On inferring liquid-liquid phase boundaries and tie lines from ternary mixture light scattering

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We investigate the possibility of using light scattering data in the single-phase regions of a ternary liquid mixture phase diagram to infer ternary mixture coexistence curves, and to infer tie lines joining the compositions of isotropic liquid phases in thermodynamic equilibrium. Previous analyses of a nonlinear light scattering partial differential equation (LSPDE) show that it provides for reconstruction of ternary [D. Ross, G. Thurston, and C. Lutzer, *J. Chem. Phys.* **129**, 064106 (2008); C. Wahle, D. Ross, and G. Thurston, *J. Chem. Phys.* **137**, 034201 (2012)] and quaternary [C. Wahle, D. Ross, and G. Thurston, *J. Chem. Phys.* **137**, 034202 (2012)] mixing free energies from light scattering data, and that if the coexistence curves are already known, it can also yield ternary tie lines and triangles [D. Ross, G. Thurston, and C. Lutzer, *J. Chem. Phys.* **129**, 064106 (2008)]. Here, we show that the LSPDE can be used more generally, to infer phase boundaries and tie lines from light scattering data in the single-phase region, without prior knowledge of the coexistence curve, if the single-phase region is connected. The method extends the fact that the reciprocal light scattering intensity approaches zero at the thermodynamic spinodal. Expressing the free energy as the sum of ideal and excess parts leads to a natural family of Padé approximants for the reciprocal Rayleigh ratio. To test the method, we evaluate the single-phase reciprocal Rayleigh ratio resulting from the mean-field, regular solution model on a fine grid. We then use a low-order approximant to extrapolate the reciprocal Rayleigh ratio into metastable and unstable regions. In the metastable zone, the extrapolation estimates light scattering prior to nucleation and growth of a new phase. In the unstable zone, the extrapolation produces a negative function that in the present context is a computational convenience. The original and extrapolated reciprocal light scattering are jointly used as input to solving the LSPDE to deduce the mixing free energy and its convex hull. When projected onto the composition triangle, the boundary of the convexified part of the free energy is the phase boundary, and lines on the convexified region along which the second directional derivative is zero are the tie lines. We find that the tie lines and phase boundaries so deduced agree well with their exact values. This work is a step toward developing methods for inferring phase boundaries from real light scattering intensities measured with noise, from mixtures having compositions on a coarser grid. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4731710>]

I. INTRODUCTION

The present work stems from the fact that second composition derivatives of the intensive Gibbs free energy, g , can express both the intensity of the scattered light in the single-phase regions, and the conditions for thermodynamic equilibrium between two or more isotropic liquid phases. These facts suggest a natural question: to what extent can light scattering data in the single-phase region of a ternary liquid mixture be used to determine phase boundaries and tie lines?

In the case of thermodynamic equilibrium between two or more phases, the chemical potentials of each component must be the same in all phases, and for ternary liquid mixtures this corresponds to having a plane doubly or triply tangent to the graph of the intensive Gibbs free energy, g . The question of the existence of such a plane can be expressed in terms of second composition derivatives of g . This follows because adding a function l , linear in composition, both to g and to any function whose graph is a doubly or triply tangent plane will create a new set of planes, tangent to the new function g

+ l at the same compositions. In the case of static light scattering, the excess Rayleigh ratio of the light scattered towards forward angles, $\Delta R(0)$, is given by the inverse of the Hessian matrix of second compositional derivatives of g , pre- and post-multiplied by the gradient of the dielectric coefficient, for liquid mixtures in which the volumes of the constituents are essentially additive.¹

Without further analysis it is not clear whether $\Delta R(0)$ will suffice for determining phase boundaries, as it only gives a combination of second derivatives of g . However, work on a light-scattering partial differential equation (LSPDE) has shown that $\Delta R(0)$ can be used to deduce ternary^{1,2} and quaternary³ mixing free energies, and can yield ternary tie lines and triangles when coexistence curves are already known.¹ Here, we extend the previous work to study whether tie lines and triangles can be deduced from $\Delta R(0)$ in the single phase region, without prior knowledge of precise phase boundary locations. We find that phase boundaries, spinodals, and tie lines can indeed be inferred accurately from

FIG. 1. *Upper left:* The excess Rayleigh ratio in the single-phase region, $R(x, y) > 0$, is the starting point for the present method of inferring phase boundaries and tie lines. R diverges at the spinodal (dashed blue); the part $R(x, y) < 0$ is not a light scattering intensity, but would result from using Eq. (9) on the test free energy model at locations inside its spinodal. *Upper right:* The blue part of the reciprocal light scattering, $1/R$, is accessible to experiment. Padé extrapolation of $1/R$ into metastable and unstable regions is shown in red, and produces a complete input function to the light scattering PDE, Eq. (11). *Lower left:* The free energy (blue) and its convexified part, shown in red by tie lines and phase boundary lifted to the free energy, from PDE solution with the complete $1/R$ input function. *Lower right:* The coexistence curve, spinodal, and tie lines (red) inferred from light scattering in the single-phase region alone (shaded blue) agree with their exact counterparts (dashed blue).

single-phase light scattering, in principle, if the single-phase region is connected.

A pictorial introduction to the present method is given in Fig. 1. Light scattering intensity diverges at the thermodynamic spinodal (Fig. 1, *top left*), but reciprocal scattering intensity behaves well there. We extrapolate reciprocal light scattering into the metastable and unstable regions to provide a suitable, complete input to the LSPDE (Fig. 1, *top right*). Integration of the LSPDE yields a model free energy complete with concave-down portions (Fig. 1, *bottom left*), and the convex hull of this function yields the phase boundaries (Fig. 1, *bottom right*).

The phase boundaries and tie lines of ternary liquid mixtures are important in a very broad and rapidly growing variety of contexts.^{4–15} Often the chemical compositions of the separated phases are important in their own right, and are also very sensitive to interaction strength changes. For example, recent findings about concentrated liquid protein mixtures indicate that substantial rotations of tie lines can be achieved with net protein interaction energy changes as small as 0.1 kT,¹⁴ and that a small interaction strength change that rotates liquid mixture tie lines is a strong candidate for causing opacification, in a cataract type resulting from a single-

point mutation to one of the human eye lens gamma crystallin genes.¹⁵

A practical method for estimating phase boundary locations and tie line directions from non-invasive, single-phase light scattering measurements could complement other methods of determining these boundaries. Cloud point measurements are direct but can also require considerable time to limit effects of hysteresis.^{16,17} For direct measurement of tie lines, time is required to reach, and check for, equilibrium,¹⁰ in addition to good analytical methods. Here, we describe the mathematical and numerical basis of a technique for using single-phase light scattering to estimate phase boundaries, and we test it on simple cases of the regular solution free energy model, with and without added quartic composition dependence. We leave the important but involved question of how to apply this method to real data on a coarse grid, measured with noise, for further work.

II. BACKGROUND

To set the stage for the present work, we first state the conditions for phase equilibrium in terms of an intensive Gibbs free energy per molecule $g = G/N$, in order to show how, and discuss when, only second derivatives of g are needed to analyze the equilibrium conditions. Second, we restate an expression for the light scattering intensity in terms of second derivatives of g .¹

The conditions for thermodynamic equilibrium between two phases having compositions $\mathbf{w}$ and $\mathbf{z}$, that coexist at fixed temperature and pressure, are

$$\mu_i(\mathbf{w}) = \mu_i(\mathbf{z}), \quad (1)$$

where $\mu_i(\mathbf{x}) = (\partial G / \partial N_i)_{T, p, N_{j \neq i}}$ is the chemical potential of component i in a k -component mixture, where $\mathbf{x} = \{N_1/N, N_2/N, \dots, N_k/N\}$. Equations (1) can be put in terms of g with use of

$$\mu_i(\mathbf{x}) = g(\mathbf{x}) + \nabla g(\mathbf{x}) \cdot (\mathbf{v}_i - \mathbf{x}), \quad (2)$$

in which vertex $\mathbf{v}_i$ is the value of $\mathbf{x}$ for pure i ; $\mu_i(\mathbf{x})$ is the vertical coordinate of the intersection of the tangent plane to the graph of g at $\mathbf{x}$ with the vertical line through vertex $\mathbf{v}_i$. With use of Eq. (2), the equilibrium conditions expressed by Eqs. (1) can be recast as

$$\begin{aligned} \nabla g(\mathbf{z}) &= \nabla g(\mathbf{w}), \\ g(\mathbf{z}) &= g(\mathbf{w}) + \nabla g(\mathbf{w}) \cdot (\mathbf{z} - \mathbf{w}). \end{aligned} \quad (3)$$

Equations (3) imply that if phases with compositions $\mathbf{w}$ and $\mathbf{z}$ are in equilibrium, there is a plane tangent to the graph of g at both $\mathbf{w}$ and $\mathbf{z}$.

Now, in Eqs. (3), suppose we add a function l to g that is linear in $\mathbf{x}$, to form a new free energy model $g' = g + l$. Then, if $\mathbf{w}$ and $\mathbf{z}$ already satisfy Eq. (3), they will also satisfy Eq. (3) when g' replaces g ; adding l to g adds the constant vector ∇l to both $\nabla g(\mathbf{z})$ and $\nabla g(\mathbf{w})$, and the corresponding, appropriate quantity to $g(\mathbf{z}) - g(\mathbf{w})$, that is, $\nabla l \cdot (\mathbf{z} - \mathbf{w})$.

Therefore, the second derivatives of g must be sufficient to determine the phase equilibrium conditions. To write this out formally, one can start at some convenient origin $\mathbf{x}_0$ in the single phase, and note that

$$\nabla g(\mathbf{x}) - \nabla g(\mathbf{x}_0) = \int_{C[\mathbf{x}_0, \mathbf{x}]} H[g](\mathbf{x}_C(s)) \cdot \hat{e}_t ds, \quad (4)$$

where C is a curve in the composition triangle joining $\mathbf{x}_0$ to $\mathbf{x}$, at every point $\mathbf{x}_C(s)$ of which the Hessian matrix $H[g](\mathbf{x}_C(s))$ must be well-defined, $\hat{e}_t$ is a unit tangent to the curve C , and s denotes arc length along C . Likewise,

$$g(\mathbf{x}) - g(\mathbf{x}_0) = \int_{C'[\mathbf{x}_0, \mathbf{x}]} \nabla g(\mathbf{x}_C(t)) \cdot \hat{e}_t dt \quad (5)$$

for a suitable curve C' , within which Eq. (4) can be used to express $\nabla g(\mathbf{x}_C(t))$ in terms of H . Taken together, Eqs. (4) and (5) show that, in principle, all the information needed to determine $\mathbf{w}$ and $\mathbf{z}$ so as to satisfy Eqs. (3) is contained in the composition dependence of $H[g]$, as long as suitable curves C and C' can be found; for example, if C and C' are entirely in a single-phase region of the same symmetry.

In the case of a model free energy, often, but not always, $H[g]$ is defined at compositions that are in multiphase regions, and Eqs. (4) and (5) can still be used on the model free energy in the metastable and unstable regions of the phase diagram. In real systems, the meaning of g and hence H in such regions is not as clear, though it does take an important role in models of the origin and nature of surface tension.¹⁸ Also, in

the case of equilibrium between phases of different symmetry, Eqs. (4) and (5) would not apply, since g then also depends on symmetry. However, the double- or triple-tangent plane construction is still valid; see, for example, Ref. 19.

Finally, if the single-phase region were not connected, it would be possible to add *different* linear functions of composition to the free energy in the different, disconnected regions, and that would change the possible locations of the doubly- and triply-tangent planes and hence the phase boundary, even though none of the second compositional derivatives of the free energy would have changed. This is the reason for our restriction in the present work to the case of connected single-phase regions.

The fact that the second derivatives of g are sufficient to determine the phase equilibrium conditions also appears more generally in the form of a first-order, ordinary differential equation (ODE) describing continuous sets of tie lines. To see this, let s parametrize the curve $\mathbf{tl}(s) = \{x_w(s), y_w(s), x_z(s), y_z(s)\}$, a four-dimensional curve of tie lines, and suppose also that a starting tie line $\mathbf{tl}(s=0) = \{\mathbf{w}_0, \mathbf{z}_0\}$ is known that satisfies Eqs. (1). As s changes, in order to continue to satisfy each of the three Eqs. (1), the point $\mathbf{tl}(s)$ must move in a four-dimensional direction that is perpendicular to all three of the gradient vectors of the equilibrium conditions, namely, $\nabla(\mu_1(\mathbf{z}) - \mu_1(\mathbf{w}))$, $\nabla(\mu_2(\mathbf{z}) - \mu_2(\mathbf{w}))$, and $\nabla(\mu_3(\mathbf{z}) - \mu_3(\mathbf{w}))$. There are two such directions, parallel and opposite to the generalized cross product²⁰ of the three gradient vectors. Specifically,

$$d(\mathbf{tl})/ds = \pm \begin{vmatrix} \hat{e}_x & \hat{e}_y & \hat{e}_x & \hat{e}_y \\ \partial\mu_1(\mathbf{z})/\partial x & \partial\mu_1(\mathbf{z})/\partial y & -\partial\mu_1(\mathbf{w})/\partial x & -\partial\mu_1(\mathbf{w})/\partial y \\ \partial\mu_2(\mathbf{z})/\partial x & \partial\mu_2(\mathbf{z})/\partial y & -\partial\mu_2(\mathbf{w})/\partial x & -\partial\mu_2(\mathbf{w})/\partial y \\ \partial\mu_3(\mathbf{z})/\partial x & \partial\mu_3(\mathbf{z})/\partial y & -\partial\mu_3(\mathbf{w})/\partial x & -\partial\mu_3(\mathbf{w})/\partial y \end{vmatrix} \quad (6)$$

$$= \pm \begin{vmatrix} \hat{e}_x & \hat{e}_y & \hat{e}_x & \hat{e}_y \\ (1-x_z)g_{xx}^z - y_z g_{xy}^z & H_2(\mathbf{z}) \cdot (\mathbf{v}_1 - \mathbf{z}) & -H_1(\mathbf{w}) \cdot (\mathbf{v}_1 - \mathbf{w}) & -H_2(\mathbf{w}) \cdot (\mathbf{v}_1 - \mathbf{w}) \\ H_1(\mathbf{z}) \cdot (\mathbf{v}_2 - \mathbf{z}) & H_2(\mathbf{z}) \cdot (\mathbf{v}_2 - \mathbf{z}) & -H_1(\mathbf{w}) \cdot (\mathbf{v}_2 - \mathbf{w}) & -H_2(\mathbf{w}) \cdot (\mathbf{v}_2 - \mathbf{w}) \\ H_1(\mathbf{z}) \cdot (\mathbf{v}_3 - \mathbf{z}) & H_2(\mathbf{z}) \cdot (\mathbf{v}_3 - \mathbf{z}) & -H_1(\mathbf{w}) \cdot (\mathbf{v}_3 - \mathbf{w}) & -H_2(\mathbf{w}) \cdot (\mathbf{v}_3 - \mathbf{w}) \end{vmatrix}, \quad (7)$$

in which $H_1 = \{g_{xx}, g_{xy}\}$ and $H_2 = \{g_{xy}, g_{yy}\}$ denote the first and second rows (or columns) of the Hessian matrix, respectively, and the vertices of the ternary composition triangle are denoted by $\mathbf{v}_1 = \{1, 0\}$, $\mathbf{v}_2 = \{0, 1\}$, and $\mathbf{v}_3 = \{0, 0\}$; the (2, 1) entry is written out for clarity. Equation (7) is the desired ODE that describes a smooth set of tie lines, and is clearly stated using only second derivatives of g .

In fact, provided that a suitable starting point is available, numerical integration of Eq. (7), with use of occasional corrections based on Eqs. (1) and (3), provides a reasonably efficient scheme for generating phase boundaries and tie lines. With analogous use of the generalized cross product, similar ODEs can readily be obtained that describe smooth sets of tie triangles that vary in temperature in terms of the Hessian of g , or binary tie line sets that satisfy a criterion, such as varying in temperature but having one end

along a desired set of compositions that has been assayed experimentally.

Finally, to complete the description of the phase boundary in terms of second derivatives of g , we recall that the thermodynamic spinodal is given by $\det[H[g]] = 0$, and that at the critical points, the eigenvectors of H with eigenvalue 0 are parallel to the spinodal and to the coexistence curve.

The light scattering efficiency can also be expressed in terms of H .¹⁻³ For convenience we repeat the expression given in Ref. 2, while noting that the notation used here differs from that of Ref. 2, in which “ x ” was used for volume fraction variables, whereas here we use it to denote mole fractions,

$$\frac{\varepsilon_{\phi_2}^2 g_{\phi_1 \phi_1} - 2\varepsilon_{\phi_1} \varepsilon_{\phi_2} g_{\phi_1 \phi_2} + \varepsilon_{\phi_1}^2 g_{\phi_2 \phi_2}}{g_{\phi_1 \phi_1} g_{\phi_2 \phi_2} - g_{\phi_1 \phi_2}^2} = R(\phi_1, \phi_2) = \nabla \varepsilon \cdot (H[g])^{-1} \cdot \nabla \varepsilon. \quad (8)$$

Here, g is the intensive, dimensionless Gibbs free energy $\Omega_0 G/(Vk_B T)$, where G is the extensive Gibbs free energy, V is the volume, k_B is Boltzmann's constant, T is absolute temperature, $\Omega_0 = \partial V/\partial N_0$ is the volume associated with each molecule of component 0, and $\phi_1 = \Omega_1 N_1/V$ and $\phi_2 = \Omega_2 N_2/V$ are the volume fractions of components 1 and 2. Consistent with the derivation¹ from the multicomponent light scattering formulation of Kirkwood and Goldberg,²¹ each Ω_i is taken to be constant. The function $\varepsilon(\phi_1, \phi_2)$ is the real part of the dimensionless dielectric coefficient at the optical frequency used for measuring $R(\phi_1, \phi_2)$, $\varepsilon_{\phi_1} = \partial \varepsilon/\partial \phi_1$, and $\varepsilon_{\phi_2} = \partial \varepsilon/\partial \phi_2$. $R(\phi_1, \phi_2)$ is a dimensionless form of the excess Rayleigh ratio, $\Delta R(0)$, given by $R(\phi_1, \phi_2) = \lambda^4 \Delta R(0)/(\pi^2 \Omega_0)$, where λ is the vacuum wavelength of the incident and the scattered light. Here, $H[g]$ is the Hessian matrix of g with respect to the volume fraction variables, and $\nabla \varepsilon$ is the gradient of ε with respect to those variables.

In summary, to help motivate the following work, in this section we have recalled that the liquid-liquid phase boundary, the tie lines, the spinodal, and the critical point, and the intensity of the scattered light, $\Delta R(0)$, can all be expressed in terms of the Hessian matrix $H[g]$ of the intensive Gibbs free energy g . We now describe a method we have tested for using $\Delta R(0)$ from Eq. (8) to obtain numerical estimates of the phase boundary characteristics.

III. METHODS

In the following development, for simplicity, we take the partial molecular volumes of all three constituents to be the same, that is, $\Omega_0 = \Omega_1 = \Omega_2$, in addition to assuming they are constant. With these assumptions $\phi_1 = x$ and $\phi_2 = y$, and the relationship between the free energy and the excess, forward-angle Rayleigh ratio from Eq. (8) can be rewritten as

$$\frac{\varepsilon_y^2 g_{xx} - 2\varepsilon_x \varepsilon_y g_{xy} + \varepsilon_x^2 g_{yy}}{g_{xx} g_{yy} - g_{xy}^2} = R(x, y). \quad (9)$$

At the spinodal, because $\det(H[g]) = 0$, the Rayleigh ratio $R(x, y)$ in Eq. (9) is infinite, as illustrated in Figs. 1 and 3. To produce a well-behaved input function for use in the light scattering PDE to find the free energy, we instead construct an approximation to the reciprocal Rayleigh ratio, $R^{-1}(x, y)$, which approaches 0 at the spinodal. To do this we write the dimensionless, intensive free energy of mixing, $g(x, y)/(k_B T)$, as the sum of the ideal solution free energy and an excess free energy that we take to be a smooth function ϕ

$$\begin{aligned} g(x, y)/(k_B T) &= x \ln x + y \ln y + z \ln z + \phi(x, y), \\ z &= 1 - x - y. \end{aligned} \quad (10)$$

With this choice of g , Eq. (9) becomes

$$R^{-1}(x, y) = \frac{1 + x(1-x)\phi_{xx} - 2xy\phi_{xy} + y(1-y)\phi_{yy} + xyz(\phi_{xx}\phi_{yy} - \phi_{xy}^2)}{\varepsilon_y^2 y(1-y + xz\phi_{xx}) - 2\varepsilon_x \varepsilon_y xy(1 + z\phi_{xy}) + \varepsilon_x^2 x(1-x + yz\phi_{yy})}. \quad (11)$$

Equation (11) shows that at least in local neighborhoods of a particular composition (x, y) , $R^{-1}(x, y)$ naturally has the character of a ratio of polynomials, an observation that forms the basis for the numerical methods adopted here for the extension of $1/R$ into zones in which light scattering has not been, or cannot be measured. Indeed, initial attempts revealed that the use of a single polynomial for such extension typically yields phase boundary predictions that are less accurate than those resulting from the Padé-type approximations used below.

Equation (11) further suggests that the nature of the desired extension of $R^{-1}(x, y)$ into the metastable and unstable regions depends in general on the second derivatives of ϕ . If the second derivatives of ϕ are constant, as is the case for the regular solution free energy model, then at each fixed y , $R^{-1}(x, y)$ reduces to a ratio of quadratic polynomials in x . If the second derivatives of ϕ vary only moderately, then a ratio of cubic polynomials may be an adequate approximation to $R^{-1}(x, y)$. For models in which ϕ varies very rapidly – as would be the case near a critical micellar concentration, for example – it may be necessary to adopt higher order approximations to reciprocal light scattering.

We have implemented the ratio of cubic polynomials numerically along each grid line $y = y_j$ passing through

metastable or unstable regions. We see from Eq. (11) that the constant terms of the functions appearing in the numerator and denominator are independent of ϕ . That is, if ϕ_{yy} does not contribute to the constant term in the numerator, as is the case in all the examples we present here, then the constant terms are 1 and $\varepsilon_y^2 y_j(1 - y_j)$, respectively, for all ϕ . Thus, we take the cubic Padé approximation

$$\hat{R}^{-1}(x, y_j) = \frac{1 + a_1 x + a_2 x^2 + a_3 x^3}{\varepsilon_y^2 y_j(1 - y_j) + b_1 x + b_2 x^2 + b_3 x^3}. \quad (12)$$

We impose six conditions on $\hat{R}^{-1}(x, y_j)$ to determine the six coefficients ($a_1, a_2, a_3, b_1, b_2, b_3$). Suppose at some fixed y_j , we wish to construct the rational function approximation of $R^{-1}(x, y_j)$ over an interval (x_l, x_m) , where x_l and x_m are grid points on the x axis. We demand that $\hat{R}^{-1}(x, y_j)$ agree with $R^{-1}(x, y_j)$ and its first two derivatives at the endpoints, x_l and x_m , of the interval. That is, we impose the six conditions

$$\begin{aligned} \hat{R}^{-1}(x_i, y_j) &= R^{-1}(x_i, y_j), \\ \frac{\partial}{\partial x} \hat{R}^{-1}(x_i, y_j) &= \frac{\partial}{\partial x} R^{-1}(x_i, y_j), \\ \frac{\partial^2}{\partial x^2} \hat{R}^{-1}(x_i, y_j) &= \frac{\partial^2}{\partial x^2} R^{-1}(x_i, y_j), \end{aligned} \quad (13)$$

for $i = l, m$. We approximate the derivatives of $R^{-1}(x, y_j)$ with second-order finite difference formulas. We set

$$\begin{aligned}\rho_{ij} &= R^{-1}(x_i, y_j), \\ \rho'_{ij} &= \frac{R^{-1}(x_{i+1}, y_j) - R^{-1}(x_{i-1}, y_j)}{2\Delta x} \\ &= \frac{\partial}{\partial x} R^{-1}(x_i, y_j) + O(\Delta x^2), \\ \rho''_{ij} &= \frac{R^{-1}(x_{i+1}, y_j) - 2R^{-1}(x_i, y_j) + R^{-1}(x_{i-1}, y_j)}{\Delta x^2} \\ &= \frac{\partial^2}{\partial x^2} R^{-1}(x_i, y_j) + O(\Delta x^2).\end{aligned}$$

The conditions given by (13) yield a linear system of six equations which determines the six coefficients. The equations are

$$\begin{aligned}a_1x_i + a_2x_i^2 + a_3x_i^3 - b_1x_i\rho_{ij} - b_2x_i^2\rho_{ij} - b_3x_i^3\rho_{ij} \\ = \varepsilon_y^2 y_j(1 - y_j)\rho_{ij} - 1,\end{aligned}$$

$$\begin{aligned}a_1 + 2a_2x_i + 3a_3x_i^2 - b_1(x_i\rho'_{ij} + \rho_{ij}) - b_2x_i(x_i\rho'_{ij} + 2\rho_{ij}) \\ - b_3x_i^2(x_i\rho'_{ij} + 3\rho_{ij}) = \varepsilon_y^2 y_j(1 - y_j)\rho'_{ij},\end{aligned}$$

$$\begin{aligned}2a_2 + 6a_3x_i - b_1(x_i\rho''_{ij} + 2\rho'_{ij}) - b_2(x_i^2\rho''_{ij} + 4x_i\rho'_{ij} + 2\rho_{ij}) \\ - b_3x_i(x_i^2\rho''_{ij} + 6x_i\rho'_{ij} + 6\rho_{ij}) = \varepsilon_y^2 y_j(1 - y_j)\rho''_{ij},\end{aligned}$$

for $i = l, m$. We solve the system using Gaussian elimination with partial pivoting, thus yielding a rational function approximation of $R^{-1}(x, y_j)$ along the grid line $y = y_j$ over the interval (x_l, x_m) .

By the same method we construct a quartic Padé-type approximant, of the form

$$\hat{R}^{-1}(x, y_j) = \frac{1 + a_1x + a_2x^2 + a_3x^3 + a_4x^4}{\varepsilon_y^2 y_j(1 - y_j) + b_1x + b_2x^2 + b_3x^3 + b_4x^4}. \quad (14)$$

The quartic has eight, rather than six, parameters to be determined; we add the analogous third-derivative conditions to get a system of eight equations for the eight parameters. We use both cubic and quartic cases below. Having extended the quantity $R^{-1}(x, y)$ to cover the entire triangle, we now solve Eq. (11) as described previously^{1,2} to find g , its convex hull, and the corresponding tie lines.

IV. RESULTS

We have tested the method described above on several types of free energy models: regular solution ternary free energy models having multiphase regions that intersect one binary axis; models that have closed-loop phase separation, that is, models with multiphase regions that are entirely inside the ternary composition triangle; and an augmented regular solution model to which a quartic term has been added that cannot be exactly represented by Eq. (12). In each case, the Rayleigh ratio was evaluated both in the entire single-phase region, and in reduced portions of the single-phase region, and its reciprocal was extended into the metastable and unstable regions

FIG. 2. *Upper left*: The excess Rayleigh ratio in the single-phase region, $R(x, y) > 0$, for a free energy that corresponds to a closed-loop coexistence curve. *Upper right*: As in Fig. 1, the blue reciprocal light scattering, $1/R$, is accessible to experiment; Padé approximation to extend $1/R$ into metastable and unstable regions is shown in red. *Lower left*: The free energy (blue) and its convexified part, shown in red by tie lines and the phase boundary lifted to the free energy, from the PDE solution with the complete $1/R$ input function. *Lower right*: The closed-loop coexistence curve, spinodal, and tie lines (red) inferred from light scattering in the single-phase region alone (shaded blue) agree with their exact counterparts (dashed blue).

with a Padé approximant, before PDE integration to obtain the mixing free energy. We considered reduced portions of the single-phase region in order to investigate how far from a phase boundary reciprocal Rayleigh ratio extrapolation combined with the light scattering PDE can effectively infer phase boundary locations and tie lines.

Figures 1 and 2 illustrate the entire process for constructing inferred phase boundaries, for the binary axis-intersecting and closed-loop phase separation cases, respectively. Clearly, the x -direction of extrapolation could be rotated as needed, to study phase separations that intersect the other axes.

We have also studied phase boundary inference in cases in which the Rayleigh ratio is known only in a portion of the single-phase region. The results are shown in Figs. 3 and 4, for phase separations that touch the binary axis and ones that form closed loops, respectively. Figures 3 and 4 illustrate that phase boundaries can be inferred accurately using light scattering data in parts of the composition triangle that are not immediately adjacent to the boundary, and also illustrate some numerical issues that can arise in this process.

While the inferred phase boundaries in Fig. 3 are close to the exact ones, the *center* panel shows that deviations can result if the light scattering exclusion zone is too close to the composition triangle vertices. This is not surprising, for the excess light scattering becomes a nearly linear function of composition near the vertices, while Eq. (12) is set up to capture second derivatives of $1/R$ at the exclusion zone boundaries.

FIG. 3. Phase boundaries and tie lines inferred from single-phase light scattering data only in the regions shaded blue, using the cubic Padé approximant, Eq. (12) (red—inferred; dashed blue—exact). *Left and right* panels show precise inference. Small deviations at *center*, near the axis, result from using an exclusion region too close to the vertices, unlike that at *left and right*, leading to an inaccurate extrapolant.

In Fig. 4, we added the term $C_{xxzz}x^2z^2$ to the free energy, to study the effects of a term that is not captured by the cubic Padé-type approximant, Eq. (12). Figure 4 (*left*) shows that if light scattering is evaluated up to the phase boundary, the cubic approximant is able to generate an extrapolated $1/R$ function that, when integrated, correctly captures the properties of this closed-loop coexistence, including the two critical point locations, the spinodal, the tie lines, and the phase boundary.

Figure 4 (*center*) shows, however, that if the light scattering exclusion zone is now enlarged, eventually the cubic approximant does give phase boundary errors. However, if one now leaves the exclusion zone at the same size, but instead makes use of the quartic Padé approximant given by Eq. (14) instead of the cubic approximant to $1/R$, integration of the PDE yields a phase boundary that returns to the correct properties.

If the challenges of accounting for experimental noise and coarser experimental coverage of the composition triangle can be overcome, observations of the type demonstrated in Figs. 3 and 4 may prove to be of particular use in facilitating experimental work on ternary liquid mixtures.

Figure 5 explores discrepancies between the inferred and exact phase boundaries that occur near the binary, x - z axis, with use of the $C_{xxzz}x^2z^2$ augmentation to the regular solution free energy. The *top left* panel of Fig. 5 illustrates a discrepancy, near the axis, between the exact phase boundaries

FIG. 4. Phase boundaries and tie lines for closed-loop coexistence with $C_{xxzz} = 1$, inferred from single-phase light scattering evaluated only in the regions shaded blue (red—inferred; dashed blue—exact). The *left* panel shows precise inference, with use of the cubic Padé approximant, Eq. (12); the inner, regular solution phase diagrams corresponding to $C_{xxzz} = 0$ are shown with thin lines. *Center*: If the exclusion zone for light scattering (white) is made large enough, deviations between inferred and exact phase boundaries start to occur, with use of the cubic approximant. *Right*: If a quartic Padé approximant is used instead, with the same exclusion zone as at *center*, inference improves. In the process of applying Eq. (14), we used a 6th-order finite difference formula to estimate third derivatives of $1/R$ with enough accuracy at the exclusion zone boundaries, for the chosen grid spacing.

FIG. 5. Reducing C_{xxzz} in the added term $C_{xxzz}x^2z^2$ (*top right*) reduces the discrepancy between the exact phase boundaries corresponding to the augmented test regular solution model (*top left*), and those inferred with use of the cubic Padé approximant, as does reducing the magnitude of C_{xz} (*bottom left*), or using the quartic Padé approximant, Eq. (14) (*bottom right*). The inner, regular solution phase diagrams are shown with thin lines (cyan=exact, magenta=inferred from light scattering), while thick lines correspond to the augmented free energy (blue=exact, red=inferred).

corresponding to the augmented test regular solution model and the ones inferred with use of the cubic Padé approximant. The other three panels in Fig. 5 show that this discrepancy is reduced for smaller values of C_{xxzz} (*top right*), for phase separations that remain closer to the x - z axis (*bottom left*), or with use of the quartic Padé approximant, Eq. (14) (*bottom right*).

In Fig. 6 we have plotted the inferred coexistence curve error near the binary axis, Δx , as a function of the numerical evaluation grid point spacing, $1/n$, where n is the number of grid points in either direction within the triangle. As before, $1/R$ is evaluated only in the region shaded blue, prior to

FIG. 6. For the test model and exclusion zone considered in the *center* panel of Fig. 3, the inferred coexistence curve error near the binary axis, Δx , decreases in proportion to the square of the numerical evaluation grid point spacing, $1/n$, where n is the number of grid points in either direction within the triangle. Thus, in this case the numerical errors in estimating the location of the coexistence curve at $y = 0$ scale with $1/n$ in the same fashion as do the numerical errors in approximating the second x derivatives of $1/R$.

cubic Padé approximation (Eq. (12)) and numerical extension of $1/R$. Figure 6 shows that the numerical error in estimating the location of the coexistence curve at $y = 0$ scales with $1/n$ in the same fashion as do the numerical errors in approximating the second x derivatives of $1/R$, the highest order derivatives that are evaluated at the boundaries of the exclusion zone, for use in the cubic Padé approximation, Eq. (12). This strongly suggests that, in this case, the numerical approximation of the second derivatives is the primary source of error in the extrapolation of $1/R$, and hence, the only source of error in inferring $g(x, y)$ and the coexistence curve. This is consistent with the statement made in connection with the middle panel of Fig. 3; namely, that the source of the error there, and here, is that the exclusion zone comes very near to the composition triangle vertices, where the second derivative of R is very small. By increasing the grid resolution, the needed second derivative of $1/R$ can nevertheless be adequately discerned, improving the accuracy of the inferred coexistence curve. Note that there is very little error near the critical point.

As formulated in the present work, the accuracy of phase boundaries inferred from single-phase light scattering experiments hinges on the accuracy with which $1/R$ can be extended towards and into the metastable region. A full analysis of the effects of experimental uncertainty on the inferred phase boundaries is beyond the scope of this paper. However, to begin to gain some insight into the accuracy required of the light scattering, we have artificially altered specific coefficients in the Padé approximant, to see the effects on the phase boundary. Figure 7 shows a cross-section of results for alteration of a_1 , appearing in Eq. (12), to $a_1(1 + \varepsilon)$, for a series of positive and negative values of ε . Figure 7 shows that significant errors in the inferred coexistence curve will result unless a_1 is determined to within a few percent. Continuing in this fashion, Fig. 8 shows the dependence of coexistence curve error on forced variation of the coefficient a_1 in Eq. (12). As shown there, we found an approximately linear relationship between the co-

FIG. 7. Sensitivity of inferred phase boundaries to artificially varying a Padé coefficient in Eq. (12) from its fitted value, a_1 , to $a_1(1 + \varepsilon)$. Top left: $\varepsilon = -0.04$, Top middle: $\varepsilon = -0.02$, Top right: $\varepsilon = -0.01$, Bottom left: $\varepsilon = 0.01$, Bottom middle: $\varepsilon = 0.02$, Bottom right: $\varepsilon = 0.04$. For this coefficient, the most sensitive of the set of 6 in Eq. (12), substantial errors in the coexistence curve will result unless it is determined to within just a few percent. The sensitivity of this coefficient is detailed further in Fig. 8.

FIG. 8. Dependence of coexistence curve error on forced variation of the coefficient a_1 in Eq. (12). As a measure of the shift we use Δx as shown on the left, and varied ε in $(1 + \varepsilon)a_1$, as shown on the right.

existence curve shift and the fractional change in a_1 , with a slope of -0.35 . Thus, roughly speaking, an 8% error in a_1 alone would be expected to result in a change of about 0.03 in the mole fraction of one end of a tie line. We expect results of this type to be useful for analyzing the effects of experimental noise in light scattering determination of liquid-liquid phase boundaries.

V. DISCUSSION

It is important to note that despite the success of the method described above for inferring phase boundaries and tie lines, we have not achieved a rigorous mathematical foundation identifying circumstances under which the method works. The method is essentially a numerical method inspired by (i) the relationships among the Hessian matrix, the phase boundaries, and the Rayleigh ratio, as expressed by Eqs. (4)–(8), and (ii) the fact that the single-phase Rayleigh ratio alone, combined with *prior* knowledge of the phase boundaries, allows the computation of the tie lines through solution of the light scattering PDE, as shown in Ref. 1. It remains an interesting problem to study the possibility of supplying a more rigorous framework for the success of the method demonstrated above, and in the following we make a few possibly relevant remarks.

Clearly, if one had the composition dependence of all of the entries of the Hessian matrix in the entire single phase region, judicious use of Eqs. (3)–(7) would, in principle, yield the phase boundaries. But the Rayleigh ratio is only a cross-section of the Hessian matrix, and as a scalar function of composition, it cannot in a *local* sense carry the full information about the Hessian that would be needed to carry out the integrations formally given in Eqs. (4) and (5).

However, in a mean-field model such as the ones tested above, near the critical point the width of the coexistence curve is close to $\sqrt{3}$ times the width of the spinodal curve.¹⁹ Therefore, if one regards the Padé extrapolant, Eq. (12), as a way of locating the spinodal, then at least near the critical point it may be regarded as a means of *effectively* locating the coexistence curve as well – which would then provide the prior information we have previously found to enable one to deduce the tie lines through solution of the light scattering PDE.¹ On the other hand, near enough to the critical point of a real system, the mean-field analysis will not apply, and the

extent to which an apparent spinodal may be observed will need to be analyzed in considerably more detail.^{22,23}

Clearly, an important further step toward practical implementation of the method described here will be to test it using simulations of real data evaluated on a coarse grid, measured with noise, as we have done for the cases of ternary and quaternary mixing free energy inference from light scattering when there is no phase separation.^{2,3} We anticipate that with real data, because of the high-order derivatives that are essential to determining phase boundaries,¹⁹ some degree of smoothing²⁴ before extrapolating is likely to be needed.

It will also be important to test the method with some of the many other free energy models for ternary solutions that are in common use,^{6,7} to investigate the effectiveness of more sophisticated approximants, and to apply the model with use of non-mean-field scaling near the critical point.²²

VI. CONCLUSIONS

In this work we have examined the potential for deducing ternary isotropic liquid mixture phase boundaries by extrapolating static light scattering data from the single-phase region and PDE solution. We have used a family of Padé approximants for the reciprocal Rayleigh ratio, that results from expressing the free energy as the sum of ideal and excess parts. After extrapolating the single-phase Rayleigh ratio into the metastable and unstable zones, and integrating the light scattering PDE, we can calculate inferred free energy model functions and corresponding phase boundaries. With finely spaced sampling of the exact Rayleigh ratio, we find that phase boundaries can be accurately reproduced. We have illustrated situations in which the inferred boundaries become less accurate. In summary, static light scattering investigations of single-phase liquid ternary mixtures can provide considerable information about liquid-liquid phase boundaries in those mixtures.

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