilibrium systems. The reduction of higher-order density operators to lower-order ones is accomplished by taking a partial trace

$$\mathrm{Tr}_n \rho^{(n)}_{1\cdots n} = (N-n+1)\rho^{(n-1)}_{1\cdots n-1}. \tag{9}$$

This is referred to here as a chain relation.

Motivated by the cluster expansion of Ursell,[18] an expansion in terms of correlation operators is often used for the further analysis of the reduced density operators. A formal expression for the reduced density operators in terms of one-particle reduced density operators and correlation operators $c^{(n)}_{12\cdots n}$ has been given according to

$$\rho^{(2)}_{12} = \rho^{(1)}_1 \rho^{(1)}_2 + c^{(2)}_{12}, \tag{10}$$

$$\rho^{(3)}_{123} = \rho^{(1)}_1 \rho^{(1)}_2 \rho^{(1)}_3 + \rho^{(1)}_1 c^{(2)}_{23} + \rho^{(1)}_2 c^{(2)}_{13} + \rho^{(1)}_3 c^{(2)}_{12} + c^{(3)}_{123}, \tag{11}$$

$$\begin{aligned}\rho^{(4)}_{1234} = {} & \rho^{(1)}_1 \rho^{(1)}_2 \rho^{(1)}_3 \rho^{(1)}_4 + \rho^{(1)}_1 \rho^{(1)}_2 c^{(2)}_{34} + \rho^{(1)}_2 \rho^{(1)}_3 c^{(2)}_{14} \\ & + \rho^{(1)}_3 \rho^{(1)}_4 c^{(2)}_{12} + \rho^{(1)}_1 \rho^{(1)}_3 c^{(2)}_{24} + \rho^{(1)}_2 \rho^{(1)}_4 c^{(2)}_{13} \\ & + \rho^{(1)}_1 \rho^{(1)}_4 c^{(2)}_{23} + \rho^{(1)}_1 c^{(3)}_{234} + \rho^{(1)}_2 c^{(3)}_{134} + \rho^{(1)}_3 c^{(3)}_{124} \\ & + \rho^{(1)}_4 c^{(3)}_{123} + c^{(2)}_{12} c^{(2)}_{34} + c^{(2)}_{23} c^{(2)}_{14} + c^{(2)}_{13} c^{(2)}_{24} + c^{(4)}_{1234},\end{aligned} \tag{12}$$

or in general,

$$\rho^{(n)}_{1\cdots n} = \sum_{\{\alpha,\beta_2,\cdots,\beta_l,\cdots,\beta_n\}} \prod_{i\in\alpha} \rho^{(1)}_i \prod_{l=2}^{n} \prod_{(j,\cdots,s)\in\beta_l} c^{(l)}_{j\cdots s}. \tag{13}$$

Here α is a listing of single particle labels and β_l a listing of sets of l-particle labels, while the sum is over all possible partitions of the n labeled particles into sets $\alpha,\beta_2,\ldots,\beta_n$. This decomposition breaks down the structure of the reduced density operator $\rho^{(n)}$ into contributions from the one-particle reduced density operator $\rho^{(1)}$ and the correlation operators $c^{(n)}_{1\cdots n}$. The motivation for this is twofold. First, it is assumed that greater knowledge of the lower order correlation operators can be experimentally available. Second, it is hoped that the main contributions to $\rho^{(n)}$ arise from products of lower order terms and that the contribution of the n-particle correlation operator is small and may be treated as a perturbation.[19] The n-particle correlation operator $c^{(n)}_{1\cdots n}$ can thus be either neglected, or approximated by some function without incurring too much error in $\rho^{(n)}$. This treatment may appear equivalent to interpreting the correlation operators $c^{(n)}_{1\cdots n}$ as describing isolated n-particle physical clusters in the system, or in other words, as giving the probability for the existence of physical clusters in the system. But the normalization of these correlation operators, as will now be discussed, implies that one must be very careful in pursuing this type of interpretation.

Even though the exact form of the correlation operators $c^{(n)}_{1\cdots n}$ may be unknown, the normalization property, Eq. (2), and the chain relation, Eq. (9), impose certain constraints on them. This can be of help both in introducing approximate forms for the correlation operators of a physical system and in understanding existing theoretical results. The normalization of the correlation operators is one constraint which follows from the normalization conditions, Eq. (2), of the reduced density operators. In particular, from the normalization of $\rho^{(2)}$, $c^{(2)}_{12}$ is normalized according to Eq. (6). If as stated above, $c^{(2)}_{12}$ is interpreted as describing the probability of having two-particle physical clusters in the system, the negative normalization of Eq. (6) will appear to be an inconsistent result. In Sec. IV it will be demonstrated that $c^{(2)}_{12}$ is a complicated factor, which incorporates many physical effects, not just two-particle clusters. Balescu[6] noted this negative normalization but did not comment on its interpretation. After recognizing that the total trace of each correlation operator scales linearly with N, equating various powers of N in the normalization of Eq. (13) gives a straightforward way of showing that the normalization for a general n-particle correlation operator is

$$\mathrm{Tr}_{1\cdots n} c^{(n)}_{1\cdots n} = (-1)^{n-1}(n-1)!N. \tag{14}$$

Since the $c^{(n)}_{1\cdots n}$ are not associated with a single physical effect, the negative values for even n in Eq. (14) do not give rise to any problem of interpretation. In contrast, the association of correlations with physical effects, namely clustering, is commonly assumed in the literature.

Relations between correlation operators of different orders can be obtained. The first few of these are

$$\mathrm{Tr}_2 c^{(2)}_{12} = -\rho^{(1)}_1, \tag{15}$$

$$\mathrm{Tr}_3 c^{(3)}_{123} = -2c^{(2)}_{12}, \quad \mathrm{Tr}_{23} c^{(3)}_{123} = 2\rho^{(1)}_1. \tag{16}$$

A general chain relation between the correlation operators can be derived from the chain relation, Eq. (9), namely

$$\mathrm{Tr}_n c^{(n)}_{1\cdots n} = -(n-1)c^{(n-1)}_{1\cdots n-1}, \tag{17}$$

or more generally,

$$\mathrm{Tr}_{n\cdots n+\ell} c^{(n+\ell)}_{1\cdots n+\ell} = (-1)^{\ell+1}\frac{(n+\ell-1)!}{(n-2)!} c^{(n-1)}_{1\cdots n-1}. \tag{18}$$

This is the classic result of Lebowitz and Percus,[20] who only discuss the generic normalization condition (1). It also implies, used along with Eq. (6), the normalization of Eq. (14). An obvious approximation method would appear to be to ignore higher correlation operators, for example, to retain the two-particle correlation operator but to assume there is no three-particle (or higher) correlation operator. Clearly such an approach is inconsistent with the above chain relations for the correlation operators. Such a truncation of the correlation operators must be contrasted with the truncation of the Ursell operators at some order. The latter truncation of ''physical'' clusters must be carried out while describing the total system, that is, at the N-particle level, which is both mathematically consistent and can often lead to a physically reasonable approximation. This has been used for describing a chemically reactive ideal gas of monomers and dimers[12] and also for the nonideal gas having only binary clusters[21] [therein called the ''binary correlation approximation,'' a designation which is not in agreement with the notation used in the present paper].

Besides the normalization convention discussed above, a number of other related normalizations for reduced density

operators may be found in the literature. The common aspect of these normalizations is the combination of factorials, $N!/(N-n)!$, that they all contain, which keeps them of the generic type. One related normalization for reduced distribution functions, see the books by Hill[5] and McQuarrie,[22] is

$$\frac{N^n}{V^n}\tilde{\rho}^{(n)}_{1\cdots n}=\frac{N!}{(N-n)!}\,\mathrm{Tr}_{n+1\cdots N}\rho^{(N)}_{1\cdots N}. \tag{19}$$

This normalization is identical to that of the equilibrium ''radial'' distribution functions. By using the definition of Eq. (10), along with its higher order analogs, correlation operators for this normalization convention may be obtained. It is straightforward to derive a general expression for the traced correlation operators for this normalization scheme. Thus for example,

$$\mathrm{Tr}_{12}\tilde{c}^{(2)}_{12}=-V^2/N. \tag{20}$$

It was pointed out[23] that the two-particle correlation function associated with Debye–Hückel theory obeys the classical analog of this equation. The chain relation for this set of correlation operators can be seen to be

$$\begin{aligned}&\mathrm{Tr}_n\tilde{c}^{\,(n)}_{1\cdots n}=-\frac{V(n-1)}{N}\,\tilde{c}^{\,(n-1)}_{1\cdots n-1}\quad (n\geqslant 3),\\ &\mathrm{Tr}_2\tilde{c}^{\,(2)}_{12}=-\frac{V}{N}\tilde{\rho}^{\,(1)}_{1}.\end{aligned} \tag{21}$$

The same general classification for the various terms in the expansions of the reduced density operators according to their order of magnitude in N, as stated in the paragraph preceding Eq. (14), applies for this normalization. Even though there are differences in detail, this normalization and that of Eq. (1) are similar in nature.

An alternate normalization[12] is

$$\hat{\rho}^{(n)}_{1\cdots n}=\frac{N!}{(N-n)!n!}\,\mathrm{Tr}_{n+1\cdots N}\rho^{(N)}_{1\cdots N}. \tag{22}$$

This was introduced[12] so that the bound state part of the pair density operator directly reproduces the number and density of bound states. If $\hat{\rho}^{(n)}_{1\cdots n}$ is expanded in the same structure as the correlation expansion of Eqs. (10)–(12), with the correlation operators labeled as $\hat{c}(n)$, the resulting correlation operators have a different structure from those of $c^{(2)}_{12}$, for example,

$$\mathrm{Tr}_2\hat{c}^{(2)}_{12}=-\frac{(N+1)}{2}\hat{\rho}^{(1)}_1,\quad \mathrm{Tr}_{12}\hat{c}^{(2)}_{12}=-\frac{N(N+1)}{2}. \tag{23}$$

In order to obtain correlation operators for this normalization that have chain relations similar to the other correlation operators in this section, $\hat{\rho}^{(n)}_{1\cdots n}$ needs to be expressed in terms of correlations, labeled as $\check{c}^{(n)}$, using a different expansion from that of Eqs. (10)–(12), in particular, for the pair and triplet reduced density operators

$$\hat{\rho}^{(2)}_{12}=\tfrac{1}{2}\hat{\rho}^{(1)}_1\hat{\rho}^{(1)}_2+\check{c}^{(2)}_{12}, \tag{24}$$

$$\hat{\rho}^{(3)}_{123}=\tfrac{1}{6}\hat{\rho}^{(1)}_1\hat{\rho}^{(1)}_2\hat{\rho}^{(1)}_3+\tfrac{1}{3}\hat{\rho}^{(1)}_1\check{c}^{(2)}_{23}+\tfrac{1}{3}\hat{\rho}^{(1)}_2\check{c}^{(2)}_{13}+\tfrac{1}{3}\hat{\rho}^{(1)}_3\check{c}^{(2)}_{12}+\check{c}^{(3)}_{123}, \tag{25}$$

or in general

$$\hat{\rho}^{(n)}_{1\cdots n}=\frac{1}{n!}\sum_{\{\alpha,\beta_2,\cdots,\beta_l,\cdots,\beta_n\}}\prod_{i\in\alpha}\hat{\rho}^{(1)}_i\prod_{l=2}^{n}\prod_{(j,\cdots,s)\in\beta_l} l!\check{c}^{(l)}_{j\cdots s}. \tag{26}$$

See the discussion following Eq. (13) for an elaboration of the notation. With this definition of the correlation expansion, the resulting correlation operators have properties that parallel the $c^{(n)}_{1\cdots n}$ but with different detailed numerical factors. For example, instead of Eq. (6) one has

$$\mathrm{Tr}_{12}\check{c}^{(2)}_{12}=-N/2. \tag{27}$$

The chain rule for these correlation operators becomes

$$\begin{aligned}&\mathrm{Tr}_n\check{c}^{(n)}_{1\cdots n}=-\frac{(n-1)}{n}\check{c}^{(n-1)}_{1\cdots n-1}\quad (n\geqslant 3)\\ &\mathrm{Tr}_2\check{c}^{(2)}_{12}=-\hat{\rho}^{(1)}_1/2.\end{aligned} \tag{28}$$

It is thus seen that the structure of the correlation operators depends on the choice of both the particular normalization convention and the form for the correlation expansion.

III. SPECIFIC REDUCED DENSITY OPERATORS

The standard definition of specific reduced density operators is given in Eq. (3) with normalization (4). Following Bogoliubov,[24] various classic treatments of gas kinetic theory[24–27] define the reduced density operators in a manner which gives them similar properties, namely,

$$\varrho^{(n)}_{1\cdots n}=V^n\mathrm{Tr}_{n+1\cdots N}\rho^{(N)}_{1\cdots N}. \tag{29}$$

The common property of these normalizations is the absence of the factorials contained in the numerical factor in the definition of the generic reduced distribution functions. Clearly these distribution functions satisfy the chain relations

$$\mathrm{Tr}_n\varrho^{(n)}=V\varrho^{(n-1)},\quad \mathrm{Tr}_n\wp^{(n)}=\wp^{(n-1)}. \tag{30}$$

The correlation operators derived using the reduced density operators of Eq. (3) have very different properties from those described in Sec. II. On expanding the reduced density operators in terms of correlations according to Eqs. (10)–(12), with the corresponding correlation operators labeled as $\mathscr{C}^{(n)}$, it follows that the trace over any arbitrary particle i of the set $\{1,2,\cdots,n\}$ gives

$$\mathrm{Tr}_i\mathscr{C}^{(n)}_{1\cdots i\cdots n}=0. \tag{31}$$

This constraint was first recognized by Liboff,[28] who referred to the corresponding full trace as the ''antinormalization'' property. Equation (31) shows that, in contrast to Eq. (17), there are no chain relations between correlation operators when this normalization convention is used for the definition of reduced density operators. Obviously, the antinormalization property prevents any direct association of $\mathscr{C}^{(n)}_{1\cdots n}$

with the probability of a physical clustering of particles, since any quantity measuring a probability must have a positive value (namely its probability).

IV. REDUCED DENSITY OPERATORS IN THE PRESENCE OF BOUND STATES

If dimerization occurs in the gas phase, the gas becomes a molecular mixture. From an atomic point of view, dimers are two-particle clusters. This chemical clustering must be reflected in the (atomic) reduced density operators for the system. Treating the gas molecules as noninteracting gives a system that is very simple, yet illustrates the differing roles of molecular clustering and mathematical correlations. These differences are discussed here in terms of both the generic and specific definitions of reduced density operators.

A. Generic density operators

Lowry and Snider[12] formulated a gas kinetic theory for a system in which monomer–dimer interconversions occur. From a monomer (atomic) point of view, the only correlations that are present are associated with pair bound states. Thus the N-particle system can be considered as consisting of a mixture of M unbound particles (monomers) and D bound pairs (dimers). This methodology has recently been used to motivate a description of the kinetic properties of a moderately dense gas,[21] where the bound states have been replaced by general pair correlations associated with the second virial coefficient. The generalization to higher-order correlations is straightforward. The arguments presented here regarding the normalization of reduced density operators and correlation operators apply to both monomer–dimer and moderately dense gas systems as long as the correlations are attractive. For simplicity of presentation, only the monomer–dimer gas system is discussed.

If bound states exist, they can be considered as a separate chemical species so that the system now is appropriately treated as a binary mixture. One way of representing such a system is to explicitly recognize the two species. An equilibrium binary ideal gas canonical density operator for a system containing M molecules of species M and D of D is[29]

$$\rho_{1\cdots N}^{(M,D)}=\frac{1}{M!D!Q_{M,D}}\prod_{i=1}^{M} e^{-\beta H_i^M}\prod_{j=1}^{D} e^{-\beta H_j^D} \tag{32}$$

with partition function

$$Q_{M,D}=\frac{(Q_M)^M(Q_D)^D}{M!D!}, \tag{33}$$

expressed in terms of the molecular partition functions Q_M and Q_D and molecular Hamiltonians H^M and H^D. But if species D is to be the dimer (diatomic) of monomer (atom) M, then there should be a symmetry between all atoms, whether they are free (M), or bound to another atom to form a diatomic (D). Equation (32) does not express this (Boltzmann) indistinguishability. Given that there are M unbound and $2D$ bound atoms, indistinguishability requires that it can be any set of D pairs of the $N=M+2D$ atoms that are bound. To represent this, it is appropriate to label all N atoms consecutively and consider all partitions $\{\alpha,\gamma\}$ of the N particles into a set α of M unbound monomers and a set γ of D (ordered) bound pairs. The labeling of a bound pair is naturally ordered, i.e., if $(jk)\in\gamma$, then $j<k$, and the number of such partitions of N particles is

$$\mathrm{g}(N,M,D)=\frac{N!}{M!D!2^D}. \tag{34}$$

This symmetry can be incorporated by replacing Eq. (32) for the N-particle (equilibrium ideal gas) density operator by

$$\rho_{1\cdots N}^{(M,D)}=\frac{1}{\mathrm{g}(N,M,D)M!D!Q_{M,D}} \times\sum_{\{\alpha,\gamma\}}\prod_{i\in\alpha} e^{-\beta H_i^M}\prod_{(jk)\in\gamma} e^{-\beta H_{jk}^D}. \tag{35}$$

An alternate notation may be used in this equation to emphasize the numbers of monomer and dimer species in the system,

$$\rho_{1\cdots N}^{(M,D)}=\frac{1}{\mathrm{g}(N,M,D)M^M(2D)^D}\sum_{\{\alpha,\gamma\}}\prod_{i\in\alpha}\rho_{fi}\prod_{(jk)\in\gamma}\rho_{bjk}. \tag{36}$$

The form of Eq. (36) was used as a frame of reference for formulating a kinetic theory of recombination and decay.[12] Here ρ_{fi} is the density operator for a free particle i, normalized to the number of free particles

$$\mathrm{Tr}_i\rho_{fi}=M, \tag{37}$$

and ρ_{bjk} is the bound pair density operator of particles jk, with normalization to the number of particles that are bound,

$$\mathrm{Tr}_{jk}\rho_{bjk}=2D. \tag{38}$$

Expressions for the reduced density operators $\rho^{(n)}$ can be derived using Eq. (1).

In $\rho_1^{(1)}$ the single extant particle can be either free, or part of a bound pair, in which case it is bound to another traced-over particle (ghost). The form of the one-particle reduced density operator is thus

$$\begin{aligned}\rho_1^{(1)}&\equiv\frac{N!}{(N-1)!}\mathrm{Tr}_{2\cdots N}\rho_{1\cdots N}^{(M,D)}\\&=\mathrm{g}(N,M,D)^{-1}NM^{-M}(2D)^{-D}\\&\quad\times\Big\{\mathrm{g}(N-1,M-1,D)M^{M-1}(2D)^D\rho_{f1}\\&\quad+\mathrm{g}(N-2,M,D-1)M^M(2D)^{D-1}\sum_{i=2}^{N}\mathrm{Tr}_i\rho_{b1i}\Big\}\\&=\rho_{f1}+\mathrm{Tr}_2\rho_{b12}\equiv\rho_{f1}+\rho_{b1}.\end{aligned} \tag{39}$$

The partial trace of ρ_{b12}, shown as ρ_{b1}, describes the properties of a particle that is bound to a ghost (particle whose state is not explicitly defined), and is normalized to the number of bound particles,

$$\mathrm{Tr}_1\rho_{b1}\equiv\mathrm{Tr}_{12}\rho_{b12}=2D. \tag{40}$$

For $n=1$, the normalization of Eq. (1) is recovered from Eqs. (39), (37), and (40),

$$\mathrm{Tr}_1\rho_1^{(1)}=\mathrm{Tr}_1(\rho_{f1}+\rho_{b1})=M+2D=N. \tag{41}$$

In the same manner, the two-particle reduced density operator $\rho_{12}^{(2)}$ is obtained as

$$\rho_{12}^{(2)}\equiv\frac{N!}{(N-2)!}\mathrm{Tr}_{3\cdots N}\rho_{1\cdots N}^{(M,D)}$$
$$=\rho_1^{(1)}\rho_2^{(1)}+\rho_{b12}-\frac{1}{M}\rho_{f1}\rho_{f2}-\frac{1}{D}\rho_{b1}\rho_{b2}. \tag{42}$$

Here use has been made of Eqs. (39) and (38). Comparing this equation with Eq. (10), the correlation operator $c_{12}^{(2)}$ can be identified as

$$c_{12}^{(2)}=\rho_{b12}-\frac{1}{M}\rho_{f1}\rho_{f2}-\frac{1}{D}\rho_{b1}\rho_{b2}. \tag{43}$$

This correlation operator contains contributions from the density operators of both the free and the bound particles. It is thus seen that the *mathematical* definition of *correlation* between particles 1 and 2, $c_{12}^{(2)}$, must be distinguished from the *physical* notion of *clustering* in an N-particle system, as exemplified by ρ_{b12}. Also note that, even though particles 1 and 2 may be far away from each other so that they are physically independent, $\rho_{b12}=0$, the correlation function can be nonzero. This is because the correlation function contains a sum of products of terms, each of which reflects a different manner in which the particles are independent of one another.

The partial trace over particle 2 of $c_{12}^{(2)}$ is seen to satisfy the chain relation, Eq. (15), i.e.,

$$\mathrm{Tr}_2c_{12}^{(2)}=\mathrm{Tr}_2\left\{\rho_{b12}-\frac{1}{M}\rho_{f1}\rho_{f2}-\frac{1}{D}\rho_{b1}\rho_{b2}\right\}$$
$$=\rho_{b1}-\rho_{f1}-2\rho_{b1}=-\rho_1^{(1)}. \tag{44}$$

Thus the correct normalization of Eq. (43) is easily obtained,

$$\mathrm{Tr}_{12}c_{12}^{(2)}=-N. \tag{45}$$

The $-N$ value of $\mathrm{Tr}_{12}c_{12}^{(2)}$ is thus the result of $c_{12}^{(2)}$ being the composite of a number of different terms. Equation (42) reproduces the thermodynamic limit for a moderately dense gas system

$$\lim_{V,N,M,D\to\infty}\rho_{12}^{(2)}\to\rho_1^{(1)}\rho_2^{(1)}+\rho_{b12} \tag{46}$$

on the basis that the ''small terms'' containing factors of $1/M$ and $1/D$ can be neglected in comparison with the dominant product factor $\rho_1^{(1)}\rho_2^{(1)}$. But these neglected terms can be of importance, especially if the trace is taken, when it is recognized that their traces are comparable in size to the trace of the bound pair density operator ρ_{b12}. Thus it is important to keep in mind those terms which have been left out in using the thermodynamic limit expression such as Eq. (46) for $\rho_{12}^{(2)}$.

Similar considerations lead to an expression for the three-particle reduced density operator

$$\rho_{123}^{(3)}\equiv\frac{N!}{(N-3)!}\mathrm{Tr}_{4\cdots N}\rho_{1\cdots N}^{(M,D)}$$
$$=\rho_1^{(1)}\rho_2^{(1)}\rho_3^{(1)}+\rho_1^{(1)}\rho_{b23}+\rho_2^{(1)}\rho_{b13}+\rho_3^{(1)}\rho_{b12}$$
$$+\frac{2}{M^2}\rho_{f1}\rho_{f2}\rho_{f3}-\frac{1}{M}[\rho_1^{(1)}\rho_{f2}\rho_{f3}+\rho_{f1}\rho_2^{(1)}\rho_{f3}$$
$$+\rho_{f1}\rho_{f2}\rho_3^{(1)}]+\frac{2}{D^2}\rho_{b1}\rho_{b2}\rho_{b3}-\frac{1}{D}$$
$$\times[(\rho_1^{(1)}\rho_{b2}+\rho_{b12})\rho_{b3}+(\rho_3^{(1)}\rho_{b1}+\rho_{b13})\rho_{b2}$$
$$+(\rho_2^{(1)}\rho_{b3}+\rho_{b23})\rho_{b1}]. \tag{47}$$

The first four terms on the right-hand side of the last equality are the terms that remain in the thermodynamic limit. By expressing $\rho_{123}^{(3)}$ in terms of correlation operators and comparing with Eq. (11), the three-particle correlation operator $c_{123}^{(3)}$ can be identified as

$$c_{123}^{(3)}=\frac{2}{M^2}\rho_{f1}\rho_{f2}\rho_{f3}+\frac{2}{D^2}\rho_{b1}\rho_{b2}\rho_{b3}$$
$$-\frac{1}{D}(\rho_{b12}\rho_{b3}+\rho_{b13}\rho_{b2}+\rho_{b23}\rho_{b1}). \tag{48}$$

A correct normalization can only be obtained by taking into account all the ''small terms'' that are divided by a power of either M or D. Taking the trace of Eq. (48) over all three particles gives

$$\mathrm{Tr}_{123}c_{123}^{(3)}=2M+16D-12D=2N. \tag{49}$$

It is straightforward to show that $\rho_{123}^{(3)}$ satisfies the chain relation Eq. (9):

$$\mathrm{Tr}_3\rho_{123}^{(3)}=(N-2)\left[\rho_1^{(1)}\rho_2^{(1)}+\rho_{b12}-\frac{1}{M}\rho_{f1}\rho_{f2}\right.$$
$$\left.-\frac{1}{D}\rho_{b1}\rho_{b2}\right]=(N-2)\rho_{12}^{(2)}. \tag{50}$$

The chain relation for correlation operators, Eq. (16), can also be easily verified. Higher-order reduced density operators can be treated in a similar manner.

Equation (35) can similarly be used in the other generic normalization conventions given by Eqs. (19) and (22). Even though there are differences in detail, the properties of the correlation operators in these conventions are similar to those already given in this section.

B. Specific density operators

The structure of the reduced density operators are different in this normalization. If one uses the Lowry–Snider form

$\rho^{(M,D)}$, Eq. (35), for the N-particle density operator with the normalization convention (29) for the reduced density operators, the expressions for the one- and two-particle reduced density operators are

$$\varrho_1^{(1)}=\frac{V}{N}(\rho_{f1}+\rho_{b1}) \tag{51}$$

and

$$\varrho_{12}^{(2)}=\varrho_1^{(1)}\varrho_2^{(1)}+\frac{V^2}{N(N-1)}\Big[\rho_{b12}+\frac{N}{V^2}\varrho_1^{(1)}\varrho_2^{(1)} - \frac{1}{M}\rho_{f1}\rho_{f2}-\frac{1}{D}\rho_{b1}\rho_{b2}\Big]. \tag{52}$$

The last four terms on the right-hand side of Eq. (52) can be identified with $\mathscr{C}_{12}^{(2)}$, whose trace gives zero as predicted by Eq. (31). This behavior is contrasted with Eq. (15). The structure of the correlation operator using this normalization is more complicated than that of Eq. (43). In the thermodynamic limit of $V,N,M,D\to\infty$ with each of N/V, M/V, and D/V constant, the ''standard'' expression for the two-particle reduced density operator is equivalent to

$$\lim_{V,N,M,D\to\infty}\varrho_{12}^{(2)}\to\varrho_1^{(1)}\varrho_2^{(1)}+\frac{V^2}{N^2}\rho_{b12}. \tag{53}$$

The three-particle reduced density operator is

$$\begin{aligned}\varrho_{123}^{(3)}=&\frac{V^3}{N(N-1)(N-2)}\Big\{\frac{N^3}{V^3}\varrho_1^{(1)}\varrho_2^{(1)}\varrho_3^{(1)}+\frac{N}{V}[\varrho_1^{(1)}\rho_{b23}\\ &+\varrho_2^{(1)}\rho_{b13}+\varrho_3^{(1)}\rho_{b12}]+\frac{2}{M^2}\rho_{f1}\rho_{f2}\rho_{f3}\\ &-\frac{N}{VM}[\varrho_1^{(1)}\rho_{f2}\rho_{f3}+\rho_{f1}\varrho_2^{(1)}\rho_{f3}+\rho_{f1}\rho_{f2}\varrho_3^{(1)}]\\ &+\frac{2}{D^2}\rho_{b1}\rho_{b2}\rho_{b3}-\frac{1}{D}\Big[\Big(\frac{N}{V}\varrho_1^{(1)}\rho_{b2}+\rho_{b12}\Big)\rho_{b3}\\ &+\Big(\frac{N}{V}\varrho_3^{(1)}\rho_{b1}+\rho_{b13}\Big)\rho_{b2}+\Big(\frac{N}{V}\varrho_2^{(1)}\rho_{b3}\\ &+\rho_{b23}\Big)\rho_{b1}\Big]\Big\}.\end{aligned} \tag{54}$$

In the thermodynamic limit the expression for $\varrho_{123}^{(3)}$ reduces to

$$\lim_{V,N,M,D\to\infty}\varrho_{123}^{(3)}\to\varrho_1^{(1)}\varrho_2^{(1)}\varrho_3^{(1)}+\frac{V^2}{N^2}[\varrho_1^{(1)}\rho_{b23}+\varrho_2^{(1)}\rho_{b13}+\varrho_3^{(1)}\rho_{b12}]. \tag{55}$$

Equation (54) can be rearranged in terms of the correlation expansion. The result is

$$\begin{aligned}\varrho_{123}^{(3)}=&\varrho_1^{(1)}\varrho_2^{(1)}\varrho_3^{(1)}+\varrho_1^{(1)}\mathscr{C}_{23}^{(2)}+\varrho_2^{(1)}\mathscr{C}_{13}^{(2)}+\varrho_3^{(1)}\mathscr{C}_{12}^{(2)}\\ &-\frac{2}{(N-1)(N-2)}\varrho_1^{(1)}\varrho_2^{(1)}\varrho_3^{(1)}+\frac{2}{N-2}[\varrho_1^{(1)}\mathscr{C}_{23}^{(2)}\\ &+\varrho_2^{(1)}\mathscr{C}_{13}^{(2)}+\varrho_3^{(1)}\mathscr{C}_{12}^{(2)}]+\frac{V^3}{N(N-1)(N-2)}\\ &\times\Big[\frac{2}{M^2}\rho_{f1}\rho_{f2}\rho_{f3}+\frac{2}{D^2}\rho_{b1}\rho_{b2}\rho_{b3}\\ &-\frac{1}{D}(\rho_{b12}\rho_{b3}+\rho_{b13}\rho_{b2}+\rho_{b23}\rho_{b1})\Big].\end{aligned} \tag{56}$$

By comparing with Eq. (11), $\mathscr{C}_{123}^{(3)}$ can be identified. Explicit calculation verifies that its trace over any particle vanishes. The form of the correlation function $\mathscr{C}_{123}^{(3)}$ for this normalization is seen to be more complicated than the corresponding expression given in Eq. (48). Clearly, in all cases, whatever the normalization convention, care must be taken when trying to assign physical meanings to the corresponding correlation operators.

V. COHEN'S CLUSTER EXPANSION

The difficulty of imposing the chain relations and thus the normalization requirement once the thermodynamic limit has been taken, can also be illustrated with reference to the classic formalism of Cohen,[27,10] which uses the specific reduced distribution functions of Eq. (29). For this convention, the chain relation between consecutive reduced distribution functions is given by

$$\int F^{(s+1)}(x_1\cdots x_{s+1})dx_{s+1}=VF^{(s)}(x_1\cdots x_s). \tag{57}$$

Cohen expanded the N-body distribution function D_N in terms of s-body distribution functions D_s and the $U_s(x_1\cdots x_s)$ defined in his work. Exact expressions for the reduced distribution functions, $F^{(s)}$, and their corresponding correlation functions, $G^{(s)}$, were then derived in terms of a density expansion of functions $U_s(x_1\cdots x_s)$. The chain relation Eq. (57) shows that

$$\int G^{(s)}(x_1\cdots x_i\cdots x_s)dx_i=0, \tag{58}$$

which is similar to Eq. (31). In the thermodynamic limit, the expressions for the first and second reduced distribution functions were obtained as (here n is the density),

$$F^{(1)}(x_1)=U_1(x_1)+\frac{n}{1!}\int U_2(x_1x_2)dx_2 + \frac{n^2}{2!}\int U_3(x_1x_2x_3)dx_2dx_3+\cdots \tag{59}$$

and,

$$F^{(2)}(x_1x_2)=U_2(x_1x_2)+\frac{n}{1!}\int U_3(x_1x_2x_3)dx_3+\frac{n^2}{2!}\int U_4(x_1x_2x_3x_4)dx_3dx_4+\cdots+\Bigg[U_1(x_2)+\frac{n}{1!}\int U_2(x_2x_3)dx_3$$
$$+\frac{n^2}{2!}\int U_3(x_2x_3x_4)dx_3dx_4+\cdots\Bigg]U_1(x_1)+\frac{n}{1!}\Bigg[U_1(x_2)+\frac{n}{1!}\int U_2(x_2x_4)dx_4+\frac{n^2}{2!}\int U_3(x_2x_4x_5)dx_4dx_5+\cdots\Bigg]$$
$$\times\int U_2(x_1x_3)dx_3+\frac{n^2}{2!}\Bigg[U_1(x_2)+\frac{n}{1!}\int U_2(x_2x_5)dx_5+\frac{n^2}{2!}\int U_3(x_2x_5x_6)dx_5dx_6+\cdots\Bigg]$$
$$\times\int U_3(x_1x_3x_4)dx_3dx_4+\cdots\ . \tag{60}$$

Cohen defined the U_1 and U_s for $s>1$ such that $\int U_1(x_i)dx_i=V$ and $\int U_s(x_1\cdots x_s)dx_1\cdots dx_s=0$. Note that this normalization prevents the U_s from being identical to the Ursell functions. On integrating $F^{(2)}(x_1x_2)$ over the phase space coordinates of particle 2 we get

$$\frac{1}{V}\int F^{(2)}(x_1x_2)dx_2=U_1(x_1)+\left(\frac{n}{1!}+1\right)\int U_2(x_1x_2)dx_2$$
$$+\left(\frac{n^2}{2!}+\frac{n}{1!}\right)\int U_3(x_1x_2x_3)dx_2dx_3$$
$$+\cdots\ , \tag{61}$$

which is not equal $F_1^{(1)}$, as given in Eq. (59). Thus the use of these expressions for $F^{(1)}$ and $F^{(2)}$ in the same theory leads to questions of consistency. In contrast, the exact expressions for $F^{(2)}(x_1x_2)$ and $F^{(1)}(x_1)$ will of course satisfy the chain relations, Eq. (57).

VI. DISCUSSION

The object of this paper has been to clarify the structure of reduced distribution functions and their associated correlation functions, in particular with regard to the (chain) relations between reduced distribution functions of different orders. In general only a limited set of these relations have appeared in the literature at any one time. For example, the chain relations for the generic correlation functions are discussed by Lebowitz and Percus,[20] but neither the thermodynamic limit nor the specific correlation functions are mentioned. In contrast, Liboff[28] discusses only the specific reduced distribution functions. This paper has attempted to give a broader perspective of the contrasting properties of the chain relations which result when different normalization conventions are used for the definition of the reduced distribution functions. The different normalizations give rise to correlation functions which obey different mathematical constraints. It has also been shown in great detail that the normalization requirements disallow the *direct* association between correlation functions and physical clusters for all normalizations.

Historically there seems to have been some controversy over the validity of the Debye–Hückel theory arising from whether its pair correlation function obeys the ''antinormalization'' property. The discussion given by Schram on this topic[23] can be interpreted as stating that in the Debye–Hückel theory, the generic normalization of Eq. (19) was used in defining the reduced density operator and so its corresponding two particle correlation function will obey Eq. (20).

The chain relations stated here are exact, but in many applications the asymptotic behavior (large-N limit), $N\gg 1$, is used to simplify theoretical equations. The relations derived above illustrate that the stage at which the asymptotic limit is taken is of importance. An extreme example is taking the large-N limit of Eq. (1), which gives

$$\rho_{1\cdots n}^{(n)}=N^n\ \mathrm{Tr}_{n+1\cdots N}\rho_{1\cdots N}^{(N)}. \tag{62}$$

In this limit one obtains,

$$\mathrm{Tr}_i\ c_{1\cdots i\cdots n}^{(n)}=0, \tag{63}$$

which is similar to the result of (31), and very different from the exact form in (6). By taking the large-N limit, one neglects factors of the type n/N. These are very important for the validity of the chain relations, so neglecting them destroys the chain relations. The authors became aware of the possible inconsistencies between the large-N forms for the different reduced distribution functions when generalizing gas kinetic equations to higher density with the rigorous inclusion of bound states. In such work it is necessary to involve reduced distribution functions of different orders and if these are not consistent, the resulting kinetic equations can be impossible to interpret.

The question now arises as to when is it justified to neglect the terms in the reduced density and correlation operators containing factors such as $1/M$ or $1/D$ in the monomer–dimer problem? Certainly the operation of taking a trace requires their presence in order to properly account for the makeup of lower order reduced density and correlation operators, in particular their normalization. Otherwise these terms always involve $1/M$ or $1/D$ factors and are of lower order in the thermodynamic limit, so they act as (presumably minor) corrections to the product terms that have no $1/M$ or $1/D$ factors. On the other hand, it is desirous to retain the term ρ_{b12} in the two-particle density operator $\rho_{12}^{(2)}$ since it has a different structure, namely, that it describes the binding between the two specific particles 1 and 2. Thus it needs to be retained in the $M,D\to\infty$ limit even though its norm has a magnitude of comparable size to the neglected terms. It

seems that the answer to the question posed above is: it depends on the use being made of the reduced density or correlation operator. But if ''small'' terms are neglected, it must not be forgotten to check that their neglect is done in a manner consistent with the use put to the non-neglected terms.

The magnitudes and signs of the traced over correlation operators also merit some discussion. For the ''specific'' normalization these all vanish while in a closed system for the ''generic'' normalization, Eq. (14) shows that the total trace of any correlation function is N, multiplied by a signed numerical factor. Thus, since the reduced density operators $\rho^{(n)}$ are of order N^n, the significance of the n-particle correlation functions can be seen to be negligible for large N (in trace magnitude) and become of even less importance as n increases. For this normalization, the signs of the traced over correlation operators are also of interest. In particular, the traced over two-particle correlation operator is always negative, irrespective of the ''attractive'' or ''repulsive'' nature of the intermolecular potential. Similar constraints hold for higher order correlation operators. The signs of the traced over correlation operators indicate that in the total trace of the n-particle reduced density operator, all terms excluding the n-particle correlation operator $c^{(n)}$ overestimate $\mathrm{Tr}_{1\ldots n}\rho^{(n)}$ for even n, and underestimate it for odd n. These properties arise from the $N!/(N-n)!$ normalization chosen for $\rho^{(n)}$. Similar arguments can be given for the other correlation operators of Sec. II.

As discussed by Liboff,[28] modeling the correlation functions is a difficult task. The normalization relations stated here provide constraints which any model functions must satisfy in order to give consistent results. Thus, for example, as stressed by Liboff for the classical correlation function $\mathscr{C}_{12}^{(2)}$, this function must have at least one zero at some interparticle separation between 0 and ∞ in order for Eq. (31) to be satisfied. The different constraints also show that one must be consistent in choosing the proper normalization for the correlation functions and the reduced distribution functions. For example, the discussion given by Schram[23] can be interpreted as stating that the normalization for the pair correlation function was not consistent with the normalization of the original reduced distribution function.

The normalization constraint can provide a test of the consistency of existing kinetic theory formalisms. Usually, this constraint is *not* emphasized in the literature. Cohen's classic dense gas theory has been analyzed as an illustration. It has shown that his normalization prevents his U_s from being identical to the Ursell cluster functions and that his $F^{(1)}$ and $F^{(2)}$ do not satisfy the corresponding chain relation. It is also noted that the normalization constraint has actually been included in the density functional theory for the cluster expansion of a finite number of electrons.[30]

The results obtained in this paper show that the normalization convention chosen for the reduced density operator has an important effect on the properties of the correlation operators. This must be carefully considered when the correlation operators are being modeled analytically or derived from simulations where the large-N limit cannot be taken.

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