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Ensemble transformation in the fluctuation theory

Seishi Shimizu[1,*] and Nobuyuki Matubayasi[2]

[1]York Structural Biology Laboratory, Department of Chemistry, University of York, Heslington, York YO10 5DD, United Kingdom

[2]Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

Corresponding Author: Seishi Shimizu

Tel: +44 1904 328281, Fax: +44 1904 328281, Email: seishi.shimizu@york.ac.uk

Abstract

Interactions in complex solutions that consist of multiple components can be quantified via number correlations observed within an isochoric subsystem. The fluctuation solution theory carries out a conversion between experimental data, under isobaric conditions, and the isochoric number correlations, through cumbersome thermodynamic variable transformations. In contrast, we have recently demonstrated heuristically that direct transformation of statistical variables (i.e., those variables fluctuating in statistical ensembles such as volume and particle numbers) can lead to equivalent results via simple algebra. This paper reveals the geometrical basis of fluctuation and invariants underlying the equivalence between thermodynamic and statistical variable transformations. Based on the quasi-thermodynamic fluctuation theory and the postulate that concentration and its fluctuation are invariant under ensemble transformation, we show that the thermodynamic and statistical variable transformations correspond to the change of basis on a Hessian and statistical variables, respectively, under which the quadratic form of fluctuation is invariant. Statistical variable transformation can also be used in cases when a set of experimental data do not belong to the same ensemble. When combined with the order-of-magnitude analysis, our formalism shows that the quasi-thermodynamic formalism of fluctuation at the thermodynamic limit is valid only for extensive variables and cannot be applied to intensive variables.

Keywords: fluctuation solution theory; Hessian; thermodynamic variable transformation; tensor; intensive; extensive

1. Introduction

Quantifying interactions in complex solutions, that are composed of multiple components, is a challenging scientific question with many applications, such as colloids and surfactants [1,2], microemulsions [3], nanoparticles [4], and polymers including biopolymers [5]. The most general theoretical foundation is the fluctuation solution theory, initiated by Kirkwood and Buff [6], which quantifies interactions between constituent species via number covariance, related to the molecular distribution function [6–10]. The physical meaning of the fluctuation solution theory can be best illustrated by setting up within a multiple component solution an open, isochoric subsystem as (a theoretical device as) an observatory for particle numbers and their fluctuations and covariances therein [9,11,12]. However, the discrepancy between the isochoric "observatory" subsystem and the ensemble of experimental convenience (i.e., isobaric) necessitated thermodynamic variable transformation between the two ensembles, leading to significant calculus and algebra [6–10]. For the fluctuation solution theory to remain a useful tool for even more complex solutions [5,13,14], facilitating calculation [15,16] is indispensable.

Our goal is to facilitate thermodynamic variable transformation in the fluctuation theory, based on a geometrical perspective. A reasonable strategy would be to circumvent the isobaric to isochoric transformation required by the route initiated by Kirkwood and Buff [6,8,17,18]. We have recently proposed the statistical or "algebraic" transformation rules for number correlations as a facile alternative to the thermodynamic route [19]. This was conceived as a multiple-component generalization of the following short-cut technique found in textbooks [20,21],

$$\langle \delta V \delta V \rangle_{\{T,P,N\}} = \frac{V^2}{N^2} \langle \delta N \delta N \rangle_{\{T,V,\mu\}} \tag{1.1}$$

which directly transforms the number fluctuation in a grand canonical ensemble $\langle \delta N \delta N \rangle_{\{T,V,\mu\}}$ (with the chemical potential μ, number N, and temperature T) to the volume fluctuation in an isobaric ensemble $\langle \delta V \delta V \rangle_{\{T,P,N\}}$ (where P is the pressure). The crux of this approach is the algebraic relationship between the two deviations [19–21],

$$\delta V = -\frac{V}{N} \delta N \tag{1.2}$$

which we will refer to as the *statistical variable transformation*. Eq. (1.2) provides a facile alternative to deriving the following relationship on the isothermal compressibility

$$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_N = \frac{V}{N^2}\left(\frac{\partial N}{\partial \mu}\right)_P \tag{1.3}$$

The derivation of Eq. (1.3) purely from the *thermodynamic variable transformation* of partial derivatives requires several careful steps, in contrast to the short-cut afforded by Eq. (1.2) [19–21].

The statistical variable transformation, i.e., the generalization of Eq. (1.2) to multiple-component solutions [19], has exhibited considerable ease in re-deriving the Kirkwood-Buff theory, compared to the more cumbersome route via thermodynamic variable transformation [19]. An even more difficult problem of cooperative solubilization by hydrotropes and micelles [22–26], which requires the variable transformation on multiple-body correlation and higher-order thermodynamic derivatives, has been simplified by the statistical variable transformation [19]. Furthermore, the statistical variable transformation was proven to be useful for the questions beyond the remit of macroscopic chemical thermodynamics, such as the thermodynamic stability condition for a mixture in mesoscale confinement (which involves an additional degree of freedom coming from the boundary effect [27]) and in clarifying the similarity and difference between sorption on/into solid and liquid sorbents [28]. However, the theoretical foundation of the statistical variable transformation has remained rather ad-hoc. The present paper will show that the equivalence between the statistical and thermodynamic transformations can be established from the invariance of the quadratic form.

To clarify the geometric foundation of fluctuation, the quasi-thermodynamic formalism [21,29–35] of von Smoluchowski [36–38] and Einstein [38–40] will provide a useful perspective complementary to the ensemble-based formalism of Gibbs [41] which is used commonly as the foundation of the Kirkwood-Buff theory [6,8,17]. The quasi-thermodynamic formalism employs the minimum work associated with moving a molecule from the reservoir into the system, which is expressed in a quadratic form involving the Hessian matrix and the deviation vector of thermodynamic variables [25,27].

Based on the quasi-thermodynamic formalism, the goal of this paper is to reveal the geometrical structure underlying the equivalence between the thermodynamic and statistical variable transformations. We will prove that a change of basis acts on the Hessian as thermodynamic variable transformation and the deviation vector as statistical variable transformation.

transforming in the same manner as the metric tensor and displacement vector in geometry, respectively. Furthermore, statistical variable transformation can be used even in non-geometric cases when a set of experimental data have not been obtained within the same ensemble. However, intensive variables cannot be statistical variables within the quasi-thermodynamic formalism at the thermodynamic limit. This can be shown straightforwardly and intuitively via the order-of-magnitude analysis within our formalism, thereby shedding light onto the much-debated topic [31,32,35,42,43] despite its entry into standard textbooks [21,44].

2. A quasi-thermodynamic formulation of size-invariant fluctuation

Our goal is to facilitate thermodynamic variable transformation in the fluctuation solution theory from a geometrical perspective. The geometric basis of fluctuation will become apparent when one reformulates the Kirkwood-Buff solution theory [6,8,11] based on the quasi-thermodynamic formalism of fluctuation by von Smoluchowski and Einstein [36–40], which has been refined since then [21,29–35,45]. Let us consider an isochoric system, which consists of a small, open isochoric (constant volume) subsystem and a reservoir (denoted as r). The use of a small, open isochoric subsystem plays a key role in the observation of particle numbers and their correlations as the measure of solution structure [9,11,12]. Such a subsystem will be referred to as the isochoric (constant volume) observatory subsystem. What is essential is that the molecular species can go in and out of the observatory subsystem, so that their concentration and their fluctuations reflect intermolecular interaction [9,11,12]. Following Landau and Lifshitz [21], the minimum work done by the external medium on the isochoric system (i.e., the observatory subsystem and the reservoir),

δR_v, which accompanies the exchange of matter between the observatory subsystem and the reservoir can be written as

$$\delta R_v = \delta e + \delta E^{(r)} \tag{2.1}$$

where δe is the change in the internal energy of the observatory subsystem and $\delta E^{(r)}$ is that of the reservoir. In this setup, $\delta E^{(r)}$ which accompanies the exchange of matter is expressed as [21]

$$\delta E^{(r)} = T^{(r)}\delta S^{(r)} + \mu_1^{(r)}\delta N_1^{(r)} + \mu_2^{(r)}\delta N_2^{(r)} \tag{2.2}$$

For simplicity, we consider a two-component mixture consisting of species 1 and 2. μ_i and N_i are the chemical potential and the number of species i, respectively; T is the temperature and the superscript (r) represents the reservoir. Appendix A presents a justification, based on an order-of-magnitude argument, why it suffices to consider only the change of numbers, δN_i, up to the first order. The observatory subsystem and the reservoir are in equilibrium, hence $\mu_1^{(r)} = \mu_1$, $\mu_2^{(r)} = \mu_2$, $T^{(r)} = T$. We use the corresponding symbols without the superscript to denote quantities pertaining to the observatory subsystem. In addition, the conservation relationships hold between the subsystem and the reservoir, such that $\delta N_1^{(r)} = -\delta n_1$, $\delta N_2^{(r)} = -\delta n_2$, and $\delta S^{(r)} = -\delta s$. We use the lower case characters to represent the thermodynamic quantities for the observatory subsystem. This is to reflect the small size of the observatory subsystem, even though it is still macroscopic [9,11,12]. Thus, the minimum work done by the external medium on the isochoric system that accompanies the exchange of matter between the subsystem and the reservoir can be obtained from Eqs. (2.1) and (2.2) as

$$\delta R_v = \delta e - T\delta s - \mu_1\delta n_1 - \mu_2\delta n_2 = \delta a + s\delta T - \mu_1\delta n_1 - \mu_2\delta n_2 \tag{2.3}$$

where $a = e - Ts$ is the Helmholtz free energy. (Note that Eq. (2.3) corresponds to the well-known result from thermodynamics that the Helmholtz free energy is the minimum work under constant T, v, n_1 and n_2). Equilibrium thermodynamics is recovered under $\delta R_v = 0$, which leads to the familiar differential relationship. Our interest, however, is in the minimum work done by the external medium that accompanies the slight deviation (δn_1 and δn_2) from the equilibrium distribution of the molecules inside the isochoric observatory subsystem. Expanding δa in Eq. (2.3) up to the second-order under constant temperature and volume,

$$\delta a = \mu_1 \delta n_1 + \mu_2 \delta n_2 + \left(\frac{\partial^2 a}{\partial n_1^2}\right) \delta n_1 \delta n_1 + 2\left(\frac{\partial^2 a}{\partial n_1 \delta n_2}\right) \delta n_1 \delta n_2 + \left(\frac{\partial^2 a}{\partial n_2^2}\right) \delta n_2 \delta n_2 \tag{2.4}$$

Note that the variables for the second-order derivatives are n_1 and n_2. Appendix A presents an order-of-magnitude argument, justifying why up to the second-order terms should be incorporated for δa. Combining Eqs. (2.3) and (2.4), we obtain the following quadratic form for the minimum work under constant temperature and volume:

$$\delta R_v = (\delta n_1 \quad \delta n_2)_{\{T,v,\mu_1,\mu_2\}} \begin{pmatrix} \dfrac{\partial^2 a}{\partial n_1^2} & \dfrac{\partial^2 a}{\partial n_1 \partial n_2} \\ \dfrac{\partial^2 a}{\partial n_1 \partial n_2} & \dfrac{\partial^2 a}{\partial n_2^2} \end{pmatrix}_{\{T,v\}} \begin{pmatrix} \delta n_1 \\ \delta n_2 \end{pmatrix}_{\{T,v,\mu_1,\mu_2\}} \tag{2.5}$$

The deviations, δn_i, in Eq. (2.5) pertains to the observatory subsystem, whose ensemble variables are $\{T, v, \mu_1, \mu_2\}$. For the Hessian matrix in Eq. (2.5), we have emphasized the isothermal-isochoric condition, $\{T, v\}$, common to all the elements. Evaluating the thermodynamic derivatives in the Hessian matrix leads to the following form:

$$\delta R_v = (\delta n_1 \quad \delta n_2)_{\{T,v,\mu_1,\mu_2\}} \begin{pmatrix} \dfrac{\partial \mu_1}{\partial n_1} & \dfrac{\partial \mu_1}{\partial n_2} \\ \dfrac{\partial \mu_2}{\partial n_1} & \dfrac{\partial \mu_2}{\partial n_2} \end{pmatrix}_{\{T,v\}} \begin{pmatrix} \delta n_1 \\ \delta n_2 \end{pmatrix}_{\{T,v,\mu_1,\mu_2\}} \tag{2.6}$$

Now we show that Eq. (2.6) is size invariant, which plays a key role in deriving the statistical variable transformation rules [19] as will be shown in Section 4. This can be carried out most effectively by employing the so-called A matrix in the Kirkwood-Buff theory [6,8], denoted here as $\boldsymbol{A_v}$ to emphasise its isochoric nature, defined as

$$\boldsymbol{A_v} = \frac{v}{kT}\begin{pmatrix} \frac{\partial \mu_1}{\partial n_1} & \frac{\partial \mu_1}{\partial n_2} \\ \frac{\partial \mu_2}{\partial n_1} & \frac{\partial \mu_2}{\partial n_2} \end{pmatrix}_{\{T,v\}} \tag{2.7}$$

All the elements of $\boldsymbol{A_v}$ are intensive. Using Eq. (2.7), Eq. (2.6) can be rewritten as

$$\beta \delta R_v = \boldsymbol{b_v^T A_v b_v} \tag{2.8}$$

with $\beta = \frac{1}{kT}$where $\boldsymbol{b_v}$ is now a vector, whose elements are intensive, defined as

$$\boldsymbol{b_v} = \frac{1}{\sqrt{v}}\begin{pmatrix} \delta n_1 \\ \delta n_2 \end{pmatrix}_{\{T,v,\mu_1,\mu_2\}} \tag{2.9}$$

Since $\delta n_i = O(\sqrt{v})$ for $n = O(v)$ (see, for example, Chapter 2 of Ref [21]), the elements of $\boldsymbol{b_v}$ are also intensive. (Here we have used Landau's symbol; $O(v)$ signifires "in the order of v"). Consequently, δR_v is intensive and size-invariant. This is because the order of magnitude (with respect to v) for the terms in Eq. (2.4) decreases by half when the order of the deviations (δn_1 and δn_2) is increased by 1. Consequently, the first-order terms with respect to δn_1 and δn_2 in Eq. (2.4) are $O(\sqrt{v})$ whereas the second order terms are $O(1)$. The orders of magnitude consideration on the expansion of δR_v in Eq. (2.6) will play a crucial role in understanding whether the quasi-thermodynamic formalism can be applied to the fluctuation of intensive variables (Section 8).

This paper aims to exploit the geometric feature of Eq. (2.8) to facilitate thermodynamic variable transformation, which will be presented in Sections 4 and 5. The conventional approach, instead, aims to calculate the correlation between particle numbers, through the ensemble average of the following matrix constructed from the deviation vectors

$$\boldsymbol{B_v} = \frac{1}{v}\begin{pmatrix} \delta n_1 \delta n_1 & \delta n_1 \delta n_2 \\ \delta n_2 \delta n_1 & \delta n_2 \delta n_2 \end{pmatrix}_{\{T,v,\mu_1,\mu_2\}} = \boldsymbol{b_v b_v^T} \tag{2.10}$$

The ensemble average of $\boldsymbol{B_v}$ is referred to as the Kirkwood-Buff B matrix [6,8]. Assuming a Gaussian probability distribution, the following relationship can be derived for the B matrix

$$\langle \boldsymbol{B_v} \rangle = \boldsymbol{A_v^{-1}} \tag{2.11}$$

(The derivation can be found in Section 3.1 of Ref [27] and Section 111 of Ref [21]). Hence the Kirkwood-Buff theory involves inverting $\boldsymbol{A_v}$ and evaluating the thermodynamic derivatives in Eq. (2.7) under constant volume. Note that the experimental data on solutions are measured under constant pressure. This necessitates a successive series of thermodynamic variable transformations, and the resultant forms are algebraically complex, as can be seen in Refs [7,8]; it took more than two decades for the Kirkwood-Buff theory to be applied to solution thermodynamic data [46,47]. We will show in Sections 4-6 how such complex thermodynamic variable transformations involved in the fluctuation theory can be facilitated by a geometrical perspective.

3. A statistical approach to ensemble transformation

To circumvent thermodynamic variable transformation from isochoric to isobaric, it is convenient to define an isobaric fluctuation observatory subsystem, which contains the constant number of species 1. Such a subsystem is denoted in our notation as $\{T, P, n_1, \mu_2\}$; species 2 can freely come in and out of the subsystem under constant μ_2. In this setup, $\delta E^{(r)}$ is expressed as

$$\delta E^{(r)} = T^{(r)} \delta S^{(r)} - P^{(r)} \delta V^{(r)} + \mu_2^{(r)} \delta N_2^{(r)} \tag{3.1a}$$

The reservoir is in thermodynamic equilibrium with the subsystem, namely, $T^{(r)} = T$, $P^{(r)} = P$ and $\mu_2^{(r)} = \mu_2$, together with the conservation relationships, $\delta V^{(r)} = -\delta v$, $\delta N_2^{(r)} = -\delta n_2$. Following the same argument as in Section 2, Eq. (3.1) leads to

$$\delta R_P = \delta e - T\delta s + P\delta v - \mu_2 \delta n_2 = \delta a + s\delta T + P\delta v - \mu_2 \delta n_2 \tag{3.1b}$$

again with the Helmholtz free energy, $a = e - Ts$. Under constant T, we obtain the following quadratic form for the minimum work, denoted as δR_P:

$$\delta R_P = \begin{pmatrix} \delta v & \delta n_2 \end{pmatrix}_{\{T,P,n_1,\mu_2\}} \begin{pmatrix} \dfrac{\partial^2 a}{\partial v^2} & \dfrac{\partial^2 a}{\partial v \partial n_2} \\ \dfrac{\partial^2 a}{\partial v \partial n_2} & \dfrac{\partial^2 a}{\partial n_2^2} \end{pmatrix}_{\{T,n_1\}} \begin{pmatrix} \delta v \\ \delta n_2 \end{pmatrix}_{\{T,P,n_1,\mu_2\}} \tag{3.2}$$

Note, again, that the thermodynamic variables for the deviation vector are $\{T, P, n_1, \mu_2\}$, identical to those of the observatory subsystem. For the Hessian matrix in Eq. (3.2), we have emphasized the constant $\{T, n_1\}$ as the common constraint for all the elements. Evaluating the thermodynamic derivatives, Eq. (3.2) becomes

$$\delta R_P = \begin{pmatrix} \delta v & \delta n_2 \end{pmatrix}_{\{T,P,n_1,\mu_2\}} \begin{pmatrix} -\dfrac{\partial P}{\partial v} & -\dfrac{\partial P}{\partial n_2} \\ \dfrac{\partial \mu_2}{\partial v} & \dfrac{\partial \mu_2}{\partial n_2} \end{pmatrix}_{\{T,n_1\}} \begin{pmatrix} \delta v \\ \delta n_2 \end{pmatrix}_{\{T,P,n_1,\mu_2\}} \tag{3.3}$$

In a parallel manner to δR_v in Section 2, Eq. (3.3) can be rewritten in a size-invariable manner, by introducing the size-invariant matrices composed of only intensive variables,

$$\boldsymbol{A_P} = \frac{\langle v \rangle}{kT} \begin{pmatrix} -\dfrac{\partial P}{\partial v} & -\dfrac{\partial P}{\partial n_2} \\ \dfrac{\partial \mu_2}{\partial v} & \dfrac{\partial \mu_2}{\partial n_2} \end{pmatrix}_{\{T,n_1\}} \tag{3.4}$$

$$\boldsymbol{b_P} = \frac{1}{\sqrt{\langle v \rangle}} \begin{pmatrix} \delta v \\ \delta n_2 \end{pmatrix}_{\{T,P,n_1,\mu_2\}} \tag{3.5}$$

through which Eq. (3.3) can be written as

$$\beta \delta R_P = \boldsymbol{b_P^T A_P b_P} \tag{3.6}$$

Just as in Section 2, assuming Gaussian distribution, the following relationship can be derived [21,27] between the Hessian matrix $\boldsymbol{A_P}$ and the correlation matrix, $\langle \boldsymbol{B_P} \rangle$,

$$\langle \boldsymbol{B_P} \rangle = \boldsymbol{A_P^{-1}} \tag{3.7}$$

where B_P is defined as

$$\boldsymbol{B_P} = \frac{1}{\langle v \rangle} \begin{pmatrix} \delta v \delta v & \delta v \delta n_2 \\ \delta n_2 \delta v & \delta n_2 \delta n_2 \end{pmatrix}_{\{T,P,n_1,\mu_2\}} = \boldsymbol{b_P b_P^T} \tag{3.8}$$

The benefit of the isobaric formalism is that A_P can be obtained directly from experimental data measured in the $\{T, P, n_1, \mu_2\}$ ensemble. The volume of the observatory subsystem (on which the fluctuation matrix, $\boldsymbol{B_P}$, is defined), on the other hand, fluctuates. Using the isochoric observatory subsystem is advantageous because the effect of interaction is monitored by the particle numbers without any need to consider volume fluctuation. Therefore, particle number correlations are reported using the isochoric observatory subsystems. This necessitates a scheme to convert the isobaric correlation matrix, $\boldsymbol{B_P}$, to its isochoric counterpart, $\boldsymbol{B_v}$.

A transformation from $\boldsymbol{B_P}$ to $\boldsymbol{B_v}$ can be carried out based on the one from $\boldsymbol{b_P}$ to $\boldsymbol{b_v}$. We postulate that the concentration and its fluctuation are invariants, which do not depend on the ensembles for observation [19]. (The following intuitive approach has been proven to be equivalent to the invariance of concentration and its fluctuation [19].) Consequently, the change of solution composition, n_2/n_1, is the same in the $\{T, P, n_1, \mu_2\}$ and $\{T, v, \mu_1, \mu_2\}$ observatory subsystems

$$\frac{n_2 + (\delta n_2)_{\{T,P,n_1,\mu_2\}}}{n_1} = \frac{n_2 + (\delta n_2)_{\{T,v,\mu_1,\mu_2\}}}{n_1 + (\delta n_1)_{\{T,v,\mu_1,\mu_2\}}} \tag{3.9}$$

Eq. (3.9), via Maclaurin expansion, leads to [19]

$$(\delta n_2)_{\{T,P,n_1,\mu_2\}} = (\delta n_2)_{\{T,v,\mu_1,\mu_2\}} - C(\delta n_1)_{\{T,v,\mu_1,\mu_2\}} + O(1) \tag{3.10}$$

where we have introduced $\frac{n_2}{n_1} = \langle \frac{n_2}{n_1} \rangle + o(1) = C$ as the solution composition at the thermodynamic limit. (Here, we have used Landau's symbols, O and o, to denote orders of magnitude. $O(1)$ denotes "of the order of 1", which, in the context of Eq. (3.10), means that the order of intensive variables being lower than $O(\sqrt{v})$ of the rest in Eq. (3.10). $o(1)$ denotes "lower order than 1", which, in the above case, means that the error between the two $O(1)$ (intensive) quantities, $\frac{n_2}{n_1}$ and $\langle \frac{n_2}{n_1} \rangle$ is of a lower order of magnitude.) The fluctuation of $c_i = \frac{n_i}{v}$ does not depend on the ensembles adopted for the observatory subsystem [19], hence

$$\frac{n_1 + (\delta n_1)_{\{T,v,\mu_1\mu_2\}}}{v} = \frac{n_1}{v + (\delta v)_{\{T,P,n_1,\mu_2\}}} \tag{3.11a}$$

$$\frac{n_2 + (\delta n_2)_{\{T,v,\mu_1\mu_2\}}}{v} = \frac{n_2 + (\delta n_2)_{\{T,P,n_1\mu_2\}}}{v + (\delta v)_{\{T,P,n_1,\mu_2\}}} \tag{3.11b}$$

The Maclaurin expansion leads to

$$(\delta n_1)_{\{T,v,\mu_1,\mu_2\}} = -\frac{n_1}{v}(\delta v)_{\{T,P,n_1,\mu_2\}} + O(1) \tag{3.12a}$$

$$(\delta n_2)_{\{T,v,\mu_1,\mu_2\}} = (\delta n_2)_{\{T,P,n_1\mu_2\}} - \frac{n_2}{v}(\delta v)_{\{T,P,n_1,\mu_2\}} + O(1) \tag{3.12b}$$

From the Gibbs-Duhem equation, $V_1 \frac{n_1}{\langle v \rangle} + V_2 \frac{n_2}{\langle v \rangle} = 1$ can be derived for closed isobaric ensembles, with V_i being the partial molar volume of species i. Here we invoke the invariance of concentrations, which, in this context, is that the mean $\frac{n_i}{\langle v \rangle}$ in the closed isobaric observatory subsystem is the same as $\langle \frac{n_i}{v} \rangle_{\{T,P,n_1,\mu_2\}}$ in the partially open observatory subsystem. It follows that

$V_1 \langle \frac{n_1}{v} \rangle_{\{T,P,n_1,\mu_2\}} + V_2 \langle \frac{n_2}{v} \rangle_{\{T,P,n_1,\mu_2\}} + o(1) = 1$ at the thermodynamic limit. Eq. (3.12) leads to [19]

$$(\delta v)_{\{T,P,n_1,\mu_2\}} - V_2 (\delta n_2)_{\{T,P,n_1,\mu_2\}} = -V_1 (\delta n_1)_{\{T,v,\mu_1,\mu_2\}} - V_2 (\delta n_2)_{\{T,v,\mu_1,\mu_2\}} \tag{3.13a}$$

Using Eq. (3.10) to eliminate $(\delta n_2)_{\{T,P,n_1,\mu_2\}}$ from the left-hand side, we obtain

$$(\delta v)_{\{T,P,n_1,\mu_2\}} = -\frac{1}{c_1} (\delta n_1)_{\{T,v,\mu_1,\mu_2\}} \tag{3.13b}$$

where $c_1 = n_1/v$. We emphasize here that c_1 in Eq. (3.13) has been introduced at the thermodynamic limit. Note that Eq. (3.13) is about$\{T, v, \mu_1, \mu_2\} \to \{T, P, n_1, \mu_2\}$ transformation, instead of $\{T, v, \mu_1, \mu_2\} \to \{T, P, n_1, n_2\}$ presented in Ref [19]. This case with experimental significance will be discussed in Section 6.

The transformation scheme, Eq. (3.10), together with the $\{T, v, \mu_1, \mu_2\} \to \{T, P, n_1, n_2\}$ counterpart of Eq. (3.13) (see Section 6), was verified by their successful re-derivation of the Kirkwood-Buff theory [19]. This means that the thermodynamic variables can be converted algebraically, through the "statistical" transformation for variances [19]. However, the relationship between the two approaches to variable transformations, statistical and thermodynamic, has remained unclear. This will be resolved in the subsequent sections.

4. Geometrical foundation of the statistical and thermodynamic variable transformations

Our goal is to reveal a deeper reason as to why the statistical variable transformation (i.e., via Eqs. (3.10) and (3.13)) gives equivalent results as the thermodynamic variable transformation (i.e., between $\boldsymbol{A_v}$ and $\boldsymbol{A_P}$ via converting partial derivatives). As a first step, we combine Eqs. (3.10) and (3.13) in the following manner:

$$\boldsymbol{b_P} = \boldsymbol{D}\boldsymbol{b_v} \tag{4.1a}$$

$$\boldsymbol{D} \equiv \begin{pmatrix} -c_1^{-1} & 0 \\ -C & 1 \end{pmatrix} \tag{4.1b}$$

Here we show that Eq. (4.1) can be derived from the general approach to coordinate transformation, namely,

$$\begin{pmatrix} \delta v \\ \delta n_2 \end{pmatrix}_{\{T,P,n_1,\mu_2\}} = \begin{pmatrix} \dfrac{\partial v_{\{P\}}}{\partial n_{1\{v\}}} & \dfrac{\partial v_{\{P\}}}{\partial n_{2\{v\}}} \\ \dfrac{\partial n_{2\{P\}}}{\partial n_{1\{v\}}} & \dfrac{\partial n_{2\{P\}}}{\partial n_{2\{v\}}} \end{pmatrix} \begin{pmatrix} \delta n_1 \\ \delta n_2 \end{pmatrix}_{\{T,v,\mu_1,\mu_2\}} \tag{4.2}$$

where we have abbreviated the ensemble variables in the Hessian for calculation facility. To calculate the elements, we use the postulated invariance of concentration and density, which can be summarized using Eqs. (3.9) and (3.11) as

$$\frac{n_1}{v_{\{P\}}} = \frac{n_{1\{v\}}}{v} \tag{4.3a}$$

$$\frac{n_{2\{P\}}}{n_1} = \frac{n_{2\{v\}}}{n_{1\{v\}}} \tag{4.3b}$$

Note that the quantities without { } in the subscript are constants. Using Eqs. (4.3a) and (4.3b), the transformation matrix in Eq. (4.2) can be calculated as

$$\begin{pmatrix} \dfrac{\partial v_{\{P\}}}{\partial n_{1\{v\}}} & \dfrac{\partial v_{\{P\}}}{\partial n_{2\{v\}}} \\ \dfrac{\partial n_{2\{P\}}}{\partial n_{1\{v\}}} & \dfrac{\partial n_{2\{P\}}}{\partial n_{2\{v\}}} \end{pmatrix} = \begin{pmatrix} -\dfrac{n_1 v}{n_{1\{v\}}^2} & 0 \\ -\dfrac{n_1 n_{2\{v\}}}{n_{1\{v\}}^2} & \dfrac{n_1}{n_{1\{v\}}} \end{pmatrix} = \begin{pmatrix} -\dfrac{1}{c_1} & 0 \\ -C & 1 \end{pmatrix} \tag{4.4a}$$

To evaluate the final step, we have carried out the following expansions and retained the terms up to $O(1)$:

$$\frac{n_{i\{v\}}}{n_i} = 1 + \frac{\delta n_i}{n_i} + o\left(\frac{1}{\sqrt{v}}\right) \tag{4.4b}$$

$$\frac{n_{1\{v\}}}{v} = \frac{\langle n_{1\{v\}}\rangle}{v}\left(1 + \frac{\delta n_1}{n_1}\right) + o\left(\frac{1}{\sqrt{v}}\right) = c_1\left(1 + \frac{\delta n_1}{n_1}\right) + o\left(\frac{1}{\sqrt{v}}\right) \tag{4.4c}$$

$$\frac{n_{2\{v\}}}{n_{1\{v\}}} = \frac{\langle n_{2\{v\}}\rangle}{\langle n_{1\{v\}}\rangle}\left(1 + \frac{\delta n_2}{n_2} - \frac{\delta n_1}{n_1}\right) + o\left(\frac{1}{\sqrt{v}}\right) = C\left(1 + \frac{\delta n_2}{n_2} - \frac{\delta n_1}{n_1}\right) + o\left(\frac{1}{\sqrt{v}}\right) \tag{4.4d}$$

Eq. (4.4a) is the same as the transformation matrix *D* in Eq. (4.1b) at the thermodynamic limit.

The same matrix *D* can carry out the thermodynamic variable transformation on the Hessian. This can be seen from the following:

$$\begin{pmatrix} \frac{\partial}{\partial v} \\ \frac{\partial}{\partial n_2} \end{pmatrix}_{\{T,P,n_1,\mu_2\}} = \begin{pmatrix} \frac{\partial n_{1\{v\}}}{\partial v_{\{P\}}} & \frac{\partial n_{2\{v\}}}{\partial v_{\{P\}}} \\ \frac{\partial n_{1\{v\}}}{\partial n_{2\{P\}}} & \frac{\partial n_{2\{v\}}}{\partial n_{2\{P\}}} \end{pmatrix} \begin{pmatrix} \frac{\partial}{\partial n_1} \\ \frac{\partial}{\partial n_2} \end{pmatrix}_{\{T,v,\mu_1,\mu_2\}} = (\boldsymbol{D^T})^{-\mathbf{1}} \begin{pmatrix} \frac{\partial}{\partial n_1} \\ \frac{\partial}{\partial n_2} \end{pmatrix}_{\{T,v,\mu_1,\mu_2\}} \tag{4.5}$$

which can be proven easily via

$$\begin{pmatrix} \frac{\partial n_{1\{v\}}}{\partial v_{\{P\}}} & \frac{\partial n_{2\{v\}}}{\partial v_{\{P\}}} \\ \frac{\partial n_{1\{v\}}}{\partial n_{2\{P\}}} & \frac{\partial n_{2\{v\}}}{\partial n_{2\{P\}}} \end{pmatrix} \begin{pmatrix} \frac{\partial v_{\{P\}}}{\partial n_{1\{v\}}} & \frac{\partial v_{\{P\}}}{\partial n_{2\{v\}}} \\ \frac{\partial n_{2\{P\}}}{\partial n_{1\{v\}}} & \frac{\partial n_{2\{P\}}}{\partial n_{2\{v\}}} \end{pmatrix}^T = I \tag{4.6}$$

As a result, the Hessian transformation becomes

$$\boldsymbol{A_P} = \begin{pmatrix} \dfrac{\partial}{\partial v} \\ \dfrac{\partial}{\partial n_2} \end{pmatrix}_{\{T,P,n_1,\mu_2\}} \begin{pmatrix} \dfrac{\partial a}{\partial v} & \dfrac{\partial a}{\partial n_2} \end{pmatrix}_{\{T,P,n_1,\mu_2\}} \tag{4.7}$$

$$= (\boldsymbol{D^T})^{-1} \begin{pmatrix} \dfrac{\partial}{\partial n_1} \\ \dfrac{\partial}{\partial n_2} \end{pmatrix}_{\{T,v,\mu_1,\mu_2\}} \begin{pmatrix} \dfrac{\partial a}{\partial n_1} & \dfrac{\partial a}{\partial n_2} \end{pmatrix}_{\{T,v,\mu_1,\mu_2\}} \boldsymbol{D^{-1}}$$

$$= (\boldsymbol{D^T})^{-1} \boldsymbol{A_v} \boldsymbol{D^{-1}}$$

This leads to the relationship for the change of basis for the thermodynamic variables

$$\boldsymbol{D^T A_P D} = \boldsymbol{A_v} \tag{4.8}$$

We have obtained a complete set of transformation rules for thermodynamic fluctuations for both the Hessian matrix of thermodynamic second derivatives (Eq. (4.8)) and the deviation vector (Eq. (4.1a)). Under these rules, we can show that

$$\beta\delta R_P = \boldsymbol{b_P^T A_P b_P} = \boldsymbol{b_v^T D^T A_P D b_v} = \boldsymbol{b_v^T A_v b_v} = \beta\delta R_v \tag{4.9}$$

Thus, we have established that the quadratic form of fluctuation, $\delta R = \delta R_P = \delta R_v$, is invariant under ensemble transformation. The transformation rules (Eqs. (4.1a) and (4.8)) belong to a universal mathematical formalism encountered for the change of basis and the consequent transformation of the Hessian metric tensor in differential geometry.

Even though the geometrical structure underlying classical thermodynamics has been recognized for a long time [33,48,49], the significance here is of practical value; the considerable reduction of calculation demonstrated via the statistical variable transformation for the fluctuation solution theory [19] was essentially the application of tensor calculus for the change of basis, applied directly on the deviation vector instead of the Hessian.

5. Isothermal compressibility

So far, we have been focusing on a transformation between the two open systems, $\{T, v, \mu_1, \mu_2\}$ and $\{T, P, n_1, \mu_2\}$. Under isothermal conditions, both observatory subsystems have two statistical variables. Because of the same dimensionality, conversion between the two was straightforward via the change of basis. In the Kirkwood-Buff theory of solutions, the isothermal compressibility, κ_T, plays an important role in connecting thermodynamic measurements to number fluctuations [6–8,50]. Due to its wide availability, the use of isothermal compressibility is sensible also from a practical point of view. Unlike the osmotic nature of $\{T, v, \mu_1, \mu_2\}$ and $\{T, P, n_1, \mu_2\}$, isothermal compressibility refers to the $\{T, P, n_1, n_2\}$ ensemble, which enables a symmetrical treatment of species 1 and 2. However, because of an additional constraint on the particle number, only v is the remaining statistical variable. This requires a separate theoretical treatment.

The minimum work $\delta E^{(r)}$ for the $\{T, P, n_1, n_2\}$ subsystem is expressed as

$$\delta E^{(r)} = T^{(r)} \delta S^{(r)} - P^{(r)} \delta V^{(r)} \tag{5.1}$$

The reservoir is in thermodynamic equilibrium with the subsystem, namely, $T^{(r)} = T$ and $P^{(r)} = P$, together with the conservation relationship, $\delta V^{(r)} = -\delta v$. Following the same argument as in Sections 2 and 3, Eq. (5.1) leads to the following quadratic form for the minimum work under constant temperature, denoted as δR_κ:

$$\delta R_{\kappa} = \left(\frac{\partial^2 a}{\partial v^2}\right)_{\{T,n_1,n_2\}} (\delta v)^2_{\{T,P,n_1,n_2\}} = -\left(\frac{\partial P}{\partial v}\right)_{\{T,n_1,n_2\}} (\delta v)^2_{\{T,P,n_1,n_2\}} \tag{5.2}$$

The application of the Gaussian distribution [21] yields a well-known relationship,

$$kT\kappa_T = -\frac{kT}{v}\left(\frac{\partial v}{\partial P}\right)_{\{T,n_1,n_2\}} = \frac{\langle \delta v \delta v \rangle_{\{T,P,n_1,n_2\}}}{\langle v \rangle_{\{T,P,n_1,n_2\}}} \tag{5.3}$$

Here, the conversion rule is different from Eqs. (3.13) in that, the number of species 2 is now kept constant. A pair of relationships that maps the statistical variables in $\{T, v, \mu_1, \mu_2\}$ to the ones in $\{T, P, n_1, n_2\}$ is available, which from the invariance of concentration, just like Eq. (3.11), as

$$(\delta v)_{\{T,P,n_1,n_2\}} = -\frac{1}{c_1}(\delta n_1)_{\{T,v,\mu_1,\mu_2\}} + O(1) \tag{5.4a}$$

$$(\delta v)_{\{T,P,n_1,n_2\}} = -\frac{1}{c_2}(\delta n_2)_{\{T,v,\mu_1,\mu_2\}} + O(1) \tag{5.4b}$$

Combining Eqs. (5.4a) and (5.4b) under $c_1V_1 + c_2V_2 = 1$ leads to

$$(\delta v)_{\{T,P,n_1,n_2\}} = -V_1(\delta n_1)_{\{T,v,\mu_1,\mu_2\}} - V_2(\delta n_2)_{\{T,v,\mu_1,\mu_2\}} + O(1) \tag{5.5}$$

Using Eqs. (5.4a) and (5.5), we obtain the following equivalent expressions:

$$\begin{aligned} \langle \delta v \delta v \rangle_{\{T,P,n_1,n_2\}} & \\ &= V_1^2 \langle \delta n_1 \delta n_1 \rangle_{\{T,v,\mu_1,\mu_2\}} + 2V_1V_2 \langle \delta n_1 \delta n_2 \rangle_{\{T,v,\mu_1,\mu_2\}} \\ &+ V_2^2 \langle \delta n_2 \delta n_2 \rangle_{\{T,v,\mu_1,\mu_2\}} \end{aligned} \tag{5.6a}$$

$$\langle \delta v \delta v \rangle_{\{T,P,n_1,n_2\}} = \frac{V_1}{c_1} \langle \delta n_1 \delta n_1 \rangle_{\{T,v,\mu_1,\mu_2\}} + \frac{V_2}{c_1} \langle \delta n_1 \delta n_2 \rangle_{\{T,v,\mu_1,\mu_2\}} \tag{5.6b}$$

Because both n_1 and n_2 change in the $\{T, v, \mu_1, \mu_2\}$, the expression for $\langle \delta v \delta v \rangle_{\{T,P,n_1,n_2\}}$ must contain both δn_1 and δn_2. Eq. (5.6) was shown to be equivalent to the well-known expression from the Kirkwood-Buff theory [19].

If isothermal compressibility is chosen as one of the links between experiment and number fluctuation, Eq. (5.6) can be used in place of one of three equations for the determination of $\boldsymbol{B}_v$. The disadvantage of this approach, however, is that the tensor transformation, which has led to clarity and facility in Section 5, can no longer be applied.

6. Statistical variable transformation in inhomogeneous solutions

We have demonstrated in the previous section that the determination of the number correlation matrix from experimental data sometimes requires a combination of different ensembles/bases, beyond the simplicity afforded by a geometrical formalism. The most logical approach would be to keep the geometry of the theory by processing experimental data through thermodynamic variable conversion. Here we propose a practical alternative using a mixed deviation vector belonging to two different bases. Such a vector can no longer be treated geometrically as in the previous section but reflects the practice of thermodynamic data analysis in multiple-component solutions.

Let us construct a mixed deviation vector by combining Eqs. (3.10) and Eq. (5.5a),

$$\begin{pmatrix} (\delta v)_{\{T,P,n_1,n_2\}} \\ (\delta n_2)_{\{T,P,n_1,\mu_2\}} \end{pmatrix} = \begin{pmatrix} -V_1 & -V_2 \\ -C & 1 \end{pmatrix} \begin{pmatrix} \delta n_1 \\ \delta n_2 \end{pmatrix}_{\{T,v,\mu_1,\mu_2\}} \tag{6.1}$$

which exhibits a striking similarity to the fundamental relationship for the preferential solvation theory [9,12,51], namely, how the solvation free energy of a dilute solute (μ_u^*, solute denoted as u) depends on P and μ_2, as

$$\begin{pmatrix} \left(\frac{\partial \mu_u^*}{\partial P}\right)_{T,n_1,n_2} \\ -\left(\frac{\partial \mu_u^*}{\partial \mu_2}\right)_{T,P,n_1} \end{pmatrix} = \begin{pmatrix} -V_1 & -V_2 \\ -C & 1 \end{pmatrix} \begin{pmatrix} \langle n_1 \rangle_u - \langle n_1 \rangle \\ \langle n_2 \rangle_u - \langle n_2 \rangle \end{pmatrix}_{\{T,v,\mu_1,\mu_2\}} \tag{6.2}$$

which was obtained by swapping the indexes 1 and 2 in Eq. (15) of Ref [15]. Here, $\langle\ \rangle_u$ refers to the ensemble average in an inhomogeneous ensemble around a solute, whose centre of mass is fixed in position and can be treated as an external field [52,53]. The fixed solute can be converted to a component in a homogeneous ensemble, via [15,22]

$$\frac{\langle \delta n_i \delta n_u \rangle}{\langle n_u \rangle} = \langle n_i \rangle_u - \langle n_i \rangle \tag{6.3}$$

which is a relationship valid for infinitely dilute solute, through which Eq. (6.2) can be rewritten as

$$\langle n_u \rangle \begin{pmatrix} \left(\frac{\partial \mu_u^*}{\partial P}\right)_{T,n_1,n_2} \\ -\left(\frac{\partial \mu_u^*}{\partial \mu_2}\right)_{T,P,n_1} \end{pmatrix} = \begin{pmatrix} -V_1 & -V_2 \\ -C & 1 \end{pmatrix} \begin{pmatrix} \langle \delta n_1 \delta n_u \rangle \\ \langle \delta n_2 \delta n_u \rangle \end{pmatrix}_{\{T,v,\mu_1,\mu_2\}} \tag{6.4a}$$

By now, the right-hand side of Eq. (6.4a) clearly shows its relations with the correlation between δn_u and Eq. (6.1), as

$$\begin{pmatrix} \langle \delta v \delta n_u \rangle_{\{T,P,n_1,n_2\}} \\ \langle \delta n_2 \delta n_u \rangle_{\{T,P,n_1,\mu_2\}} \end{pmatrix} = \begin{pmatrix} -V_1 & -V_2 \\ -C & 1 \end{pmatrix} \begin{pmatrix} \langle \delta n_1 \delta n_u \rangle \\ \langle \delta n_2 \delta n_u \rangle \end{pmatrix}_{\{T,v,\mu_1,\mu_2\}} \tag{6.4b}$$

Now we show that the transformation of the mixed deviation vector, Eq. (6.1), is indeed the foundation of the preferential solvation theory (Eq. (6.2)). To demonstrate this, we need to show the following relationship arising from the combination of Eqs. (6.3), (6.4a), and (6.4b):

$$\begin{pmatrix} \left(\dfrac{\partial \mu_u^*}{\partial P}\right)_{T,n_1,n_2} \\ -\left(\dfrac{\partial \mu_u^*}{\partial \mu_2}\right)_{T,P,n_1} \end{pmatrix} = \frac{1}{\langle n_u \rangle} \begin{pmatrix} \langle \delta v \delta n_u \rangle_{\{T,P,n_1,n_2\}} \\ \langle \delta n_2 \delta n_u \rangle_{\{T,P,n_1,\mu_2\}} \end{pmatrix} = \begin{pmatrix} (\langle v \rangle_u - \langle v \rangle)_{\{T,P,n_1,n_2\}} \\ (\langle n_2 \rangle_u - \langle n_2 \rangle)_{\{T,P,n_1,\mu_2\}} \end{pmatrix} \tag{6.5}$$

Justifying Eq. (6.5) is straightforward, using only the basics of statistical thermodynamics. The solvation free energy of a solute in infinite dilution, μ_u^*, can be expressed in terms of the inhomogeneous and homogeneous partition functions in two different ways, as [54]

$$e^{-\beta\mu_u^*} = \frac{Y_u(T,P,n_1,n_2)}{Y(T,P,n_1,n_2)} \tag{6.6a}$$

$$e^{-\beta\mu_u^*} = \frac{\Gamma_u(T,P,n_1,\mu_2)}{\Gamma(T,P,n_1,\mu_2)} \tag{6.6b}$$

where Γ and Y are the partition functions in the $\{T,P,n_1,\mu_2\}$ and $\{T,P,n_1,n_2\}$ ensembles, respectively, and the inhomogeneous ensemble with a fixed solute is denoted by the subscript u. Differentiating Eq. (6.6a) with respect to P and Eq. (6.6b) by μ_2 proves Eq. (6.5) straightforwardly.

We have thus demonstrated that the statistical variable transformation can be used beyond the strictly defined geometrical foundation of the change of basis. The basic equation of the preferential solvation theory (Eq. (6.2)) [9,11,12,15,16] was revealed to be the statistical variable transformation on a mixed deviation vector. This picture is much more straightforward than the approaches based on thermodynamic variable transformation from the Kirkwood-Buff tradition [55].

7. Fluctuation of intensive variables

So far, our deviation vectors have been composed exclusively of extensive variables, and the statistical variable transformation has been concerned only with the transformation between such deviation vectors. Consequently, our focus so far was on the correlations between extensive variables. However, the fluctuations of intensive variables, such as pressure and temperature, have been calculated using the quasi-thermodynamic formalism, which has been promulgated in the standard textbooks [21,44] yet has been debated [31,32,35,42,43].

Here we show that the deviation vectors for the quasi-thermodynamic formalism of fluctuation must be composed exclusively of extensive variables at the thermodynamic limit. To this end, let us take the $\{T, P, n_1, n_2\}$ ensemble as an example. In Section 6, the quadratic form consisted only of one extensive variable, δv; the deviation vector is one dimensional, in contrast to the two-dimensional vectors for the $\{T, v, \mu_1, \mu_2\}$ and $\{T, P, n_1, \mu_2\}$ ensembles in Sections 2-4. If the deviation of an intensive variable, say, $\delta\mu_2$, can be considered, the $\{T, v, \mu_1, \mu_2\} \to \{T, P, n_1, n_2\}$ conversion could be carried out via a change of basis.

We start by assuming the following change of basis:

$$\begin{pmatrix} \delta v \\ \delta\mu_2 \end{pmatrix}_{\{T,P,n_1,n_2\}} = \begin{pmatrix} \dfrac{\partial v_{\{P\}}}{\partial n_{1\{v\}}} & \dfrac{\partial v_{\{P\}}}{\partial n_{2\{v\}}} \\ \dfrac{\partial \mu_{2\{P\}}}{\partial n_{1\{v\}}} & \dfrac{\partial \mu_{2\{P\}}}{\partial n_{2\{v\}}} \end{pmatrix} \begin{pmatrix} \delta n_1 \\ \delta n_2 \end{pmatrix}_{\{T,v,\mu_1,\mu_2\}} \tag{7.1}$$

where the ensembles in the elements of the Hessian matrix were abbreviated as $\{v\}$ and $\{P\}$ for simplicity. Now we apply the order-of-magnitude analysis on Eq. (7.1). To do so, let us remember that the elements of the deviation vectors in Sections 2-5 were $O(\sqrt{v})$ and those of the transformation matrix D (see Eq. (4.1)) were $O(1)$. To facilitate the comparison, we rewrite Eq. (7.1) into the following form to make all the deviation vector elements $O\left(\sqrt{v}\right)$:

$$\begin{pmatrix} \delta v \\ \sqrt{\langle v\rangle}\delta\mu_2 \end{pmatrix}_{\{T,P,n_1,n_2\}} = \begin{pmatrix} \dfrac{\partial v_{\{P\}}}{\partial n_{1\{v\}}} & \dfrac{\partial v_{\{P\}}}{\partial n_{2\{v\}}} \\ \sqrt{\langle v\rangle_{\{P\}}}\dfrac{\partial \mu_{2\{P\}}}{\partial n_{1\{v\}}} & \sqrt{\langle v\rangle_{\{P\}}}\dfrac{\partial \mu_{2\{P\}}}{\partial n_{2\{v\}}} \end{pmatrix} \begin{pmatrix} \delta n_1 \\ \delta n_2 \end{pmatrix}_{\{T,v,\mu_1,\mu_2\}} \tag{7.2a}$$

Consequently, the deviation matrix elements have the following orders of magnitude:

$$\begin{pmatrix} \dfrac{\partial v_{\{P\}}}{\partial n_{1\{v\}}} & \dfrac{\partial v_{\{P\}}}{\partial n_{2\{v\}}} \\ \sqrt{\langle v\rangle_{\{P\}}}\dfrac{\partial \mu_{2\{P\}}}{\partial n_{1\{v\}}} & \sqrt{\langle v\rangle_{\{P\}}}\dfrac{\partial \mu_{2\{P\}}}{\partial n_{2\{v\}}} \end{pmatrix} = \begin{pmatrix} O(1) & O(1) \\ O\left(\dfrac{1}{\sqrt{v}}\right) & O\left(\dfrac{1}{\sqrt{v}}\right) \end{pmatrix} \tag{7.2b}$$

Therefore, at the thermodynamic limit ($v \to \infty$) required for the observatory subsystems [9,12], the transformation matrix (Eq. (7.2b)) is rank 1. This means that there is no transformation possible to form any basis sets that include intensive variables at the thermodynamic limit. In Appendix B, we have carried out a similar order-of-magnitude analysis for the statistical variable transformation underlying the calculation of $\langle \delta P\delta P\rangle$ and $\langle \delta T\delta T\rangle$ for a single component solution.

Let us apply our method for evaluating the transformation matrix, based on the postulate of invariant concentration and its fluctuation, to Eq. (7.1). The invariance relationships are

$$\frac{n_1}{v_{\{P\}}} = \frac{n_{1\{v\}}}{v} \tag{7.3a}$$

$$\frac{n_2}{v_{\{P\}}} = \frac{n_{2\{v\}}}{v} \tag{7.3b}$$

$$\frac{n_{2\{\mu_2\}}}{n_{1\{\mu_2\}}} = \frac{n_2}{n_{1\{n_2\}}} \tag{7.3c}$$

through which we obtain

$$\begin{pmatrix} \frac{\partial v_{\{P\}}}{\partial n_{1\{v\}}} & \frac{\partial v_{\{P\}}}{\partial n_{2\{v\}}} \\ \sqrt{\langle v\rangle_{\{P\}}}\frac{\partial \mu_{2\{P\}}}{\partial n_{1\{v\}}} & \sqrt{\langle v\rangle_{\{P\}}}\frac{\partial \mu_{2\{P\}}}{\partial n_{2\{v\}}} \end{pmatrix} = \begin{pmatrix} -\frac{1}{c_1} & -\frac{1}{c_2} \\ -\frac{\sqrt{\langle v\rangle_{\{P\}}}}{c_1}\frac{\partial \mu_{2\{P\}}}{\partial v_{\{P\}}} & -\frac{\sqrt{\langle v\rangle_{\{P\}}}}{c_2}\frac{\partial \mu_{2\{P\}}}{\partial v_{\{P\}}} \end{pmatrix} \tag{7.4a}$$

To derive Eq. (7.4a), we have carried out the following expansions and retained their leading terms:

$$\frac{\partial v_{\{P\}}}{\partial n_{1\{v\}}} = -\frac{1}{c_1}\left(1 - \frac{2\delta n_1}{n_1}\right) + o\left(\frac{1}{\sqrt{v}}\right) \tag{7.4b}$$

$$\frac{\partial v_{\{P\}}}{\partial n_{2\{v\}}} = -\frac{1}{c_2}\left(1 - \frac{2\delta n_2}{n_2}\right) + o\left(\frac{1}{\sqrt{v}}\right) \tag{7.3c}$$

$$\sqrt{\langle v\rangle_{\{P\}}}\frac{\partial \mu_{2\{P\}}}{\partial n_{i\{v\}}} = \frac{\sqrt{\langle v\rangle_{\{P\}}}}{c_i}\frac{\partial \mu_{2\{P\}}}{\partial v_{\{P\}}}\left(1 + \frac{2\delta v}{v}\right) + o\left(\frac{1}{v}\right) \tag{7.3d}$$

At the thermodynamic limit, the rank of Eq. (7.4a) reduces 1, because the second-row elements are both $O\left(\frac{1}{\sqrt{v}}\right)$, compared to the first row elements which are $O(1)$.

Thus, at the thermodynamic limit, statistical variables must be extensive in the quasi-thermodynamic formalism. However, for smaller systems, intensive variables may also be statistical variables. Yet it is important to recognize that the quadratic form of fluctuation is founded upon the exchange of matter and/or entropy between the observatory subsystem and the reservoir, as well as the conservation of volume under isobaric conditions. Note that these conditions (written down only for extensive variables) alongside the small size of the observatory subsystem are the key for δR to take a quadratic form of the variables pertaining only to the subsystem (Appendix A).

8. Conclusion

According to the fluctuation solution theory, interactions in multiple component solutions are quantified via number correlations using an open isochoric subsystem [6–8]. A considerable mathematical complication arises when calculating such correlations from experiments, due to the need for converting the experimental data measured under isobaric conditions to the grand canonical ensemble, usually through a series of cumbersome thermodynamic variable transformations [6–8]. Extending the fluctuation theory to cooperative solubilization (which requires multiple-body correlations) [22–26] has required even more complicated calculus for thermodynamic variable transformation. Recently, we have proposed a significantly simpler alternative, i.e., a direct algebraic transformation of variances and number correlations between ensembles [19]. Our statistical variable transformation was demonstrated to be equivalent to the conventional Kirkwood-Buff theory [19], to lead to a significant simplification of cooperative solubilization theory [19,26], and to be applicable even for mesoscopic systems [27], yet the precise relationship between the two transformations remained unclear.

The present paper has established a geometrical foundation underlying the equivalence between the statistical and thermodynamic variable transformation. Based on the quasi-thermodynamic fluctuation theory [21,36,38–40] and the postulate that concentration and its fluctuation is invariant under the change of ensembles [19], we have proven that the minimum work accompanying particle exchange is also invariant. Consequently, ensembles can be changed just like the change of basis in the quadratic form of fluctuation, which transforms the Hessian as thermodynamic variable transformation and the deviation vector (consequently, the correlation matrix) as the statistical variable transformation. We have thus shown that a geometrical elucidation of fluctuation was the reason behind the significant reduction in the calculation via statistical variable transformation.

The statistical variable transformation provides an intuitive insight into the fluctuation of intensive variables within the quasi-thermodynamic formalism, which has been debated [31,32,35,42,43]. A simple argument based on the order-of-magnitude analysis has shown that conversion from an extensive to intensive statistical variable at the thermodynamic limit leads to the reduction in rank of the transformation matrix. At the thermodynamic limit, the statistical variables within the quasi-thermodynamic formalism should therefore be exclusively extensive.

The geometrical foundation of classical thermodynamics has been recognized for a long time [33,48,49]. However, fluctuations in multiple component solutions have been studied without it, leading to mathematical complications [6–8]. Thus, the statistical variable transformation [19], proven here to be equivalent to thermodynamic variable transformation, is an efficient alternative, which is straightforward to generalize to n-component solutions in general. Even for a combination of experimental data that do not belong to the same ensemble, statistical variable transformation can be applied with a facility.

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Appendix A

To derive Eq. (2.5), δa in Eq. (2.4) was taken up to the second-order while $\delta E^{(r)}$ in Eq. (2.2) was retained only up to the first order. This can be justified by comparing the orders of magnitude. Following the notation of the main text, let v and $V^{(r)}$ be the volumes of the observatory subsystem and the reservoir, respectively, with $v \ll V^{(r)}$. Expanding Eq. (2.2) up to the second-order yields

$$\delta E^{(r)} = T^{(r)}\delta S^{(r)} + \mu_1^{(r)}\delta N_1^{(r)} + \mu_2^{(r)}\delta N_2^{(r)} + \sum_{i,j}\frac{\partial^2 E^{(r)}}{\partial N_i \partial N_j}\delta N_i^{(r)}\delta N_j^{(r)} + \sum_i \frac{\partial^2 E^{(r)}}{\partial N_i \partial S^{(r)}}\delta N_i^{(r)}\delta S^{(r)} + \frac{\partial^2 E^{(r)}}{\partial S^{(r)}\partial S^{(r)}}\delta S^{(r)}\delta S^{(r)} \tag{A.1}$$

Carrying out the order of magnitude analysis, $\frac{\partial^2 E^{(r)}}{\partial N_i \partial N_j} = O\left(\frac{1}{V^{(r)}}\right)$. However, from the number conservation relationship, $\delta N_i^{(r)} = -\delta n_i$, it follows that $\delta N_i^{(r)} = O(\sqrt{v})$. Consequently, $\delta N_i^{(r)}\delta N_j^{(r)} = O(v)$, which leads to $\frac{\partial^2 E^{(r)}}{\partial N_i \partial N_j}\delta N_i^{(r)}\delta N_j^{(r)} = O\left(\frac{v}{V^{(r)}}\right)$. Likewise, $\frac{\partial^2 E^{(r)}}{\partial N_i \partial S^{(r)}} = O\left(\frac{1}{V^{(r)}}\right)$ and $\frac{\partial^2 E^{(r)}}{\partial S^{(r)}\partial S^{(r)}} = O\left(\frac{1}{V^{(r)}}\right)$. Combining these with the entropy conservation relationship, $\delta S^{(r)} = -\delta s$, according to which $\delta S^{(r)} = O(\sqrt{v})$, we also obtain $\frac{\partial^2 E^{(r)}}{\partial N_i \partial S^{(r)}}\delta N_i^{(r)}\delta S^{(r)} = O\left(\frac{v}{V^{(r)}}\right)$ and $\frac{\partial^2 E^{(r)}}{\partial S^{(r)}\partial S^{(r)}}\delta S^{(r)}\delta S^{(r)} = O\left(\frac{v}{V^{(r)}}\right)$.

In contrast, the second-order terms in Eq. (2.5) are all $O(1)$, because $\left(\frac{\partial^2 e}{\partial n_i \delta n_j}\right) = O\left(\frac{1}{v}\right)$ and $\delta n_i \delta n_j = O(v)$. Because of $v \ll V^{(r)}$, $O\left(\frac{v}{V^{(r)}}\right)$ is lower in order than $O(1)$. Consequently, the second-order terms of Eq. (A.1) are negligible when we incorporate up to the $O(1)$ contributions in Eq. (2.5).

The same argument applies to Section 3, where we need to consider the following additional terms:

$$-P^{(r)}\delta V^{(r)} + \sum_i \frac{\partial^2 E^{(r)}}{\partial N_i \partial V^{(r)}} \delta N_i^{(r)} \delta V^{(r)} + \frac{\partial^2 E^{(r)}}{\partial S^{(r)} \partial V^{(r)}} \delta S^{(r)} \delta V^{(r)} + \frac{\partial^2 E^{(r)}}{\partial V^{(r)} \partial V^{(r)}} \delta V^{(r)} \delta V^{(r)} \tag{A.2}$$

Here we include $\delta V^{(r)} = -\delta v$ into our consideration, according to which $\delta V^{(r)} = O\left(\sqrt{v}\right)$. Repeating the same argument leads to the conclusion that Eq. (A.2) is of $O\left(\frac{v}{V^{(r)}}\right)$, which is negligible under $v \ll V^{(r)}$. The expansions in Appendix B can be done in a similar manner.

Appendix B

At the thermodynamic limit, the statistical variables for the quadratic form of fluctuation must be exclusively extensive where no intensive variables are permitted. Let us illustrate this point through the calculation of $\langle \delta P \delta P \rangle$ and $\langle \delta T \delta T \rangle$ for a single component solution, starting carefully from setting up the observatory subsystem and the reservoir that are in equilibrium, $T^{(r)} = T$ and $P^{(r)} = P$, with the conservation relationships, $\delta V^{(r)} = -\delta v$, $\delta S^{(r)} = -\delta s$. The number of particles, n, in the subsystem is kept constant. The minimum work in this system is

$$\delta R = \delta e - T\delta s + P\delta v \tag{B.1}$$

Expanding δe in Eq. (B.1) up to the second-order,

$$\delta e = T\delta s - P\delta v + \left(\frac{\partial^2 e}{\partial s^2}\right)\delta s\delta s + 2\left(\frac{\partial^2 e}{\partial s\delta v}\right)\delta s\delta v + \left(\frac{\partial^2 e}{\partial v^2}\right)\delta v\delta v \tag{B.2}$$

As before, Eqs. (B.1) and (B.2) are combined in a quadratic form, with the Hessian matrix evaluated in the following format:

$$\delta R = (\delta s \quad \delta v)_{\{n\}}\begin{pmatrix} \dfrac{\partial T}{\partial s} & \dfrac{\partial T}{\partial v} \\ -\dfrac{\partial P}{\partial s} & -\dfrac{\partial P}{\partial v} \end{pmatrix}_{\{n\}} \begin{pmatrix} \delta s \\ \delta v \end{pmatrix}_{\{n\}} \tag{B.3}$$

The quadratic form can be simplified by noting the following set of thermodynamic relationships [21,44] that correspond to the Hessian matrix in Eq. (B.3):

$$\begin{pmatrix} \delta T \\ \delta P \end{pmatrix}_{\{n\}} = \begin{pmatrix} \dfrac{\partial T}{\partial s} & \dfrac{\partial T}{\partial v} \\ \dfrac{\partial P}{\partial s} & \dfrac{\partial P}{\partial v} \end{pmatrix} \begin{pmatrix} \delta s \\ \delta v \end{pmatrix}_{\{n\}} \tag{B.4}$$

To facilitate a comparison with the extensive-to-extensive coordinate transformation, here we make the intensive deviation vectors in the same order of magnitude as the extensive, as

$$\begin{pmatrix} \sqrt{n}\delta T \\ \sqrt{n}\delta P \end{pmatrix}_{\{n\}} = \begin{pmatrix} \sqrt{n}\dfrac{\partial T}{\partial s} & \sqrt{n}\dfrac{\partial T}{\partial v} \\ \sqrt{n}\dfrac{\partial P}{\partial s} & \sqrt{n}\dfrac{\partial P}{\partial v} \end{pmatrix} \begin{pmatrix} \delta s \\ \delta v \end{pmatrix}_{\{n\}} \tag{B.5a}$$

Applying the order-of-magnitude analysis on Eq. (B.5a) shows

$$\begin{pmatrix} \sqrt{n}\dfrac{\partial T}{\partial s} & \sqrt{n}\dfrac{\partial T}{\partial v} \\ \sqrt{n}\dfrac{\partial P}{\partial s} & \sqrt{n}\dfrac{\partial P}{\partial v} \end{pmatrix} = \begin{pmatrix} O\left(\dfrac{1}{\sqrt{v}}\right) & O\left(\dfrac{1}{\sqrt{v}}\right) \\ O\left(\dfrac{1}{\sqrt{v}}\right) & O\left(\dfrac{1}{\sqrt{v}}\right) \end{pmatrix} \tag{B.5b}$$

that the transformation matrix is in fact a zero matrix at the thermodynamic limit, unlike the $O(1)$ elements for the extensive-to-extensive transformation. Consequently, at the thermodynamic limit, Eq. (B.5) ceases to be a statistical variable transformation that preserves dimensionality.

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