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Implicit function theorem and Jacobians in solvation and adsorption

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Abstract

The use of Jacobians in chemical thermodynamics has focused chiefly on explicit functions. We generalize this powerful method to incorporate implicit functions. Considering a slight deviation from equilibrium, governed by the Gibbs-Duhem equations, can simplify the theories of preferential solvation and adsorption significantly. Since these deviations are zero at equilibrium, the implicit function theorem can be applied by postulating their differentiability. A generalization to multiple component solutions is straightforward by virtue of Jacobians and the implicit function theorem.

1. Introduction

In equilibrium thermodynamics, the stability of a reaction or a system depends on a set of thermodynamic variables. Experiments carried out in one set of thermodynamic variables often need to be converted to another [1,2]. This is carried out via variable changes in partial derivatives, which can be quite tedious and lengthy [3,4]. However, the use of Jacobians has eased the calculations significantly [5–9].

The application of the Jacobian method has so far been limited chiefly to explicit functions and the conversions of variables in between [5–9]. However, the thermodynamics of chemical equilibria essentially involves implicit functions [10–13]. For example, consider two phases in equilibrium. The discussion of phase equilibria starts by considering the difference in the chemical potential of each species, $\Delta\mu_i$, between the two phases (See Appendix A). Phase equilibrium corresponds to $\Delta\mu_i = 0$; however, allowing $\Delta\mu_i$ to deviate from equilibrium is crucial in deriving the Clausius equation, Clausius-Clapeyron equation, and their multiple-component generalizations such as the Gibbs-Konovalov theorem [10–13], as well as in interpreting conformational phase diagrams via the fluctuation solution theory [14–17]. The key is to write down the derivatives of $\Delta\mu_i$ with respect to temperature, pressure, and composition, for which the differentiability of $\Delta\mu_i$ around zero is essential [10–17]. Thus, the implicit function theorem [18,19] is the key to relate the phase diagram to these derivatives (see Appendix A). In this paper, we will generalize this lesson to solvation and adsorption in solvent mixtures.

Thermodynamic variable conversions have made the statistical thermodynamic approach to solvation and adsorption in solvent mixtures complicated with significant demand for calculations

[20–28]. Despite this, classical concepts in biomolecular solvation (such as preferential solvation [29,30], pressure [31] and volumetric [32] analyses), based originally on a purely phenomenological basis (such as stoichiometric binding or exchange models [33–35]), have been reformulated rigorously via fluctuation theory [36–40]. They became an essential tool for biomolecular stability [36,37,41–43] and hydrotropic solubilization [44–48], applicable to small molecules, macromolecular assemblies and nanoparticles alike [16,49–52]. (Biomolecular stability, for example, can be understood from the difference in preferential solvation between folded and denatured conformations of a protein [37,53,54].) Such an approach has also been extended to the analysis of adsorption isotherm [55] and solution in mesoscale confinement [56].

Here we demonstrate that a slight deviation from equilibrium, when postulated to be differentiable, can simplify the theories of preferential solvation and adsorption significantly via implicit function theorem. Calculations on preferential solvation and adsorption isotherm can be simplified significantly via Jacobians and rules of determinant evaluation, with straightforward generalization to multiple-component solutions.

2. Preferential solvation and adsorption under constant temperature or constant pressure

2.1. Setup

Consider a two-component mixture consisting of species 1 and 2 at temperature T and pressure P . We keep the temperature constant throughout. Through Legendre transformation of the Gibbs free

energy $G(T, P, N_1, N_2)$, where N_i is the number of species i , let us introduce a thermodynamic function

$$D(T, P, \mu_1, \mu_2) = G - N_1\mu_1 - N_2\mu_2 \quad (1)$$

where μ_i is the chemical potential of the species i . For a macroscopic system at equilibrium, $D(T, P, \mu_1, \mu_2) = 0$ must hold true. However, when $D(T, P, \mu_1, \mu_2) \neq 0$, the system is not at equilibrium, and the chemical potentials, μ_1 and μ_2 , are allowed to deviate from their equilibrium values. Eq. (1) can be expressed also in a differential form

$$dD = VdP - SdT - N_1d\mu_1 - N_2d\mu_2 \quad (2a)$$

At equilibrium, $dD = 0$, when Eq. (2a) reduces to the Gibbs-Duhem equation. However, when the system is not at equilibrium, $dD \neq 0$, which means that the system violates the Gibbs-Duhem equation. Let us also consider an inhomogeneous solution with a solute whose centre-of-mass is fixed at the origin [36,46,57]. Here, we can also define the corresponding function, $D^*(T, P, \mu_1, \mu_2, \mu_u^*)$, where μ_u^* is the chemical potential of the fixed solute, via Legendre transform. μ_u^* is commonly referred to as the ‘‘pseudo chemical potential’’ and adopted widely as the free energy to quantify the solvation effects [36,43,58,59]. The excess solvation numbers and the Kirkwood-Buff integrals are routinely determined from how μ_u^* changes with μ_1 or μ_2 [36,43,57–59]. We therefore adopt μ_u^* in our approach to preferential solvation. Using this quantity, the differential expression for the inhomogeneous solution is

$$dD^* = V^*dP - S^*dT - N_1^*d\mu_1 - N_2^*d\mu_2 - N_u^*d\mu_u^* \quad (2b)$$

where the asterisks were introduced to signify the quantities for the inhomogeneous solution. For a macroscopic system in equilibrium, $D^*(T, P, \mu_1, \mu_2, \mu_u^*) = 0$ must hold true. Since our goal is to quantify the effect of the solute on N_i as the measure of interaction with the solute, the volume of

the inhomogeneous solution is chosen to be equal to that of the bulk solution, such that $V^* = V$ [46]. From Eqs. (1) and (2), we obtain

$$\frac{\partial D}{\partial \mu_1} = -N_1 \quad \frac{\partial D}{\partial \mu_2} = -N_2 \quad \frac{\partial D}{\partial \mu_u^*} = 0 \quad \frac{\partial D}{\partial P} = V \quad (3a)$$

$$\frac{\partial D^*}{\partial \mu_1} = -N_1^* \quad \frac{\partial D^*}{\partial \mu_2} = -N_2^* \quad \frac{\partial D^*}{\partial \mu_u^*} = -N_u^* \quad \frac{\partial D^*}{\partial P} = V \quad (3b)$$

We could derive Eqs. (3) by considering $D(T, P, \mu_1, \mu_2, \mu_u^*)$ and $D^*(T, P, \mu_1, \mu_2, \mu_u^*)$ slightly off equilibrium and postulated that they are differentiable. Although Eq. (2a) shows that D is a function of T , P , μ_1 , and μ_2 , we write its dependence further on μ_u^* in Eq (3a). Actually, the third equation of Eq (3a) means that D does not depend on μ_u^* . By writing D in the form of $D(T, P, \mu_1, \mu_2, \mu_u^*)$, D and D^* can be treated in a parallel manner in the following.

The derivatives in Eq. (3) were not taken while the values of μ_i , μ_u^* and P were restricted to maintain equilibrium. μ_i , μ_u^* and P deviate from their equilibrium values when $D(T, P, \mu_1, \mu_2, \mu_u^*)$ and $D^*(T, P, \mu_1, \mu_2, \mu_u^*)$ are not zero, as emphasized before. Therefore, Eq. (3) does not lead to an apparent paradox, i.e., the existence of extensive $D(T, P, \mu_1, \mu_2, \mu_u^*)$ and $D^*(T, P, \mu_1, \mu_2, \mu_u^*)$ that are the functions exclusively of intensive variables. N_i , N_i^* and V recover their extensive nature only at equilibrium under $D(T, P, \mu_1, \mu_2, \mu_u^*) = D^*(T, P, \mu_1, \mu_2, \mu_u^*) = 0$.

The number of independent variables of the functions D and D^* should agree with the degrees of freedom at equilibrium (even though the independent variables are allowed to deviate from their values at equilibrium). According to the Gibbs phase rule, there are three independent variables for the homogeneous solution at equilibrium. For the inhomogeneous solution, the number of independent variables at equilibrium is also three, because the fixed solute is treated as an external field on the solution in the inhomogeneous solution theory [60,61]. Accordingly, there are three

independent variables in $(T, P, \mu_1, \mu_2, \mu_u^*)$ while the remaining two are dependent on the three. Such a conclusion on the number of independent variables is incorporated already in the implicit function theorem: on a submanifold Σ in $(T, P, \mu_1, \mu_2, \mu_u^*)$ -space, on which $D(T, P, \mu_1, \mu_2, \mu_u^*) = D^*(T, P, \mu_1, \mu_2, \mu_u^*) = 0$, the number of independent variables is three, and the two remaining variables are uniquely determined by the others.

2.2. Preferential solvation under constant temperature

Our goal is to derive basic thermodynamic relationships for preferential solvation of a solute in a two-component solvent mixture. Such relationships are dependent on thermodynamic variables specified by different experimental conditions; converting from one set of conditions to another requires thermodynamic variable conversion which may be cumbersome [57]. We will demonstrate here that implicit function theorem facilitates not only the derivation of preferential solvation theory but also thermodynamic variable conversion.

Here we consider a binary solvent mixture in a single phase. To conform to a common experimental practice [40,57], under constant temperature, let us choose μ_2 and P as the independent variables while μ_u^* and μ_1 are the functions of μ_2 and P . The independent variables are allowed deviate slightly from their equilibrium values. We express this emphatically as $(\mu_2, P; \mu_1, \mu_u^*)$. At equilibrium, i.e., $D(\mu_2, P; \mu_1, \mu_u^*) = D^*(\mu_2, P; \mu_1, \mu_u^*) = 0$, the implicit function theorem [18,19] can be applied. With the help of Eq. (3) to evaluate the partial derivatives, we obtain the four thermodynamic relationships in total. The first is

$$\left(\frac{\partial \mu_u^*}{\partial \mu_2}\right)_P = -\frac{\frac{\partial(D, D^*)}{\partial(\mu_1, \mu_2)}}{\frac{\partial(D, D^*)}{\partial(\mu_1, \mu_u^*)}} = -\frac{\frac{\partial D}{\partial \mu_1} \frac{\partial D^*}{\partial \mu_2} - \frac{\partial D}{\partial \mu_2} \frac{\partial D^*}{\partial \mu_1}}{\frac{\partial D}{\partial \mu_1} \frac{\partial D^*}{\partial \mu_u^*} - \frac{\partial D}{\partial \mu_u^*} \frac{\partial D^*}{\partial \mu_1}} = -\frac{N_2^* - N_2}{N_u^*} + \frac{N_2 N_1^* - N_1}{N_1 N_u^*} \quad (4)$$

where $\frac{\partial(D, D^*)}{\partial(\mu_1, \mu_2)}$ and $\frac{\partial(D, D^*)}{\partial(\mu_1, \mu_u^*)}$ are Jacobians, defined in terms of partial derivatives, as has been shown in the second equality in Eq. (4). Eq. (4) is indeed the well-known relationship that links preferential solvation (l.h.s.) to the excess solvation numbers of species 1 and 2 (r.h.s.). Note that the standard application of the Jacobian based on explicit function relationships alone, starting from $\left(\frac{\partial \mu_u^*}{\partial \mu_2}\right)_P = \frac{\partial(\mu_u^*, P)}{\partial(\mu_2, P)}$, does not lead directly to excess numbers via Jacobian operations alone; the Gibbs-Duhem equations have been incorporated to the implicit function theorem (Eq. (4)) but not in the Jacobian calculation rules that deal with explicit function relationships. The implicit function theorem with differentiable D and D^* linked $\left(\frac{\partial \mu_u^*}{\partial \mu_2}\right)_P$ to Jacobians and shortened the derivation significantly.

Thus, the differentiable D and D^* are a useful device to incorporate the Gibbs-Duhem relationships into Jacobians. The second thermodynamic relationship is

$$\left(\frac{\partial \mu_u^*}{\partial P}\right)_{\mu_2} = -\frac{\frac{\partial(D, D^*)}{\partial(\mu_1, P)}}{\frac{\partial(D, D^*)}{\partial(\mu_1, \mu_u^*)}} = -\frac{\frac{\partial D}{\partial \mu_1} \frac{\partial D^*}{\partial P} - \frac{\partial D}{\partial P} \frac{\partial D^*}{\partial \mu_1}}{\frac{\partial D}{\partial \mu_1} \frac{\partial D^*}{\partial \mu_u^*} - \frac{\partial D}{\partial \mu_u^*} \frac{\partial D^*}{\partial \mu_1}} = -\frac{V N_1^* - N_1}{N_1 N_u^*} \quad (5)$$

where the partial derivative in the l.h.s. was taken under constant μ_2 . Eq. (5) can be linked to a better-known relationship via variable conversion, this time, using the standard Jacobian approach

$$\left(\frac{\partial \mu_u^*}{\partial P}\right)_{\mu_2} = \frac{\partial(\mu_u^*, \mu_2)}{\partial(P, \mu_2)} = \frac{\frac{\partial(\mu_u^*, \mu_2)}{\partial\left(P, \frac{N_2}{N_1}\right)}}{\frac{\partial(P, \mu_2)}{\partial\left(P, \frac{N_2}{N_1}\right)}} = \left(\frac{\partial \mu_u^*}{\partial P}\right)_{\frac{N_2}{N_1}} - \left(\frac{\partial \mu_u^*}{\partial \mu_2}\right)_P \left(\frac{\partial \mu_2}{\partial P}\right)_{\frac{N_2}{N_1}} \quad (6)$$

which, with the help of the partial molar volume V_i of the species i and its relationship to the total volume, $V = N_1 V_1 + N_2 V_2$, yields

$$\left(\frac{\partial \mu_u^*}{\partial P}\right)_{\frac{N_2}{N_1}} = -V_1 \frac{N_1^* - N_1}{N_u^*} - V_2 \frac{N_2^* - N_2}{N_u^*} \quad (7)$$

This is a well-known relationship between volumetric measurement and excess numbers. Note that the same partial derivative, Eqs. (5) and (6), can be expressed in the two different Jacobian expressions: Eq. (5) incorporates the implicit Gibbs-Duhem relationships whereas Eq. (6) only concerns explicit function relationships.

The implicit function theorem yields not only the relationships regarding excess numbers but also bulk solvent phases. There is no need to consider these two classes of relationships any longer.

To demonstrate this, the third relationship derived from the implicit function theorem is

$$\left(\frac{\partial \mu_1}{\partial \mu_2}\right)_P = -\frac{\frac{\partial(D, D^*)}{\partial(\mu_2, \mu_u^*)}}{\frac{\partial(D, D^*)}{\partial(\mu_1, \mu_u^*)}} = -\frac{\frac{\partial D}{\partial \mu_2} \frac{\partial D^*}{\partial \mu_u^*} - \frac{\partial D}{\partial \mu_u^*} \frac{\partial D^*}{\partial \mu_2}}{\frac{\partial D}{\partial \mu_1} \frac{\partial D^*}{\partial \mu_u^*} - \frac{\partial D}{\partial \mu_u^*} \frac{\partial D^*}{\partial \mu_1}} = -\frac{N_2}{N_1} \quad (8)$$

Note that all the terms containing N_u^* vanish or cancel out automatically because D does not depend on μ_u^* . This is how a relationship between chemical potentials in isothermal-isobaric bulk solution was derived. The final relationship

$$\left(\frac{\partial \mu_1}{\partial P}\right)_{\mu_2} = -\frac{\frac{\partial(D, D^*)}{\partial(P, \mu_u^*)}}{\frac{\partial(D, D^*)}{\partial(\mu_1, \mu_u^*)}} = -\frac{\frac{\partial D}{\partial P} \frac{\partial D^*}{\partial \mu_u^*} - \frac{\partial D}{\partial \mu_u^*} \frac{\partial D^*}{\partial P}}{\frac{\partial D}{\partial \mu_1} \frac{\partial D^*}{\partial \mu_u^*} - \frac{\partial D}{\partial \mu_u^*} \frac{\partial D^*}{\partial \mu_1}} = -\frac{V}{N_1} \quad (9)$$

is also a property of the bulk solution under constant μ_2 and T .

We have thus shown that the Jacobian method in chemical thermodynamics can be expanded to incorporate the Gibbs-Duhem relationship via the implicit function theorem, leading to simpler calculations for solvation and bulk properties of a solution.

2.3. Preferential solvation through a semi-permeable membrane under constant temperature

Here we demonstrate that our approach significantly facilitates thermodynamic variable conversion. We demonstrate this through the several options for measuring preferential solvation that refer to different thermodynamic conditions; solubility is measured under constant P whereas dialysis and ultracentrifugation are measured under constant μ_1 [40,57]. Hence a conversion between $\left(\frac{\partial\mu_u^*}{\partial\mu_2}\right)_P$ and $\left(\frac{\partial\mu_u^*}{\partial\mu_2}\right)_{\mu_1}$ exemplifies the thermodynamic variable conversion required in the statistical thermodynamics of solvation. This conversion can be carried out using the standard Jacobian approach, starting from the Jacobian expression, followed by a division by $\partial(\mu_2, \mu_1)$

$$\left(\frac{\partial\mu_u^*}{\partial\mu_2}\right)_P = \frac{\partial(\mu_u^*, P)}{\partial(\mu_2, P)} = \frac{\frac{\partial(\mu_u^*, P)}{\partial(\mu_2, \mu_1)}}{\frac{\partial(\mu_2, P)}{\partial(\mu_2, \mu_1)}} \quad (10a)$$

Opening the Jacobians yield

$$\frac{\frac{\partial(\mu_u^*, P)}{\partial(\mu_2, \mu_1)}}{\frac{\partial(\mu_2, P)}{\partial(\mu_2, \mu_1)}} = \frac{\left(\frac{\partial\mu_u^*}{\partial\mu_2}\right)_{\mu_1} \left(\frac{\partial P}{\partial\mu_1}\right)_{\mu_2} - \left(\frac{\partial\mu_u^*}{\partial\mu_1}\right)_{\mu_2} \left(\frac{\partial P}{\partial\mu_2}\right)_{\mu_1}}{\left(\frac{\partial P}{\partial\mu_1}\right)_{\mu_2}} \quad (10b)$$

$$= \left(\frac{\partial\mu_u^*}{\partial\mu_2}\right)_{\mu_1} - \left(\frac{\partial\mu_u^*}{\partial\mu_1}\right)_{\mu_2} \left(\frac{\partial P}{\partial\mu_2}\right)_{\mu_1} \left(\frac{\partial\mu_1}{\partial P}\right)_{\mu_2}$$

Then, the use of the chain rule, $\left(\frac{\partial P}{\partial\mu_2}\right)_{\mu_1} \left(\frac{\partial\mu_1}{\partial P}\right)_{\mu_2} \left(\frac{\partial\mu_2}{\partial\mu_1}\right)_P = -1$ yields

$$\left(\frac{\partial\mu_u^*}{\partial\mu_2}\right)_P = \left(\frac{\partial\mu_u^*}{\partial\mu_2}\right)_{\mu_1} + \left(\frac{\partial\mu_u^*}{\partial\mu_1}\right)_{\mu_2} \left(\frac{\partial\mu_1}{\partial\mu_2}\right)_P \quad (10c)$$

However, both $\left(\frac{\partial\mu_u^*}{\partial\mu_1}\right)_{\mu_2}$ and $\left(\frac{\partial\mu_1}{\partial\mu_2}\right)_P$ still need to be evaluated. For this purpose, the standard approach is to go back to the pair of the Gibbs-Duhem equations (Eqs. (2a) and (2b) at $D = D^* = 0$) and evaluate the partial derivatives. The lesson from this lengthy derivation process is twofold: (i) the explicit function relationships alone are insufficient to reach the final result and (ii) the Gibbs-Duhem equations must come in to evaluate the remaining partial derivatives.

Simplification comes from the implicit function theorem. Let us choose μ_1 and μ_2 as the independent variables; P and μ_u^* are now the functions of μ_1 and μ_2 . Let us express this choice explicitly as $(\mu_1, \mu_2; P, \mu_u^*)$. Now we allow μ_1 and μ_2 to deviate from their equilibrium values. At equilibrium, $D(\mu_1, \mu_2; P, \mu_u^*) = D^*(\mu_1, \mu_2; P, \mu_u^*)$. The application of the implicit function theorem, with the partial derivatives in Eq. (3), yields

$$\left(\frac{\partial\mu_u^*}{\partial\mu_2}\right)_{\mu_1} = -\frac{\frac{\partial(D, D^*)}{\partial(P, \mu_2)}}{\frac{\partial(D, D^*)}{\partial(P, \mu_u^*)}} = -\frac{\frac{\partial D}{\partial P} \frac{\partial D^*}{\partial\mu_2} - \frac{\partial D}{\partial\mu_2} \frac{\partial D^*}{\partial P}}{\frac{\partial D}{\partial P} \frac{\partial D^*}{\partial\mu_u^*} - \frac{\partial D}{\partial\mu_u^*} \frac{\partial D^*}{\partial P}} = -\frac{N_2^* - N_2}{N_u^*} \quad (11)$$

in a single step. This is a well-known equation for dialysis equilibrium.

Implicit function theorem, with the help of Eq. (3), provides 4 relationships. However, because of the symmetry with respect to the exchange of indexes, there are essentially 2 relationships. The second relationship,

$$\left(\frac{\partial P}{\partial \mu_2}\right)_{\mu_1} = -\frac{\frac{\partial(D, D^*)}{\partial(\mu_2, \mu_u^*)}}{\frac{\partial(D, D^*)}{\partial(P, \mu_u^*)}} = -\frac{\frac{\partial D}{\partial \mu_2} \frac{\partial D^*}{\partial \mu_u^*} - \frac{\partial D}{\partial \mu_u^*} \frac{\partial D^*}{\partial \mu_2}}{\frac{\partial D}{\partial P} \frac{\partial D^*}{\partial \mu_u^*} - \frac{\partial D}{\partial \mu_u^*} \frac{\partial D^*}{\partial P}} = -\frac{N_2}{V} \quad (12a)$$

is a bulk-phase relationship; there was a cancellation of terms involving N_u^* . Eq. (12a) is essentially the bulk-phase osmotic pressure of the species 2. This can be seen easily by a straightforward transformation

$$\left(\frac{\partial P}{\partial c_2}\right)_{\mu_1} = \left(\frac{\partial P}{\partial \mu_2}\right)_{\mu_1} \left(\frac{\partial \mu_2}{\partial c_2}\right)_{\mu_1} = -\left(\frac{\partial \mu_2}{\partial \ln c_2}\right)_{\mu_1} \quad (12b)$$

Thus, we have demonstrated here that the application of the implicit function theorem on the Gibbs-Duhem equations significantly facilitates thermodynamic variable conversion.

2.4. Adsorption isotherm under constant temperature

We have demonstrated above that thermodynamic variable conversion can be facilitated significantly by the implicit function theorem. This approach can be applied straightforwardly to the adsorption isotherm at an interface. Consider a system composed of two species ($i = 1$ and 2) that form an interface between two phases (I and II). Here, the entire system with the interface is denoted by $*$. To quantify the surface effect, we also need the reference systems, namely I and II as bulk phases without the interfacial effect. We introduce three functions that describe slight

deviations from equilibrium. The first is for the entire system with the interface, $D^* = G - N_1^* \mu_1 - N_2^* \mu_2 - A\gamma$. Its differential form is

$$dD^* = V^* dP - S^* dT - A d\gamma - N_1^* d\mu_1 - N_2^* d\mu_2 \quad (13a)$$

The remaining two are for the bulk reference phases *I* and *II*, D^I and D^{II} , expressed in differential forms, as

$$dD^I = V^I dP - S^I dT - N_1^I d\mu_1 - N_2^I d\mu_2 \quad (13b)$$

$$dD^{II} = V^{II} dP - S^{II} dT - N_1^{II} d\mu_1 - N_2^{II} d\mu_2 \quad (13c)$$

Note that we introduce the conservation of volume

$$V^* - V^I - V^{II} = 0 \quad (13d)$$

and the surface excess of species *i* as

$$N_i^e = N_i^* - N_i^I - N_i^{II} \quad (13e)$$

Most importantly, we postulate that D , D^I and D^{II} are all differentiable.

Let us first designate the independent variables and dependent variables at equilibrium. There are two independent variables in the system. This can be justified in two ways. The first is from the equilibrium condition: on a submanifold Σ in a $(T, P, \mu_1, \mu_2, \gamma)$ -space, $D(T, P, \mu_1, \mu_2, \gamma) = D^I(T, P, \mu_1, \mu_2, \gamma) = D^{II}(T, P, \mu_1, \mu_2, \gamma) = 0$ as the equilibrium condition shows that there are two independent variables while three others are determined uniquely by the two independent variables. This matches our second justification from the degrees of freedom at equilibrium. There are 2 components in the system that form 2 phases. According to the Gibbs phase rule, there are 2 degrees of freedom. Let μ_2 and T be the independent variables and μ_1 , P and γ be the functions of μ_2 and T . This is expressed emphatically as $(\mu_2, T; \mu_1, P, \gamma)$. Now we allow the variables, μ_2 and T , to deviate slightly from their equilibrium values. Applying the implicit function theory for the

equilibrium condition, $D^*(\mu_2, T; \mu_1, P, \gamma) = D^I(\mu_2, T; \mu_1, P, \gamma) = D^{II}(\mu_2, T; \mu_1, P, \gamma) = 0$, the most important relationship, under constant temperature, is

$$\left(\frac{\partial\gamma}{\partial\mu_2}\right)_T = -\frac{\frac{\partial(D^*, D^I, D^{II})}{\partial(\mu_1, P, \mu_2)}}{\frac{\partial(D^*, D^I, D^{II})}{\partial(\mu_1, P, \gamma)}} = -\frac{\begin{vmatrix} \frac{\partial D^*}{\partial\mu_1} & \frac{\partial D^*}{\partial P} & \frac{\partial D^*}{\partial\mu_2} \\ \frac{\partial D^I}{\partial\mu_1} & \frac{\partial D^I}{\partial P} & \frac{\partial D^I}{\partial\mu_2} \\ \frac{\partial D^{II}}{\partial\mu_1} & \frac{\partial D^{II}}{\partial P} & \frac{\partial D^{II}}{\partial\mu_2} \end{vmatrix}}{\begin{vmatrix} \frac{\partial D^*}{\partial\mu_1} & \frac{\partial D^*}{\partial P} & \frac{\partial D^*}{\partial\gamma} \\ \frac{\partial D^I}{\partial\mu_1} & \frac{\partial D^I}{\partial P} & \frac{\partial D^I}{\partial\gamma} \\ \frac{\partial D^{II}}{\partial\mu_1} & \frac{\partial D^{II}}{\partial P} & \frac{\partial D^{II}}{\partial\gamma} \end{vmatrix}} \quad (14)$$

With the help of Eqs. (13a)–(13c), we can evaluate the partial derivatives in Eq. (14). Using Eqs. (13d) and (13e), together with well-known procedures of determinant operations, we can simplify the determinants,

$$\begin{vmatrix} -N_1^* & V^* & -N_2^* \\ -N_1^I & V^I & -N_2^I \\ -N_1^{II} & V^{II} & -N_2^{II} \end{vmatrix} = \frac{\begin{vmatrix} -N_1^e & 0 & -N_2^e \\ -N_1^I & V^I & -N_2^I \\ -N_1^{II} & V^{II} & -N_2^{II} \end{vmatrix}}{\begin{vmatrix} -N_1^* & V^* & A \\ -N_1^I & V^I & 0 \\ -N_1^{II} & V^{II} & 0 \end{vmatrix}} = \frac{\begin{vmatrix} -N_1^e & 0 & -N_2^e \\ -c_1^I & 1 & -c_2^I \\ -c_1^{II} & 1 & -c_2^{II} \end{vmatrix}}{\begin{vmatrix} -N_1^e & 0 & A \\ -c_1^I & 1 & 0 \\ -c_1^{II} & 1 & 0 \end{vmatrix}} \quad (15)$$

which automatically yields

$$\left(\frac{\partial\gamma}{\partial\mu_2}\right)_T = -\left[\frac{N_2^e}{A} - \frac{c_2^{II} - c_1^I N_1^e}{c_1^{II} - c_1^I A}\right] \quad (16)$$

namely, the Gibbs adsorption isotherm.

Note that the three implicit functions used to derive Eq. (16) were reduced to Jacobians and determinant computations by virtue of the implicit function theorem. For more discussion on solvation and adsorption under isobaric conditions, see Appendices B and C.

3. Generalization and foundation

3.1. Generalization to multiple component systems

As the number of components increases, the rank of simultaneous equations increases for preferential solvation and adsorption. Relying solely on explicit function relationships with the ad-hoc incorporation of the Gibbs-Duhem equations makes the calculation increasingly more difficult even than the case of a 2-component solution in Section 2.3. However, the implicit function theorem can facilitate the generalization into multiple components. To demonstrate this, let us first consider an n -component solution in a single phase. On a submanifold Σ in a $(T, P, \{\mu\}, \mu_u^*)$ -space, where $\{\mu\} = \mu_1, \dots, \mu_n$, the equilibrium condition $D(T, P, \{\mu\}, \mu_u^*) = D^*(T, P, \{\mu\}, \mu_u^*) = 0$ leads to the existence of $n + 1$ independent variables while two others are determined uniquely by the independent variables. This matches the degrees of freedom at equilibrium. From here onwards, we consider the isothermal condition because it is most useful. Hence there are n degrees of freedom to be chosen out of $n + 2$ candidates, namely, $(\mu_1, \mu_2, \dots, \mu_n), P$ and μ_u^* . To facilitate our discussion, let us introduce $\mu_{n+1} = P$ as a shorthand notation. The 2 dependent variables we have chosen are μ_u^* and μ_v . Here we choose μ_σ as the variable with respect to which differentiation will be carried out, and the rest of the variables are shorthanded as $\{\mu\}$. With the above designation of independent and dependent variables, and allowing the independent variables to deviate slightly from their equilibrium values, the equilibrium conditions can be written down as

$$D(\mu_\sigma, \{\mu\}; \mu_v, \mu_u^*) = 0 \quad (18a)$$

$$D^*(\mu_\sigma, \{\mu\}; \mu_v, \mu_u^*) = 0 \quad (18b)$$

Our goal is to evaluate the following n excess numbers:

$$N_i^e = \frac{N_i^* - N_i}{N_u} \quad (19)$$

Under these constraints, the implicit function theorem yields the n independent equations from

$$\left(\frac{\partial \mu_u^*}{\partial \mu_\sigma} \right)_{\{\mu\}} = - \frac{\frac{\partial(D, D^*)}{\partial(\mu_\nu, \mu_\sigma)}}{\frac{\partial(D, D^*)}{\partial(\mu_\nu, \mu_u^*)}} \quad (20a)$$

There are also n independent equations for the bulk phase from

$$\left(\frac{\partial \mu_\nu}{\partial \mu_\sigma} \right)_{\{\mu\}} = - \frac{\frac{\partial(D, D^*)}{\partial(\mu_\sigma, \mu_u^*)}}{\frac{\partial(D, D^*)}{\partial(\mu_\nu, \mu_u^*)}} \quad (20b)$$

All the necessary relationships can be obtained automatically via the determinant rules.

For adsorption isotherm, we consider, on a submanifold Σ in a $(T, \{\mu\}, \gamma)$ -space, where $\{\mu\} = \mu_1, \dots, \mu_n$, the equilibrium condition $D(T, \{\mu\}, \gamma) = D^I(T, \{\mu\}, \gamma) = D^{II}(T, \{\mu\}, \gamma) = 0$ leads to the existence of n independent variables while two others are determined uniquely by the independent variables. This matches the degrees of freedom at equilibrium: an n -component solution forming two phases has n degrees of freedom. Under constant temperature, the system has $n - 1$ remaining degrees of freedom. This means that not all surface excesses can be determined independently but only relative to one species, say, the principal solvent, 1. Under the above designation of independent and dependent variables, and allowing the independent variables to deviate slightly from their equilibrium values, the equilibrium conditions are written down as

$$D^*(\mu_\alpha, T, \{\mu\}; \mu_1, P, \gamma) = 0 \quad (21a)$$

$$D^I(\mu_\alpha, T, \{\mu\}; \mu_1, P, \gamma) = 0 \quad (21b)$$

$$D^{II}(\mu_\alpha, T, \{\mu\}; \mu_1, P, \gamma) = 0 \quad (21c)$$

Under this setup, the implicit function theorem yields:

$$\left(\frac{\partial \gamma}{\partial \mu_\alpha}\right)_T = -\frac{\frac{\partial(D^*, D^I, D^{II})}{\partial(\mu_1, P, \mu_\alpha)}}{\frac{\partial(D^*, D^I, D^{II})}{\partial(\mu_1, P, \gamma)}} \quad (22)$$

which consists of $n - 1$ independent relationships.

3.2. The origin of D and D^*

Allowing the Gibbs-Duhem equations to deviate slightly from equilibrium had a benefit in facilitating the calculations of preferential solvation and adsorption isotherm. With the help of the implicit function theorem, generalization to multiple component solutions was straightforward through Jacobians. The key to these advantages were the functions D and D^* for the deviations from equilibrium.

Here we show that D and D^* arise from the two sources of deviation from equilibrium. The first is the deviation of dG (where G is the Gibbs free energy from equilibrium

$$-dQ' = dG + SdT - VdP - \sum_i \mu_i dN_i \quad (23a)$$

quantified via dQ' . The second is the deviation from a relationship in equilibrium thermodynamics on the extensive nature of the Gibbs free energy in terms of its natural variables N_i , $G = \sum_i N_i \mu_i$.

To account for this, we introduce

$$dQ'' = dG - \sum_i N_i d\mu_i - \sum_i \mu_i dN_i \quad (23b)$$

as the deviation from equilibrium. Combining Eqs. (23a) and (23b), and using Eq. (2a), we obtain

$$dD = dQ'' + dQ' = SdT - VdP + \sum_i N_i d\mu_i \quad (24)$$

where equilibrium condition corresponds to $D = 0$. Thus, we have shown that D comes from the deviations from the equilibrium expression for dG (Eq. (23a)) and the extensive nature of G (Eq. (23b)). In this context, our postulate was that $Q' + Q''$ is a differentiable function of T , P and $\{\mu_i\}$. We postulated the same in inhomogeneous solutions. This postulate has been validated by a successful re-derivation of the preferential solvation theory and adsorption isotherm.

4. Conclusion

How can the preferential solvation [36,59] and adsorption [56,57,59] theories take full advantage of the Jacobian formalism [5–9] which has facilitated the variable transformation in the rest of thermodynamics? To this end, a useful lesson from phase equilibrium thermodynamics was that allowing the system to deviate slightly from equilibrium is crucial in deriving useful relationships. Inspired by this, we have considered a slight deviation from equilibrium in the Gibbs-Duhem equations. Having postulated the deviation to be differentiable, the implicit function theorem [18,19] can be applied at equilibrium, which enables facile and straightforward calculations of thermodynamic quantities and variable conversions. Linking thermodynamic measurements to excess numbers (solvation) or surface excesses (adsorption) [56,57,59] can be automated by the rules of determinant calculation. The generalization to multiple-component solutions was also demonstrated to be straightforward.

Together with the current use of the Jacobians through explicit function relationships [5–9], our new approach was demonstrated to simplify the intricate thermodynamic variable conversions

underlying the fluctuation theory. Together with our recent algebraic approach to variable conversions [62], the fluctuation approach to solvation and adsorption has been facilitated significantly.

Appendix A: Clapeyron equation and its generalizations as consequences of the implicit function theorem

Here we illustrate that the implicit function theorem is at work in thermodynamic phase equilibria. To this end, let us consider the simplest example of a pure component in the two phases, *I* and *II*. The chemical potential of a single component in one phase has 2 degrees of freedom, hence $\mu^I = \mu^I(T, P)$ and $\mu^{II} = \mu^{II}(T, P)$ [1,2]. The chemical potential difference,

$$\Delta\mu = \mu^{II} - \mu^I \quad (\text{A1})$$

is differentiable around $\Delta\mu = 0$ and can be expanded as

$$d\Delta\mu = \left(\frac{\partial\Delta\mu}{\partial P}\right)_T dP + \left(\frac{\partial\Delta\mu}{\partial T}\right)_P dT = \Delta v dP - \Delta s dT \quad (\text{A2})$$

where Δv and Δs are the partial molar volume and entropy, respectively. At $\Delta\mu = 0$, the implicit function theorem for 2 variables [18,19] yields

$$\frac{\partial P}{\partial T} = -\frac{\left(\frac{\partial\Delta\mu}{\partial T}\right)_P}{\left(\frac{\partial\Delta\mu}{\partial P}\right)_T} \quad (\text{A3})$$

which is the Clausius equation.

Generalization of the Clausius equation for multiple component solutions has played a key role in the interpretation of experimental data via the fluctuation solution theory [14–17]. We

demonstrate here that such a generalization can be carried out most straightforwardly via the implicit function theorem. As a simple example, consider a biomolecule (fixed at origin, denoted as u) which can take states I and II , in the presence of solvent components 1 and 2. A solution with the biomolecule in a state is considered to be an inhomogeneous solution which has 3 degrees of freedom. The chemical potential difference between the two states, $\Delta\mu_u^*$, can be expanded as [14–17]

$$\begin{aligned}\Delta\mu_u^* &= \left(\frac{\partial\Delta\mu_u^*}{\partial P}\right)_{T,c} dP + \left(\frac{\partial\Delta\mu_u^*}{\partial T}\right)_{P,c} dT + \left(\frac{\partial\Delta\mu_u^*}{\partial c}\right)_{P,T} dc \\ &= \Delta v_u^* dP - \Delta s_u^* dT + \left(\frac{\partial\Delta\mu_u^*}{\partial c}\right)_{P,T} dc\end{aligned}\tag{A4}$$

where Δv_u^* and Δs_u^* represent the volume and entropy changes accompanying the transition, respectively, and c is solution concentration (in a preferred unit).

Our goal is to obtain $\left(\frac{\partial\Delta\mu_u^*}{\partial c}\right)_{P,T}$ from the volumetric (Δv_u^*) and calorimetric (Δs_u^*) data. To do so, let us first consider the equilibrium condition

$$\Delta\mu_u^* = 0 \quad dP = 0\tag{A5}$$

Under this condition, we obtain a useful relationship,

$$\left(\frac{\partial T}{\partial c}\right)_P = -\frac{\frac{\partial(\Delta\mu_u^*, P)}{\partial(c, P)}}{\frac{\partial(\Delta\mu_u^*, P)}{\partial(T, P)}} = \frac{\left(\frac{\partial\Delta\mu_u^*}{\partial c}\right)_P}{\Delta s_u^*}\tag{A6}$$

through which $\left(\frac{\partial\Delta\mu_u^*}{\partial c}\right)_P$ can be calculated from calorimetry (Δs_u^*) and phase diagram $\left(\frac{\partial T}{\partial c}\right)$ [14–17].

Alternatively, under another equilibrium condition,

$$\Delta\mu_u^* = 0 \quad dT = 0 \quad (\text{A7})$$

we obtain another useful relationship, linking $\left(\frac{\partial\Delta\mu_u^*}{\partial c}\right)_P$ to volume change (Δv_u^*) and phase diagram $\left(\frac{\partial P}{\partial c}\right)_T$, as [14–17]

$$\left(\frac{\partial P}{\partial c}\right)_T = -\frac{\frac{\partial(\Delta\mu_u^*, T)}{\partial(c, T)}}{\frac{\partial(\Delta\mu_u^*, T)}{\partial(P, T)}} = -\frac{\left(\frac{\partial\Delta\mu_u^*}{\partial c}\right)_P}{\Delta v_u^*} \quad (\text{A8})$$

Alternatively, under another equilibrium condition,

$$\Delta\mu_u^* = 0 \quad dc = 0 \quad (\text{A9})$$

$$\left(\frac{\partial T}{\partial P}\right)_c = -\frac{\frac{\partial(\Delta\mu_u^*, c)}{\partial(P, c)}}{\frac{\partial(\Delta\mu_u^*, c)}{\partial(T, c)}} = \frac{\left(\frac{\partial\Delta\mu_u^*}{\partial P}\right)_c}{\Delta s_u^*} \quad (\text{A10})$$

This relationship is particularly useful for obtaining the volume change, $\Delta v_u^* = \left(\frac{\partial\Delta\mu_u^*}{\partial P}\right)_c$ (which is usually very difficult to obtain), from the more accessible data on calorimetry (Δs_u^*) and the phase diagram $\left(\frac{\partial T}{\partial P}\right)_c$ [14–17].

Appendix B: Preferential solvation and adsorption under isobaric conditions

Here we apply our new approach to the temperature dependence of solvation and adsorption under constant pressure. There are 2 degrees of remaining freedom when we keep the pressure constant. Let us choose μ_2 and T as the independent variables while μ_u^* and μ_1 are the functions of μ_2 and T . We express this emphatically as $D(\mu_2, T; \mu_1, \mu_u^*)$ and $D^*(\mu_2, T; \mu_1, \mu_u^*)$. At equilibrium, i.e., $D = D^* = 0$, the implicit function theorem can be applied. We again obtain the four thermodynamic relationships in total. The two relationships under an isobaric-isothermal condition

are identical to Eqs. (4) and (8). There are two relationships specific to the temperature dependence under constant pressure. The first is

$$\left(\frac{\partial \mu_u^*}{\partial T}\right)_{\mu_2} = -\frac{\frac{\partial(D, D^*)}{\partial(\mu_1, T)}}{\frac{\partial(D, D^*)}{\partial(\mu_1, \mu_u^*)}} = -\frac{\frac{\partial D}{\partial \mu_1} \frac{\partial D^*}{\partial T} - \frac{\partial D}{\partial T} \frac{\partial D^*}{\partial \mu_1}}{\frac{\partial \mathcal{E}}{\partial \mu_1} \frac{\partial \mathcal{E}^*}{\partial \mu_u^*} - \frac{\partial \mathcal{E}}{\partial \mu_u^*} \frac{\partial \mathcal{E}^*}{\partial \mu_1}} = -\frac{S^* - S}{N_u^*} + \frac{S}{N_1} \frac{N_1^* - N_1}{N_u^*} \quad (\text{B1})$$

expresses the temperature-dependence of solvation free energy in terms of the excess number of solvent $\frac{N_1^* - N_1}{N_u^*}$ and excess entropy $\frac{S^* - S}{N_u^*}$ around the solute. To derive Eq. (B1), we have used

$$\frac{\partial D}{\partial T} = -S \quad \frac{\partial D^*}{\partial T} = -S^* \quad (\text{B2})$$

that can be derived straightforwardly from Eq. (2). The second is

$$\left(\frac{\partial \mu_1}{\partial T}\right)_{\mu_2} = -\frac{\frac{\partial(D, D^*)}{\partial(T, \mu_u^*)}}{\frac{\partial(D, D^*)}{\partial(\mu_1, \mu_u^*)}} = -\frac{\frac{\partial D}{\partial T} \frac{\partial D^*}{\partial \mu_u^*} - \frac{\partial D}{\partial \mu_u^*} \frac{\partial D^*}{\partial T}}{\frac{\partial D}{\partial \mu_1} \frac{\partial D^*}{\partial \mu_u^*} - \frac{\partial D}{\partial \mu_u^*} \frac{\partial D^*}{\partial \mu_1}} = -\frac{S}{N_1} \quad (\text{B3})$$

is also a property of the bulk solution under constant P and μ_2 . Adsorption on isobaric conditions yields less useful results. See Appendix C for further discussion.

Appendix C: Adsorption “isobary”

For adsorption under constant *pressure*, where there are 2 degrees of freedom, we shall choose μ_2 and P be the independent variables and μ_1 , T and γ be the functions of μ_2 and P . We write this emphatically as $D^*(\mu_2, P; \mu_1, T, \gamma)$, $D^I(\mu_2, P; \mu_1, T, \gamma)$ and $D^{II}(\mu_2, P; \mu_1, T, \gamma)$, by simply swapping P and T in our discussion in Appendix B. The equilibrium condition is $D^I = D^{II} = D^* = 0$, when the implicit function theorem can be applied. Under constant *pressure*, the most important relationship is

$$\left(\frac{\partial\gamma}{\partial\mu_2}\right)_P = -\frac{\frac{\partial(D^*, D^I, D^{II})}{\partial(\mu_1, T, \mu_2)}}{\frac{\partial(D^*, D^I, D^{II})}{\partial(\mu_1, T, \gamma)}} = -\frac{\begin{vmatrix} \frac{\partial D^*}{\partial\mu_1} & \frac{\partial D^*}{\partial T} & \frac{\partial D^*}{\partial\mu_2} \\ \frac{\partial D^I}{\partial\mu_1} & \frac{\partial D^I}{\partial T} & \frac{\partial D^I}{\partial\mu_2} \\ \frac{\partial D^{II}}{\partial\mu_1} & \frac{\partial D^{II}}{\partial T} & \frac{\partial D^{II}}{\partial\mu_2} \end{vmatrix}}{\begin{vmatrix} \frac{\partial D^*}{\partial\mu_1} & \frac{\partial D^*}{\partial T} & \frac{\partial D^*}{\partial\gamma} \\ \frac{\partial D^I}{\partial\mu_1} & \frac{\partial D^I}{\partial T} & \frac{\partial D^I}{\partial\gamma} \\ \frac{\partial D^{II}}{\partial\mu_1} & \frac{\partial D^{II}}{\partial T} & \frac{\partial D^{II}}{\partial\gamma} \end{vmatrix}} \quad (\text{C1})$$

With the help of Eqs. (13a)–(13c), we can evaluate the partial derivatives in Eq. (B1). Instead of the volume conservation condition, Eq. (13d), we introduce the excess entropy,

$$S^e = S^* - S^I - S^{II} \quad (\text{C2})$$

Using Eqs. (13e) and (C2), together with well-known procedures of determinant operations, we can simplify the determinants as

$$\frac{\begin{vmatrix} -N_1^* & -S^* & -N_2^* \\ -N_1^I & -S^I & -N_2^I \\ -N_1^{II} & -S^{II} & -N_2^{II} \end{vmatrix}}{\begin{vmatrix} -N_1^* & -S^* & A \\ -N_1^I & -S^I & 0 \\ -N_1^{II} & -S^{II} & 0 \end{vmatrix}} = \frac{\begin{vmatrix} -N_1^e & -S^e & -N_2^e \\ -N_1^I & S^I & -N_2^I \\ -N_1^{II} & S^{II} & -N_2^{II} \end{vmatrix}}{\begin{vmatrix} -N_1^e & -S^e & A \\ -N_1^I & S^I & 0 \\ -N_1^{II} & S^{II} & 0 \end{vmatrix}} = -\frac{\begin{vmatrix} N_1^e & -S^e & N_2^e \\ N_1^I/S^I & 1 & N_2^I/S^I \\ N_1^{II}/S^{II} & 1 & N_2^{II}/S^{II} \end{vmatrix}}{\begin{vmatrix} N_1^e & -S^e & A \\ N_1^I/S^I & 1 & 0 \\ N_1^{II}/S^{II} & 1 & 0 \end{vmatrix}} \quad (\text{C3})$$

The only way to arrive at a simple and useful equation is to choose the reference systems such that $S^e = 0$. Under this condition, we obtain the adsorption “isobary” analogous to Eq. (16), as

$$\left(\frac{\partial\gamma}{\partial\mu_2}\right)_P = -\left[\frac{N_2^e}{A} - \frac{\frac{N_2^{II}}{S^{II}} - \frac{N_1^I}{S^I} N_1^e}{\frac{N_1^{II}}{S^{II}} - \frac{N_1^I}{S^I} A}\right] \quad (\text{C4})$$

The pressure-dependence of the surface free energy under constant μ_1 can be evaluated as

$$\left(\frac{\partial\gamma}{\partial P}\right)_{\mu_1} = -\frac{\frac{\partial(D^*, D^I, D^{II})}{\partial(\mu_1, T, P)}}{\frac{\partial(D^*, D^I, D^{II})}{\partial(\mu_1, T, \gamma)}} = -\frac{\begin{vmatrix} \frac{\partial D^*}{\partial \mu_1} & \frac{\partial D^*}{\partial T} & \frac{\partial D^*}{\partial P} \\ \frac{\partial D^I}{\partial \mu_1} & \frac{\partial D^I}{\partial T} & \frac{\partial D^I}{\partial P} \\ \frac{\partial D^{II}}{\partial \mu_1} & \frac{\partial D^{II}}{\partial T} & \frac{\partial D^{II}}{\partial P} \end{vmatrix}}{\begin{vmatrix} \frac{\partial D^*}{\partial \mu_1} & \frac{\partial D^*}{\partial T} & \frac{\partial D^*}{\partial \gamma} \\ \frac{\partial D^I}{\partial \mu_1} & \frac{\partial D^I}{\partial T} & \frac{\partial D^I}{\partial \gamma} \\ \frac{\partial D^{II}}{\partial \mu_1} & \frac{\partial D^{II}}{\partial T} & \frac{\partial D^{II}}{\partial \gamma} \end{vmatrix}} = \frac{\begin{vmatrix} -N_1^* & -S^* & V^* \\ -N_1^I & -S^I & V^I \\ -N_1^{II} & -S^{II} & V^{II} \end{vmatrix}}{\begin{vmatrix} -N_1^* & -S^* & A \\ -N_1^I & -S^I & 0 \\ -N_1^{II} & -S^{II} & 0 \end{vmatrix}} \quad (\text{C4})$$

Since the reference systems cannot satisfy the zero excess volume and zero excess entropy conditions at the same time, the resulting relationship is rather involved.

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