Mathematical methods for restricted domain ternary liquid mixture free energy determination using light scattering

Chris W. Wahle,¹ David S. Ross,¹ and George M. Thurston²

¹*School of Mathematical Sciences, Rochester Institute of Technology, Rochester, New York 14623, USA*

²*Department of Physics, Rochester Institute of Technology, Rochester, New York 14623, USA*

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We extend methods of solution of a light scattering partial differential equation for the free energy of mixing to apply to connected, isotropic ternary liquid composition domains that do not touch all three binary axes. To do so we mathematically analyze the problem of inferring needed Dirichlet boundary data, and solving for the free energy, with use of hypothetical static light scattering measurements that correspond to dielectric composition gradient vectors that have distinct directions. The physical idea behind the technique is that contrasting absorption properties of mixture components can result in such distinctly directed dielectric composition gradient vectors, due to their differing wavelength dependences of dielectric response. At suitably chosen wavelengths, contrasting light scattering efficiency patterns in the ternary composition triangle can then correspond to the same underlying free energy, and enlarge the scope of available information about the free energy, as shown here. We show how to use distinctly directed dielectric gradients to measure the free energy on both straight lines and curves within the ternary composition triangle, so as to provide needed Dirichlet conditions for light scattering partial differential equation solution. With use of Monte Carlo simulations of noisy light scattering data, we provide estimates of the overall system measurement time and sample spacing needed to determine the free energy to a desired degree of accuracy, for various angles between the assumed dielectric gradient vectors, and indicate how the measurement time depends on instrumental throughput parameters. The present analysis methods provide a way to use static light scattering to measure, directly, mixing free energies of many systems that contain such restricted liquid domains, including aqueous solutions of biological macromolecules, micellar mixtures and microemulsions, and many small molecule systems that are important in separation technology. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4822004>]

I. INTRODUCTION

In this paper we extend the light scattering partial differential equation (LSPDE) method of determining mixing free energies^{1–4} to apply to limited composition domains of ternary molecular mixtures. To date, we have developed the LSPDE method for mixtures that have isotropic liquid phases within a simply connected set of compositions that touches all edges of the ternary composition triangle,² or composition tetrahedron, for quaternary mixtures.³ However, many important mixtures, such as aqueous, multicomponent protein mixtures,^{5–8} micellar mixtures and microemulsions,^{9–13} polymer mixtures,¹⁴ and mixtures of small molecules^{10,15} do not always have liquid domains of this type, and instead may form liquid crystals, solids, or other states at compositions that prevent the liquid phase compositions from reaching one or more domain edges. Model examples of such regions, computed from a regular solution ternary mixture free energy,^{16,17} are shown by the clear zones in Fig. 1. In these cases, to apply light scattering and the LSPDE method to directly determine the mixing free energies calls for a limited-domain LSPDE approach like those we analyze here.

The physical basis of the present limited-domain LSPDE method is to use differing light scattering cross-sections of

mixture components vs. wavelength, or a combination of different scattering probes such as light, X-rays, or neutrons, to gain additional information about the free energy. Here we focus on the mathematical basis for such an approach, to provide the groundwork for further statistical and spectroscopic analyses. Figure 2 illustrates the basic idea behind the current paper, namely, that light scattering intensities have different composition dependences in response to different directions of normalized dielectric gradient vectors.¹ We envision rotating the dielectric gradient by changing wavelength or scattering probe. We created Fig. 2 with large rotations to illustrate the point. The answer to the question of how much rotation can be achieved in practice will depend on the system and the scattering probe; and the answer to the question of how much rotation is needed will require statistical analysis of the sort we have published for ternary and quaternary mixture LSPDEs.^{2,3} We leave both of these questions for future analysis, but we expect that in practice rotations of the dielectric gradient will be considerably smaller than those illustrated in Fig. 2.

To provide context, we briefly review the relevant mathematical formulation. We have built on the work of Kirkwood and Goldberg^{1,18} to cast the relationship between the intensive Gibbs free energy of a liquid mixture as a function of

FIG. 1. The partial differential equation method described in this work permits static light scattering to directly measure the mixing free energy, within simply connected one-phase isotropic ternary liquid regions, shown here by the clear zones, that do not touch all three binary composition axes. Regular solution model^{16,17} examples containing such regions are shown here. Two-phase tie-lines are blue, a three-phase coexistence is shown in green, thermodynamic spinodal curves are in red, and the red dot is a hidden critical point. In the case shown, two-phase tie-lines that have portions inside the three-phase coexistence triangle are metastable.

composition, $g(\mathbf{x})$, and the single-phase excess light scattering efficiency or Rayleigh ratio, $R(\omega, \mathbf{x})$ at frequency ω , as a fully nonlinear partial differential equation,^{1,3}

$$\lambda_0(\mathbf{x}) = 0, \quad (1)$$

where $\lambda_0(\mathbf{x})$ is the smallest eigenvalue of the matrix

$$H_g[g(\mathbf{x})] - \frac{1}{R(\omega, \mathbf{x})} \nabla \varepsilon^\top(\omega, \mathbf{x}) \nabla \varepsilon(\omega, \mathbf{x}). \quad (2)$$

In Eq. (2), $H_g[g(\mathbf{x})]$ is the Hessian of the free energy $g(x)$ with respect to composition $\mathbf{x}$, $\nabla \varepsilon^\top(\omega, \mathbf{x}) \nabla \varepsilon(\omega, \mathbf{x})$ is a rank-one matrix, $\varepsilon(\omega, \mathbf{x})$ is the mixture dielectric coefficient, and $g, \mathbf{x}$, ε , and R have been put in dimensionless form.^{2,3} It is important to note that Eqs. (1) and (2) apply not only in single-phase regions of composition space, but also in multiphase regions, provided R is taken to be infinite at such compositions. The formulation given in Eqs. (1) and (2) is equivalent to that given in previous work.¹⁻⁴ As formulated in Eqs. (1) and (2) this method applies to mixtures with any number of components.

The LSPDE method can be viewed as a natural extension of existing light scattering interpretation methods. At low concentration, the latter typically yield molecular weights and virial coefficients, or parameters of model free energies. We have shown that the LSPDE method is far more general in

FIG. 2. Physical basis of the present method. For the same free energy, the composition dependence of light scattering differs for different dielectric gradients, here with directions 30° , 52° , and 60° from the x -axis,¹ for a regular solution free energy model. In principle, one can combine scattering cross sections from use of three such gradients to determine the three independent components of the Hessian matrix of the mixing free energy at any given composition. By integration along boundaries of ternary liquid composition domains, the combined information can be used to establish Dirichlet data for solution of a single PDE within such a domain.

that it allows us to determine the free energies of ternary^{1,2} and quaternary³ liquid mixtures directly from static light scattering data over the entire composition triangle or tetrahedron. Perhaps surprisingly, in conjunction with determining the free energy, we have also shown that in principle the LSPDE method can provide a chemical assay-free method to determine the tie lines that join equilibrium compositions of ternary mixtures,⁴ solely by analysis of neighboring single-phase light scattering measurements. However, as we noted above, in the previous work the applicability of the method has been restricted to single-phase regions that touch all of the binary axes of the composition triangle, or that touch all of the axes and faces of the quaternary composition tetrahedron, restrictions that we aim now to remove.

In essence, by virtue of Eq. (1), the light scattering intensity represents a *latent image* of the free energy within chemical composition space. The LSPDE method can develop this latent image to produce an image of the underlying mixing free energy, at each temperature and pressure. Thus, the LSPDE method provides the basis for a *Gibbsometer* that forms images not of mixture constituents, but rather of how thermodynamic driving forces vary with composition. From Eq. (2) it is clear that the nature of this latent image will depend on the vector $\nabla \varepsilon(\omega, \mathbf{x})$, which is in principle a function of the light frequency ω . Therefore, changing $\nabla \varepsilon(\omega, \mathbf{x})$ by changing ω , or by changing between light, X-ray, or neutron scattering, has the potential to provide complementary information about $g(\mathbf{x})$.

An outline of the paper is as follows. In Sec. II, we show that a single LSPDE can be used to obtain the free energy from light scattering data, provided that Dirichlet data are given on interior boundaries of limited domains within the ternary composition triangle. This is a crucial prerequisite for our multiple dielectric gradient methods that aim to gain the needed interior domain boundary data. In Sec. III, we show how to use Rayleigh ratios obtained with three dielectric gradients that have distinct directions, to determine the needed Dirichlet data on straight boundaries in composition space, to within a linear function of composition. In Sec. IV, we generalize this approach to curved boundaries, which can be chosen for convenience to include or avoid selected composition regions. In Sec. V, we use simulations of light scattering data, as done previously,^{2,3} to make preliminary estimates of dimensionless and actual, instrument-dependent times required to measure the free energy in a restricted domain, and how the free energy error depends on overall time, the angles between the dielectric gradient vectors, and the sample spacing. In Sec. VI, we discuss some of the further steps that will be needed to bring the proposed methods into practical use. In Sec. VII, we summarize and conclude. We describe our numerical solution methods in detail in the Appendix.

II. SOLUTION OF A SINGLE LSPDE IN RESTRICTED DOMAINS

The basic idea behind our methods for solving the restricted domain problem is to obtain needed boundary data on the interior edges of such domains by using three distinctly

FIG. 3. Prerequisite for the present method: given Dirichlet data on the boundaries of the highlighted subsets of the ternary composition triangle (*left*), the single LSPDE for one dielectric gradient direction field can be numerically solved to yield the free energy (*right*) from the light scattering intensity. The free energy computed from a single LSPDE within each of the domains at *left* is shown at *right* over those same restricted domains, and agrees to within numerical accuracy with the original, test free energy function, which is shown by the lighter surface.

directed dielectric gradients, then using a single LSPDE to find the free energy from light scattering data at a single wavelength, within the domain. Figure 3 shows that our numerical LSPDE solution method establishes this basic prerequisite for the method to work, namely, that given Dirichlet data on the boundaries of subsets of the ternary composition triangle, solution of a single LSPDE is in fact sufficient to yield the free energy from the corresponding Rayleigh ratio. In particular, the free energy computed from a single LSPDE within each of the domains in Fig. 3 (*left*) is shown at *right* over those same restricted domains, and is found to agree to within numerical accuracy with the original, test free energy function. We note that measurement of a single Rayleigh ratio provides for integration of an ordinary differential equation (ODE) to yield the free energy on binary axes.¹ Thus, if by some means (scattering or otherwise) one can provide the needed Dirichlet data on each of the edges of a restricted domain, data from

only one scattering wavelength or probe will then be sufficient to determine the mixing free energy inside that domain.

III. THREE PDE SOLUTION METHOD

We now show that the use of three probes enables one to solve ordinary differential equations to yield the needed Dirichlet data on the interior boundaries of restricted domains. For this purpose we use an alternate form of Eqs. (1) and (2); for ternary mixtures one has^{1,2}

$$\frac{\varepsilon_y^2 g_{xx} - 2\varepsilon_x \varepsilon_y g_{xy} + \varepsilon_x^2 g_{yy}}{g_{xx} g_{yy} - g_{xy}^2} = R, \quad (3)$$

where $\nabla \varepsilon$ and R are as above, and g_{xx} , g_{xy} , and g_{yy} are the second composition derivatives of g . We note that Eq. (3) is a degenerate case of the Monge-Ampère equation.¹⁹ For three dielectric gradient vectors $\nabla \varepsilon = \nabla \varepsilon(\omega_1, \mathbf{x})$, $\nabla \delta = \nabla \varepsilon(\omega_2, \mathbf{x})$, and $\nabla \gamma = \nabla \varepsilon(\omega_3, \mathbf{x})$, associated, respectively, with the light scattering measurements vs. composition R_1 , R_2 , and R_3 at frequencies ω_1 , ω_2 , and ω_3 , the governing partial differential equations (PDEs) for determination of the intensive mixing free energy g are

$$\frac{\varepsilon_y^2 g_{xx} - 2\varepsilon_x \varepsilon_y g_{xy} + \varepsilon_x^2 g_{yy}}{g_{xx} g_{yy} - g_{xy}^2} = R_1, \quad (4)$$

$$\frac{\delta_y^2 g_{xx} - 2\delta_x \delta_y g_{xy} + \delta_x^2 g_{yy}}{g_{xx} g_{yy} - g_{xy}^2} = R_2, \quad (5)$$

$$\frac{\gamma_y^2 g_{xx} - 2\gamma_x \gamma_y g_{xy} + \gamma_x^2 g_{yy}}{g_{xx} g_{yy} - g_{xy}^2} = R_3. \quad (6)$$

Equations (4)–(6) constitute an algebraic system that determines the second derivatives (g_{xx} , g_{yy} , and g_{xy}) in terms of the dielectric gradients ($\nabla \varepsilon$, $\nabla \delta$, and $\nabla \gamma$) and the corresponding Rayleigh ratios (R_1 , R_2 , and R_3). The solution of Eqs. (4)–(6) is

$$\begin{aligned} g_{xx} &= 4abc \frac{\delta_x \gamma_x a R_1 + \gamma_x \varepsilon_x b R_2 + \varepsilon_x \delta_x c R_3}{a^4 R_1^2 + b^4 R_2^2 + c^4 R_3^2 - 2(a^2 b^2 R_1 R_2 + a^2 c^2 R_1 R_3 + b^2 c^2 R_2 R_3)}, \\ g_{yy} &= 4abc \frac{\delta_y \gamma_y a R_1 + \gamma_y \varepsilon_y b R_2 + \varepsilon_y \delta_y c R_3}{a^4 R_1^2 + b^4 R_2^2 + c^4 R_3^2 - 2(a^2 b^2 R_1 R_2 + a^2 c^2 R_1 R_3 + b^2 c^2 R_2 R_3)}, \\ g_{xy} &= 2abc \frac{(\delta_x \gamma_y + \delta_y \gamma_x) a R_1 + (\gamma_x \varepsilon_y + \gamma_y \varepsilon_x) b R_2 + (\varepsilon_x \delta_y + \varepsilon_y \delta_x) c R_3}{a^4 R_1^2 + b^4 R_2^2 + c^4 R_3^2 - 2(a^2 b^2 R_1 R_2 + a^2 c^2 R_1 R_3 + b^2 c^2 R_2 R_3)}, \end{aligned} \quad (7)$$

in which a , b , and c are the signed magnitudes of $\nabla \delta \times \nabla \gamma$, $\nabla \gamma \times \nabla \varepsilon$, and $\nabla \varepsilon \times \nabla \delta$, respectively.

Using Eqs. (7), any second directional derivative of the free energy g can be computed at any concentration for which

the necessary data are accessible. We note that if any one of the cross products vanishes, the method fails. Thus, dielectric gradient vectors that have three distinct directions must be used.

FIG. 4. Light scattering can be used to measure the free energy in restricted ternary composition domains, extending the LSPDE method to apply to a broader range of physical systems. A triangular restricted domain is shown at left. On the two right-hand segments of the boundary of that domain, simulated light scattering with three dielectric gradients was used with Eqs. (7), (9), and (10) to establish Dirichlet data for solution of Eq. (3) in the interior of the restricted domain, while one gradient was used to find the binary-axis Dirichlet data. The computed g is shown as the darker surface at right, and agrees with the test function, which is shown as the lighter surface.

In terms of the g_{xx} , g_{xy} , and g_{yy} so obtained, the second directional derivative of g in the direction of the unit vector $\mathbf{u} = \langle u_1, u_2 \rangle$ is given by

$$g_{uu} = \mathbf{u} H_g \mathbf{u}^T = u_1^2 g_{xx} + 2u_1 u_2 g_{xy} + u_2^2 g_{yy}, \quad (8)$$

where u is the coordinate that runs in the direction of $\mathbf{u}$. Knowing the three Rayleigh ratios corresponding to the three dielectric coefficients along any line segment in the ternary triangle, as well as the free energy at the endpoints of the line segment, the free energy $g(u)$ can be computed everywhere along the line segment according to the boundary-value problem given by

$$g_{uu} = u_1^2 g_{xx} + 2u_1 u_2 g_{xy} + u_2^2 g_{yy}, \quad a \leq u \leq b, \quad (9)$$

$$g(a) = A, \quad g(b) = B. \quad (10)$$

The right-hand side of Eq. (9) is a known function along the line segment, determined by Eqs. (7). The endpoints of the line segment correspond to $u = a$ and $u = b$, and A and B are the values of the free energy at the endpoints.

Figure 4 (left) shows a restricted domain bounded by line segments, for which we solve the boundary-value problem to obtain g on the binary axis at $x = 0$, solve Eq. (9) on each interior edge, and then solve the single LSPDE, Eq. (3), to yield the ternary free energy within the domain, as shown at right. The ternary free energy so computed agrees to within numerical accuracy with the test free energy from which the Rayleigh ratios $R_1(\mathbf{x})$, $R_2(\mathbf{x})$, and $R_3(\mathbf{x})$ were computed. The numerical method of solving the equation involved mapping the restricted domain to a right triangle, in order to make use of rectangular coordinates on a uniform grid, as described in the Appendix. Thus, Fig. 4 demonstrates that light scattering can be used to measure the free energy in restricted domains.

The extent to which A and B are known will vary with the system and data, and we now give some examples. One example is that of three such line segments bounding a sub-triangle within the composition triangle, having vertices A , B , and C . If $g(A)$, $g(B)$, and $g(C)$ are initially unknown, then the

LSPDE can be used to determine g to within a linear function. However, for a triangle with side AB on a binary axis, say, the y -axis, $g(A)$ and $g(B)$ may well be known since the binary solution free energy can be found by integrating a second-order ordinary differential equation from the light scattering intensity. In such a case the solution g to the LSPDE will be determined to within a linear function that has unknown slope in the x direction, in the absence of further information. Such further information might be gained, for example, by measuring the chemical potential $g + (1 - x)g_x - yg_y$ of the component with concentration denoted by x .

IV. SOLUTION OF THE LSPDE IN DOMAINS WITH CURVED BOUNDARIES

In some physical systems, it may be useful to integrate the LSPDE in a restricted domain that has a curved boundary. We now extend the considerations in Sec. III to apply to curved domain boundaries. In this case, the boundary-value problem given by Eqs. (9) and (10) is replaced by a series of initial and boundary-value problems. The following equations, which relate arc length derivatives to coordinate derivatives, determine a boundary condition for g on the curved portion of the boundary:

$$\dot{g}_x = \dot{x}g_{xx} + \dot{y}g_{xy}, \quad g_x(0) = g_x(x_0, 0), \quad (11)$$

$$\dot{g}_y = \dot{x}g_{xy} + \dot{y}g_{yy}, \quad g_y(L) = g_y(0, y_0), \quad (12)$$

$$\ddot{g} = (\dot{x}^2 g_{xx} + 2\dot{x}\dot{y}g_{xy} + \dot{y}^2 g_{yy}) + \ddot{x}g_x + \ddot{y}g_y, \quad (13)$$

$$g(0) = g(x_0, 0), \quad g(L) = g(0, y_0). \quad (14)$$

In Eqs. (11)–(14), the dot denotes differentiation with respect to arc length s along the curve, and the curve is envisioned as beginning on the x -axis at $(x_0, 0)$ at $s = 0$, and ending on the y -axis at $(0, y_0)$ at $s = L$, as shown in Fig. 5 (left). We assume that a light scattering ODE has been solved on each binary axis to provide the needed boundary data on those axes, including the values of $g(0)$ and $g(L)$ and their derivatives $g_x(0)$ and $g_y(L)$. Equations (13) and (14) are the generalization of the boundary-value problem given by Eqs. (9) and (10). The first derivatives of g now appear on the right-hand side of the differential equation. These quantities are not readily accessible, but they can be computed from the two initial-value problems given by Eqs. (11) and (12). We have applied this formulation to the example of a circular sector centered at the origin, as shown in Fig. 5 (center). Key details of the numerical solution methods are described in the Appendix.

V. ESTIMATED TIME REQUIRED TO MEASURE THE FREE ENERGY IN A RESTRICTED DOMAIN

We have performed simulations of noisy light scattering data that would be obtained from a ternary solution that is well-modeled by the regular solution free energy of mixing,

FIG. 5. Solution of the LSPDE for ternary composition domains having curved boundaries, by applying the three dielectric gradient approach on the curved boundary, and the one-gradient approach within the domain. As described here the method applies to curved boundaries that begin and end on the x - and y -axes, as shown at *left*. The example free energy, computed from light scattering for compositions in the circular sector at *center*, is shown as the darker surface at *right*. The computed free energy agrees with the original free energy, shown as the lighter surface.

in order to estimate the total measurement time required to deduce the free energy to a given tolerance, using a finite number of measurement compositions, for the restricted domain depicted in Fig. 6 (*upper left*). We chose parameters that yield a two-phase region nearby, shown in green, within which the present method would not apply directly; however, in earlier papers^{1,4} we have considered relevant supplemental methods.

FIG. 6. (Upper left) A restricted domain in the ternary composition triangle, outlined in red, for simulation of time requirements for light scattering free energy measurement using the three-gradient method. A two-phase region is shown in green. Thin dark blue lines are characteristics, while the thick blue line is the spinodal. (Upper right) Rayleigh ratio measurements (black dots) and Shepard-interpolated surface for use in PDE integration. The blue, green, and cyan lines correspond to use of dielectric gradients having different angles from the x -axis, as shown in the *inset*, enabling free energy determination on the internal diagonal boundary: $\pi/9$ (blue); $\pi/9 + \pi/6$ (green); $\pi/9 + \pi/3$ (cyan). (Lower left) Free energy error norm vs. the reciprocal of the light scattering measurement sample spacing, Δx_m^{-1} , for various values of $\Delta\theta$, all for fixed total dimensionless measurement time, $T = 10^{12}$. Each point in both lower left and lower right panels is the average of 20 simulation runs. (Lower right) Free energy error norm vs. the reciprocal of the light scattering measurement sample spacing, Δx_m^{-1} , for various values of the total dimensionless measurement time T , for fixed $\Delta\theta = \pi/6$. The red circle corresponds to the Rayleigh ratio results pictured at upper right. In both lower panels, the blue curve corresponds to $T = \infty$ for the given sample spacing, and thus represents the error due strictly to interpolation.

To conduct these simulations we used the methods and analysis described in Wahle *et al.*,² supplemented by simulated measurements for three assumed, distinctly directed dielectric gradients on the diagonal boundary within the ternary mixture, as indicated in Fig. 6 by the inset and the three Rayleigh ratio curves above the diagonal boundary in the upper right panel. In Wahle *et al.*,² the overall dimensionless measurement time T for the entire set of measurements is expressed in units of an instrumental time constant, τ_{inst} , that can be calculated or measured, as detailed there and described further below. We varied the angle, $\Delta\theta$, between the three assumed dielectric gradients, the linear spacing of the samples in concentration, Δx_m , and T . An example of the simulated excess Rayleigh ratio from such a domain is given in the upper right panel of Fig. 6, for which $\Delta\theta = \pi/6$, $\Delta x_m^{-1} = 25$, and $T = 10^{10}$, conditions that correspond to the red circle in the lower right panel of Fig. 6. For the purpose of the present simulation, we assumed that the binary axis free energies had been determined prior to such a ternary composition assay.

The simulations yield the average $\mathcal{L}_2$ -norm of the difference, δg , between the actual free energy and the free energy deduced using the light scattering PDE, as a function of sample spacing, for Poisson photon counting statistics in the absence of systematic errors, which are shown in the two lower panels in Fig. 6. Each point in these figures is the average of 20 simulation runs. The lower left-hand panel quantifies the measurement time and/or error advantage of increasing the angle between the dielectric gradients, $\Delta\theta$, while the lower right-hand panel shows error reduction that can be obtained by increasing overall measurement time T for fixed $\Delta\theta = \pi/6$. In each case, we note that the characteristic shape of the curves of $\mathcal{L}_2(\delta g)$ represents the fact that for each overall time T , use of a number of samples fewer than those corresponding to the “knee,” shown, for example, by the red circle, wastes measurement time, while use of more samples can waste sample, as described in more detail in Ref. 2. Thus, in the restricted triangular domain used, which extends from mole fraction 0 to 0.4 on both binary axes, the actual number of samples needed is $(n-1)(n)/2$, where $n = 0.4 \times \Delta x_m^{-1}$, or $n = 45$ for the case shown in the upper right panel of Fig. 6. It should be noted that more samples may nevertheless be needed, as one means of checking for systematic errors in sample preparation. Note that the samples pictured on the internal diagonal would need to be measured using all three

dielectric gradients, as shown by the cyan, green, and blue curves that correspond to the dielectric gradients shown in the inset. The lower right-hand plot shows that the error norm for the example given at upper right is approximately 10^{-4} .

How $T = 10^{10}$ corresponds to real time depends on τ_{inst} , which is itself a function of the input light intensity, the scattering volume, the detection solid angle, and the detector quantum efficiency, as detailed in Wahle *et al.*² In that work it is shown that

$$\tau_{inst} = \frac{\lambda^4}{\pi^2 \Omega_0 (I_{0,i}/h\nu) \varepsilon_{eff} f_{opt} \Delta\Omega_{det} V_{sca}}, \quad (15)$$

in which λ is the vacuum wavelength of the incident light, Ω_0 is the volume of a solvent molecule, $(I_{0,i}/h\nu)$ is the number of photons per unit area per unit time in the incident beam, ε_{eff} is the quantum efficiency of the detector, f_{opt} is an optical loss factor (e.g., due to reflections), $\Delta\Omega_{det}$ is the effective solid angle subtended by the scattering detector, and V_{sca} is the scattering volume.

For a modest laboratory light scattering setup having a single photomultiplier tube as the detector, it is estimated in Wahle *et al.*² that one can readily obtain $\tau_{inst} = 1.8 \mu s$, without optimizing design characteristics as suggested by Eq. (15). To extend the analysis in Wahle *et al.*² for the purpose of making an initial estimate of time requirements for the present, new method, we now presume that such an instrument is equipped with three incident light sources that result in suitably different dielectric gradients for the physical system of interest; clearly, such a possibility, as well as the appropriate choice of light sources, will be quite system-dependent. With this assumption, the Rayleigh ratio pattern of Fig. 6 (*right top*), corresponding to the red circle in Fig. 6 (*right bottom*), $T = 10^{10}$ now provides the estimate that 45 samples, spaced as pictured and measured for a total real time $1.8 \times 10^4 s$, that is, 5 h, would be sufficient to determine the free energy of mixing, over the pictured domain of compositions, to within an $\mathcal{L}_2$ -norm of 10^{-4} . Since the free energy itself in the units used² has an order of magnitude in the vicinity of 1, such a measurement time could result in a very accurate measurement, in principle. However, it is very important to emphasize that systematic errors that can occur in practice, such as could result from sample preparation difficulties including light scattering by dust, can make the actual time requirements considerably exceed this value, in a system-dependent manner. In other words, the above estimate is appropriate for clean samples having accurate compositions.

At the same time, we anticipate that the needed measurement time can be considerably reduced by addressing appropriate source, optical, and detector throughput parameters as specified by Eq. (15) for τ_{inst} . The above measurement time estimate also has not considered potential improvements in the numerical analysis procedure that may result, for example, by optimizing sample compositions with feedback from emerging free energy characteristics during measurement, and/or by use of statistical methods related to semiparametric regression²⁰ or regularization.

VI. DISCUSSION

The present method of establishing Dirichlet conditions for the free energy PDE on interior composition region boundaries assumes use of light scattering data corresponding to three, distinctly directed dielectric gradient vector fields, followed by light scattering data from just one dielectric gradient field as input for subsequent LSPDE solution. We have demonstrated a numerical method that constructs the needed Dirichlet boundary conditions, and have shown that the LSPDE can then be solved numerically within such a domain.

It is worth considering the possibility that a curved domain boundary could be a characteristic² of one or more of Eqs. (4)–(6). In such a case, one cannot prescribe *arbitrary* Dirichlet data and expect a well-posed problem; however, if one can prescribe the correct Dirichlet data, the problem will be well-posed. The present method would be viable in such a case, since the correct Dirichlet data are computed directly.

The present work begins to address measurement statistics considerations for the restricted domain problem, as we have done previously for single-phase liquid domains that touch all binary axes or ternary faces of the ternary or quaternary composition domains, respectively.^{2,3} However, we anticipate that substantial optimization can be achieved with further considerations of feedback and regularization, as indicated above. Such a statistical analysis will inform instrumentation and measurement wavelength choices for free energy measurement of given ternary mixtures, which will vary in the difficulty of rotating the dielectric gradient field by changing light scattering wavelength. For example, near absorption frequencies the dielectric response shows more rapid variation with frequency, as would a collection of driven, damped harmonic oscillators in a Sellmeier-type model for the dielectric response.²¹ Therefore, if the molecules in the mixture have different absorption patterns near practical light scattering wavelengths, in principle, one can rotate $\nabla\varepsilon$ by varying frequency. However, at the same time the absorption itself may limit practical optical path lengths and affect instrumentation design.

VII. SUMMARY AND CONCLUSIONS

In this work we have shown that, in principle, static light scattering can be used to measure the free energy in restricted ternary composition domains, thereby extending the LSPDE method to apply to a broader range of physical systems, including aqueous, multicomponent protein mixtures,^{5–8} micellar mixtures,^{12,13} microemulsions,^{9–13} polymer mixtures,¹⁴ and indeed any mixture in which solid or liquid crystalline phases prevent the liquid phase region from touching one or more binary axes of the ternary composition triangle. In addition we have begun to address corresponding statistical considerations related to experimental design, which suggest that such a method can potentially be practical. To bring the method into practice, the physical considerations of how to access the needed, distinctly directed dielectric gradient vectors are crucial and remain to be addressed.

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APPENDIX: COMPUTATIONAL DETAILS OF THE METHOD

1. Restricted triangular domain mapping and LSPDE solution

We compute solutions of Eq. (4) subject to appropriate boundary conditions on the triangular restricted domain shown in the left panel of Fig. 4. The physics behind Eq. (4) does not equip it with conventional boundary conditions. Rather, the solution g must be asymptotic to the ideal solution form near the boundary of the ternary triangle.¹ This condition is imposed explicitly by letting $g(x, y)$ be the sum of the ideal solution free energy plus the excess free energy $\phi(x, y)$,

$$g(x, y) = x \log x + y \log y + z \log z + \phi(x, y), \quad (\text{A1})$$

where $z = 1 - x - y$ and ϕ is assumed to be a twice continuously differentiable function throughout the domain. We then solve for ϕ instead of g . In this way, g will demonstrate the required asymptotic behavior near the ternary triangle boundary.

To compute solutions numerically, we first compute the solution on the boundary of the restricted domain, thus yielding a Dirichlet problem which determines the solution in the interior. The solution along each boundary segment can be computed independently of the data in the rest of the domain. Two corners of the restricted domain are assumed to lie on the y -axis, at $(0, y_1)$ and $(0, y_2)$, while the third corner at (x_0, y_0) may lie anywhere in the interior of the ternary triangle. It is assumed that the Rayleigh ratio R_1 , corresponding to the dielectric coefficient ε , is known throughout the restricted domain, including the boundary, as well as on the binary y -axis. In addition, we assume that the Rayleigh ratios R_2 and R_3 , corresponding to the dielectric coefficients δ and γ , respectively, are known along the two boundary segments that lie in the interior of the ternary triangle. Knowing a single Rayleigh ratio on the binary y -axis is sufficient to compute $\phi(0, y)$ up to an additive linear function from the one-dimensional boundary value problem¹ given by

$$\phi_{yy}(0, y) = \frac{\varepsilon_y^2(0, y)}{R_1(0, y)} - \frac{1}{y(1-y)}, \quad \phi(0, 0) = \phi(0, 1) = 0.$$

Furthermore, knowledge of the Rayleigh ratios corresponding to three distinctly directed dielectric coefficients along the interior boundary segments is sufficient to determine $\phi(x, y)$ there from Eqs. (7) and the boundary-value problem given by Eqs. (9) and (10). Thus, $\phi(x, y)$ can be computed everywhere on the boundary of the restricted domain.

Using the resulting Dirichlet problem, we can compute $g(x, y)$ in the restricted domain up to an additive linear function using a relaxation scheme similar to that introduced in Ross *et al.*¹ Relaxation schemes are commonly used for computing solutions of Dirichlet problems, such as those encountered in the present work.^{22,23} Our iterative method is a relaxation scheme, adapted to our nonlinear problem.

Since the boundary of the restricted domain does not necessarily align with a uniform grid, we introduce a coordinate transformation that maps the restricted domain into the larger triangle shown in Fig. 4. We let

$$\xi = \frac{x}{x_0} \quad \text{and} \quad \eta = \frac{x(y_1 - y_0) + x_0(y - y_1)}{x_0(y_2 - y_1)}. \quad (\text{A2})$$

The domain in the $\xi\eta$ -coordinate system is geometrically identical to the ternary triangle ($\xi, \eta \geq 0, \xi + \eta \leq 1$).

To compute solutions by way of finite differencing methods, we lay out a uniform grid over the triangular domain in the $\xi\eta$ -coordinate system, with grid size $\Delta = 1/n$. We define $\xi_i = i\Delta$ and $\eta_j = j\Delta$, with i and j taking on values between 0 and n . The triangular domain requires that $i + j \leq n$.

Because the Rayleigh ratio R_1 , corresponding to the dielectric coefficient ε , is assumed to be known everywhere in the interior of the restricted domain, we can compute its values directly at the points of the uniform grid in the transformed domain. In practice, the Rayleigh ratios may be known only at a discrete set of concentrations, in which case, the Rayleigh ratio can be interpolated to the uniform grid in the $\xi\eta$ -coordinate system.

The second derivatives $\phi_{\xi\xi}$, $\phi_{\eta\eta}$, and $\phi_{\xi\eta}$ can then be easily computed using second-order finite-difference approximations,

$$\phi_{\xi\xi}(\xi_i, \eta_j) = \frac{\phi_{i-1,j} - 2\phi_{i,j} + \phi_{i+1,j}}{\Delta^2} + O(\Delta^2), \quad (\text{A3})$$

$$\phi_{\eta\eta}(\xi_i, \eta_j) = \frac{\phi_{i,j-1} - 2\phi_{i,j} + \phi_{i,j+1}}{\Delta^2} + O(\Delta^2), \quad (\text{A4})$$

$$\phi_{\xi\eta}(\xi_i, \eta_j) = \frac{\phi_{i-1,j} + \phi_{i+1,j} + \phi_{i,j-1} + \phi_{i,j+1} - 2\phi_{i,j} - \phi_{i+1,j-1} - \phi_{i-1,j+1}}{2\Delta^2} + O(\Delta^2), \quad (\text{A5})$$

where $\phi_{ij} = \phi(\xi_i, \eta_j)$. We do not use the conventional symmetric formula for the mixed derivative since the necessary points, e.g., $\phi_{i+1,j+1}$, are not available near the

hypotenuse of the triangle. Equation (A1), together with the chain rule, yields the following expressions for the second derivatives, g_{xx} , g_{yy} , and g_{xy} , at the grid point

(ξ_i, η_j) :

$$g_{xx}(\xi_i, \eta_j) = \frac{1}{x_i} + \frac{1}{z_{ij}} + \frac{1}{x_0^2} \left[\hat{\phi}_{\xi\xi}(\xi_i, \eta_j) + 2 \frac{y_1 - y_0}{y_2 - y_1} \hat{\phi}_{\xi\eta}(\xi_i, \eta_j) + \left(\frac{y_1 - y_0}{y_2 - y_1} \right)^2 \hat{\phi}_{\eta\eta}(\xi_i, \eta_j) \right] + O(\Delta^2), \quad (\text{A6})$$

$$g_{yy}(\xi_i, \eta_j) = \frac{1}{y_{ij}} + \frac{1}{z_{ij}} + \frac{\hat{\phi}_{\eta\eta}(\xi_i, \eta_j)}{(y_2 - y_1)^2} + O(\Delta^2), \quad (\text{A7})$$

$$g_{xy}(\xi_i, \eta_j) = \frac{1}{z_{ij}} + \frac{1}{x_0(y_2 - y_1)} \times \left[\hat{\phi}_{\xi\eta}(\xi_i, \eta_j) + \frac{y_1 - y_0}{y_2 - y_1} \hat{\phi}_{\eta\eta}(\xi_i, \eta_j) \right] + O(\Delta^2), \quad (\text{A8})$$

where $x_i = x_0 \xi_i$, $y_{ij} = y_1 - (y_1 - y_0)\xi_i + (y_2 - y_1)\eta_j$, $z_{ij} = 1 - x_i - y_{ij}$, and $\hat{\cdot}$ denote the finite difference approximation of the corresponding second derivative, as given by Eqs. (A3)–(A5). The cartesian coordinate (x_i, y_{ij}) is that which is mapped into the grid point (ξ_i, η_j) under the transformation Eq. (A2). Substituting Eqs. (A6)–(A8) into Eq. (4) yields a finite difference equation at each interior grid point (ξ_i, η_j) ,

$$\frac{\varepsilon_y^2 \hat{g}_{xx} - 2\varepsilon_x \varepsilon_y \hat{g}_{xy} + \varepsilon_x^2 \hat{g}_{yy}}{\hat{g}_{xx} \hat{g}_{yy} - \hat{g}_{xy}^2} = R_1 \Big|_{(\xi_i, \eta_j)}. \quad (\text{A9})$$

We use a relaxation scheme to solve the set of finite-difference equations given by Eq. (A9). We sweep through the grid points repeatedly, updating the value of each ϕ_{ij} , in turn, until we achieve the desired accuracy. We begin with an initial guess function $\phi^1(\xi, \eta)$, and let ϕ_{ij}^k be the approximation of ϕ_{ij} as we begin the k th sweep of the grid. Suppose we are at a grid point (ξ_i, η_j) during the k th sweep. At this grid point, Eq. (A9) is satisfied only approximately. We make a correction C_{ij}^k to ϕ_{ij}^k so that the approximation becomes an equality. That is, we replace ϕ_{ij}^k in Eq. (A9) by $\phi_{ij}^{k+1} = \phi_{ij}^k + C_{ij}^k$, and ideally solve for C_{ij}^k . However, the expression that determines C_{ij}^k is nonlinear and not readily solved. If the iterations are in fact converging, we expect C_{ij}^k to be relatively small compared to ϕ_{ij}^k . Employing this notion, we linearize the equation that determines C_{ij}^k , which then allows us to solve for C_{ij}^k ,

$$C_{ij}^k = \frac{\Delta^2}{2} x_0^2 (y_2 - y_1)^2 \times \frac{R_1 [\hat{g}_{xx}^k \hat{g}_{yy}^k - (\hat{g}_{xy}^k)^2] - (\varepsilon_y^2 \hat{g}_{xx}^k - 2\varepsilon_x \varepsilon_y \hat{g}_{xy}^k + \varepsilon_x^2 \hat{g}_{yy}^k)}{R_1 [\alpha_1 \hat{g}_{xx}^k - \alpha_2 \hat{g}_{xy}^k + \alpha_3 \hat{g}_{yy}^k] - [\alpha_1 \varepsilon_x^2 - \alpha_2 \varepsilon_x \varepsilon_y + \alpha_3 \varepsilon_y^2]} \Big|_{(\xi_i, \eta_j)},$$

where $\alpha_1 = x_0^2$, $\alpha_2 = x_0(y_1 + y_2 - 2y_0)$, and $\alpha_3 = y_0^2 + y_1^2 + y_2^2 - y_0 y_1 - y_0 y_2 - y_1 y_2$.

We continue to make updates in this way as we repeatedly sweep through the grid points until the solution converges to within a specified tolerance. It should be noted that once ϕ_{ij}^k is updated in the k th sweep, the updated value is used for the

remainder of the sweep. Once the prescribed degree of accuracy is achieved, we construct an approximate solution g in the restricted domain,

$$g(x_i, y_{ij}) \approx x_i \log x_i + y_{ij} \log y_{ij} + z_{ij} \log z_{ij} + \tilde{\phi}_{ij},$$

where $\tilde{\phi}_{ij}$ is the approximation of ϕ_{ij} computed in the above iterations. Interpolation can then be used to approximate the free energy at any concentration in the restricted domain.

An example of such a computation is shown in the right panel of Fig. 4. To test the validity of the method, we make use of the regular solution model, in which the excess free energy has the simple form

$$\phi(x, y) = C_{xy}xy + C_{xz}xz + C_{yz}yz,$$

where C_{xy} , C_{xz} , and C_{yz} are prescribed constants. For convenience, we assume that the three dielectric gradients are constant, namely, $\nabla \varepsilon = \langle \sqrt{3}/2, 1/2 \rangle$, $\nabla \delta = \langle \sqrt{3}/(2\sqrt{2}), \sqrt{5}/(2\sqrt{2}) \rangle$, and $\nabla \gamma = \langle 1/2, \sqrt{3}/2 \rangle$. The free energy solution g and the three dielectric gradients are substituted into Eq. (4) to determine the three corresponding Rayleigh ratios, R_1 , R_2 , and R_3 . The chosen dielectric gradients and the corresponding Rayleigh ratios are then used as input in computing the solution ϕ , and consequently, g . Again, we assume that the Rayleigh ratio R_1 , corresponding to the dielectric coefficient ε , is known throughout the restricted domain and its boundary, as well as on the binary y -axis. In addition, it is assumed that the Rayleigh ratios R_2 and R_3 , corresponding to the dielectric coefficients δ and γ , respectively, are known along the two boundary segments that lie in the interior of the ternary triangle. For the solution shown in Fig. 4 (right), we let $x_0 = 0.5$, $y_0 = 0.15$, $y_1 = 0.05$, $y_2 = 0.3$, $C_{xy} = 1.0$, $C_{xz} = 0.5$, and $C_{yz} = 0.25$. We begin with the initial guess function $\phi^1 = 0$ for the relaxation scheme and we iterate until all updates to ϕ_{ij}^k over a given sweep are less than 10^{-8} .

Since the governing partial differential equation involves only second derivatives, the free energy g can be determined only up to an additive linear function. Thus, we must specify the values of g at three noncollinear points in the domain to select just one of the infinitely many solutions. When computing a solution over the entire ternary triangle, we fix the solution by setting g to zero at the three corners. However, this convention is not adequate for our present purposes because the condition at $(x, y) = (1, 0)$ does not come into play when solving over the restricted domain. Instead, we must select an alternative third point at which to prescribe the value of g . For the solution shown in Fig. 4 (right), we prescribed the value of g at the interior boundary corner of the restricted domain. Specifically, we set $g(x_0, y_0)$ to be equal to the value that we find it to be when solving over the entire ternary triangle, with $g = 0$ at the three corners. In this way, we can conveniently compare the solution computed from our present method over the restricted domain to that found by computing over the entire ternary triangle by a well-established method. We see from Fig. 4 (right) that the two solutions are in close agreement. The agreement can be made as close as we please by appropriately refining the grid and making the error tolerance of the relaxation scheme more stringent.

2. Circular sector boundary considerations and LSPDE solution

To test the method of Sec. IV, we constructed a simple example in which the curved portion of the boundary is a circular arc of radius r_0 , as shown in the center panel of Fig. 5. This specific domain was chosen because it can be conveniently treated in polar coordinates. We solved Eq. (4) subject to appropriate boundary conditions on the quarter-circular domain. To compute solutions numerically, we first compute the solution on the boundary of the limited domain, thus leaving us with a Dirichlet problem that determines the solution in the interior. The solution along each boundary segment can be computed independently of the data in the rest of the domain. As before, we assume that the Rayleigh ratio R_1 , corresponding to the dielectric coefficient ε , is known throughout the restricted domain, including the boundary, as well as on the binary x - and y -axes. In addition, it is assumed that the Rayleigh ratios R_2 and R_3 , corresponding to the dielectric coefficients δ and γ , respectively, are known along the curved portion of the boundary that lies in the interior of the ternary triangle.

Knowledge of the Rayleigh ratios corresponding to three distinctly directed dielectric gradients along the interior boundary curve is sufficient to determine $\phi(x, y)$ there from Eqs. (7) and Eqs. (11)–(14). The free energy g is determined on the boundary curve by Eq. (13), subject to boundary conditions (14). Each term on the right-hand side of Eq. (13) is accessible. Since it is assumed that three distinct Rayleigh ratios are known on the boundary curve, the second derivatives, g_{xx} , g_{yy} , and g_{xy} , can be determined there from Eqs. (7), while g_x and g_y can be computed from the initial-value problems Eqs. (11) and (12), respectively. Thus, we solve, in turn, the initial-value problems given by Eqs. (11) and (12), followed by the boundary-value problem given by Eqs. (13) and (14) to determine the free energy g on the curved boundary.

To compute g along the boundary curve, we parametrized the curve with respect to arc length s . We set $x(s) = r_0 \cos \theta(s)$ and $y(s) = r_0 \sin \theta(s)$, where $\theta(s) = s/r_0$. The first two derivatives of x and y with respect to s are

$$\begin{aligned}\dot{x}(s) &= -\sin \theta(s), & \dot{y}(s) &= \cos \theta(s), \\ \ddot{x}(s) &= -\frac{\cos \theta(s)}{r_0}, & \ddot{y}(s) &= -\frac{\sin \theta(s)}{r_0}.\end{aligned}$$

We lay out a uniform grid on the curve with grid size $\Delta s = L/n$, where $L = \pi r_0/2$ is the arc length of the curve. We define $s_i = i\Delta s$, with i taking on values between 0 and n . The corresponding concentrations are $x_i = r_0 \cos \theta(s_i)$, $y_i = r_0 \sin \theta(s_i)$, and $z_i = 1 - x_i - y_i$.

We first solve the initial-value problems, Eqs. (11) and (12), to determine g_x and g_y on the boundary curve. Equations (7) determine g_{xx} , g_{yy} , and g_{xy} everywhere on the curve, except at the endpoints, since they lie on the binary axes. The values of g_{xx} and g_{xy} are needed at the endpoint that sits on the binary x -axis, and the values of g_{yy} and g_{xy} are needed at the endpoint that sits on the binary y -axis. Since we now have the solution on the binary axes at hand, g_{xx} and g_{yy} can be approximated

on their respective axes using conventional finite differencing formulas. The values of g_{xy} at the endpoints of the curve are approximated by third-order extrapolation formulas,

$$g_{xy}(0) = 3[g_{xy}(s_1) - g_{xy}(s_2)] + g_{xy}(s_3) + O(\Delta s^3)$$

and

$$g_{xy}(L) = 3[g_{xy}(s_{n-1}) - g_{xy}(s_{n-2})] + g_{xy}(s_{n-3}) + O(\Delta s^3).$$

The right-hand sides of Eqs. (11) and (12) are now fully determined where needed. Rather than computing g directly, we compute ϕ , as defined in Eq. (A1). The second derivatives of ϕ at the grid points on the boundary curve are given by

$$\begin{aligned}\phi_{xx}(s_i) &= g_{xx}(s_i) - \frac{1}{x_i} - \frac{1}{z_i}, \\ \phi_{yy}(s_i) &= g_{yy}(s_i) - \frac{1}{y_i} - \frac{1}{z_i}, \\ \phi_{xy}(s_i) &= g_{xy}(s_i) - \frac{1}{z_i}.\end{aligned}$$

We outline in detail our algorithm for solving the initial-value problem Eq. (11), while the initial-value problem Eq. (12) is solved in a similar manner.

We use a fourth-order Runge-Kutta method to compute solutions of Eq. (11). The right-hand side of the equation is considered as a function of s alone along the boundary curve. In terms of ϕ , the equation is

$$\dot{\phi}_x = f(s) = \dot{x}\phi_{xx} + \dot{y}\phi_{xy}.$$

The initial condition $\phi_x(0)$ can be easily approximated from the computed solution on the binary axis using conventional finite differencing. Then,

$$\phi_x(s_i) = \phi_x(s_{i-1}) + \frac{\Delta s}{6}(k_1 + 2k_2 + 2k_3 + k_4),$$

for $i = 1, \dots, n-1$, where

$$\begin{aligned}k_1 &= f(s_{i-1}) = \dot{x}_{i-1}\phi_{xx}(s_{i-1}) + \dot{y}_{i-1}\phi_{xy}(s_{i-1}), \\ k_2 &= f(s_{i-1/2}) = \dot{x}_{i-1/2}\phi_{xx}(s_{i-1/2}) + \dot{y}_{i-1/2}\phi_{xy}(s_{i-1/2}), \\ k_3 &= k_2, \\ k_4 &= f(s_i) = \dot{x}_i\phi_{xx}(s_i) + \dot{y}_i\phi_{xy}(s_i),\end{aligned}$$

and $s_{i-1/2} = s_i - \Delta s/2$. We can compute the values of f at the intermediate points, $s_{i-1/2}$, directly since it is assumed that R_1 , R_2 , and R_3 , and consequently, g_{xx} , g_{yy} , and g_{xy} , are known everywhere along the boundary curve. In practice, with discrete data, it may be necessary to approximate the intermediate values using an interpolation scheme. We compute g_{xx} , g_{yy} , and g_{xy} only at the grid points and then used cubic Lagrange interpolation to approximate the intermediate values for the solution shown in Fig. 5 (left). As usual, the fourth-order Runge-Kutta method yields highly accurate solutions. The initial-value problem Eq. (12) that determines ϕ_y can be solved in the same way, except that we must descend through the indices, from $i = n$ to $i = 1$.

Once ϕ_x and ϕ_y have been computed on the boundary curve, we are equipped to compute ϕ on the boundary curve from the second-order boundary-value problem given by

Eqs. (13) and (14). In terms of ϕ , the boundary-value problem is given by

$$\ddot{\phi} = (\dot{x}^2 \phi_{xx} + 2\dot{x}\dot{y} \phi_{xy} + \dot{y}^2 \phi_{yy}) + \ddot{x} \phi_x + \ddot{y} \phi_y, \quad (\text{A10})$$

$$\phi(0) = \phi(x_0, 0), \quad \phi(L) = \phi(0, y_0). \quad (\text{A11})$$

The solution ϕ can be computed using a straightforward finite-differencing scheme. At this point, $\phi(x, y)$ is known everywhere on the boundary of the restricted domain, thus yielding a Dirichlet problem that determines g in the interior of the restricted domain.

To compute g in the interior of the restricted domain, it is convenient to make use of the polar coordinate system, in which the restricted domain is rectangular ($0 \leq r \leq r_0$, $0 \leq \theta \leq \pi/2$). We lay out a uniform grid in each direction:

$$r_i = i \Delta r \text{ for } i = 0, 1, \dots, m, \text{ where } \Delta r = r_0/m,$$

$$\theta_j = j \Delta \theta \text{ for } j = 0, 1, \dots, n, \text{ where } \Delta \theta = \pi/(2n).$$

The corresponding cartesian coordinates are $x_{ij} = r_i \cos \theta_j$ and $y_{ij} = r_i \sin \theta_j$. Again, it may be necessary in practice to interpolate discrete input data to the uniform polar grid. We reserve that consideration for future work. Here, it is assumed that the Rayleigh ratio R_1 and the boundary data are known where needed, in which case, their values can be computed exactly on the uniform polar grid.

The problem, as described above, determines the free energy g in the restricted domain up to an additive linear function. As in Subsection I of the Appendix, we must prescribe the value of g at three non-collinear points in the domain. Here, it suffices to set g equal to zero at the three corners of the ternary triangle. These values serve as boundary conditions for the ordinary differential equations that determine the free energy on the binary x - and y -axes, thus selecting one of the infinitely many linear functions that can be added to g .

We use a relaxation scheme similar to that described in Subsection I of the Appendix to compute the excess free energy ϕ , from which the free energy g can be obtained using Eq. (A1). The derivatives of ϕ with respect to the polar coordinates, r and θ , are computed using the following conventional second-order finite-differencing formulas:

$$\phi_r(r_i, \theta_j) = \frac{\phi_{i+1,j} - \phi_{i-1,j}}{2\Delta r} + O(\Delta r^2), \quad (\text{A12})$$

$$\phi_\theta(r_i, \theta_j) = \frac{\phi_{i,j+1} - \phi_{i,j-1}}{2\Delta \theta} + O(\Delta \theta^2), \quad (\text{A13})$$

$$\phi_{rr}(r_i, \theta_j) = \frac{\phi_{i+1,j} - 2\phi_{i,j} + \phi_{i-1,j}}{\Delta r^2} + O(\Delta r^2), \quad (\text{A14})$$

$$\phi_{\theta\theta}(r_i, \theta_j) = \frac{\phi_{i,j+1} - 2\phi_{i,j} + \phi_{i,j-1}}{\Delta \theta^2} + O(\Delta \theta^2), \quad (\text{A15})$$

$$\begin{aligned} \phi_{r\theta}(r_i, \theta_j) &= \frac{\phi_{i+1,j+1} - \phi_{i+1,j-1} - \phi_{i-1,j+1} + \phi_{i-1,j-1}}{4\Delta r \Delta \theta} \\ &\quad + O(\Delta r^2, \Delta \theta^2), \end{aligned} \quad (\text{A16})$$

where $\phi_{ij} = \phi(r_i, \theta_j)$. Equation (A1), together with the chain rule, yields the following expressions for the second derivatives, g_{xx} , g_{yy} , and g_{xy} , at the grid point (r_i, θ_j) :

$$\begin{aligned} g_{xx}(r_i, \theta_j) &= \frac{1}{x_{ij}} + \frac{1}{z_{ij}} + (\cos \theta_j)^2 \hat{\phi}_{rr} - \frac{\sin 2\theta_j}{r_i^2} (r_i \hat{\phi}_{r\theta} - \hat{\phi}_\theta) \\ &\quad + \frac{(\sin \theta_j)^2}{r_i^2} (\hat{\phi}_{\theta\theta} + r_i \hat{\phi}_r) + O(\Delta r^2, \Delta \theta^2), \end{aligned} \quad (\text{A17})$$

$$\begin{aligned} g_{yy}(r_i, \theta_j) &= \frac{1}{y_{ij}} + \frac{1}{z_{ij}} + (\sin \theta_j)^2 \hat{\phi}_{rr} + \frac{\sin 2\theta_j}{r_i^2} (r_i \hat{\phi}_{r\theta} - \hat{\phi}_\theta) \\ &\quad + \frac{(\cos \theta_j)^2}{r_i^2} (\hat{\phi}_{\theta\theta} + r_i \hat{\phi}_r) + O(\Delta r^2, \Delta \theta^2), \end{aligned} \quad (\text{A18})$$

$$\begin{aligned} g_{xy}(r_i, \theta_j) &= \frac{1}{z_{ij}} + \frac{\sin 2\theta_j}{2r_i^2} (r_i^2 \hat{\phi}_{rr} - \hat{\phi}_{\theta\theta} - r_i \hat{\phi}_r) \\ &\quad + \frac{\cos 2\theta_j}{r_i^2} (r_i \hat{\phi}_{r\theta} - \hat{\phi}_\theta) + O(\Delta r^2, \Delta \theta^2), \end{aligned} \quad (\text{A19})$$

where $x_{ij} = r_i \cos \theta_j$, $y_{ij} = r_i \sin \theta_j$, $z_{ij} = 1 - x_{ij} - y_{ij}$, and $\hat{\cdot}$ denote the finite difference approximation of the corresponding derivative at the grid point (r_i, θ_j) , as given by Eqs. (A12)–(A16).

Substituting Eqs. (A17)–(A19) into Eq. (4) yields a finite difference equation at each interior grid point (r_i, θ_j) ,

$$\frac{\varepsilon_y^2 \hat{g}_{xx} - 2\varepsilon_x \varepsilon_y \hat{g}_{xy} + \varepsilon_x^2 \hat{g}_{yy}}{\hat{g}_{xx} \hat{g}_{yy} - \hat{g}_{xy}^2} = R_1 \Big|_{(r_i, \theta_j)}. \quad (\text{A20})$$

We use a relaxation scheme to solve the set of finite-difference equations given by (A20). As in Subsection I of the Appendix, we sweep through the grid points repeatedly, updating the value of each ϕ_{ij} , in turn, until the desired accuracy is achieved. We begin with an initial guess function $\phi^1(r, \theta)$, and let ϕ_{ij}^k be the approximation of ϕ_{ij} as we begin the k th sweep of the grid. Suppose we are at a grid point (r_i, θ_j) during the k th sweep. At this grid point, Eq. (A20) is satisfied only approximately. We make a correction C_{ij}^k to ϕ_{ij}^k so that the approximation becomes an equality. That is, we replace ϕ_{ij}^k in Eq. (A20) by $\phi_{ij}^{k+1} = \phi_{ij}^k + C_{ij}^k$, and ideally solve for C_{ij}^k . However, the expression that determines C_{ij}^k is nonlinear and is not readily solved. If the iterations are in fact converging, we expect C_{ij}^k to be relatively small compared with ϕ_{ij}^k . Employing this notion, we linearize the equation that determines C_{ij}^k , which then allows us to solve for C_{ij}^k ,

$$\begin{aligned} C_{ij}^k &= \frac{1}{2} \\ &\quad \cdot \frac{R_1 [\hat{g}_{xx}^k \hat{g}_{yy}^k - (\hat{g}_{xy}^k)^2] - (\varepsilon_y^2 \hat{g}_{xx}^k - 2\varepsilon_x \varepsilon_y \hat{g}_{xy}^k + \varepsilon_x^2 \hat{g}_{yy}^k)}{R_1 [\alpha_1 \hat{g}_{xx}^k - \alpha_2 \hat{g}_{xy}^k + \alpha_3 \hat{g}_{yy}^k] - [\alpha_1 \varepsilon_x^2 - \alpha_2 \varepsilon_x \varepsilon_y + \alpha_3 \varepsilon_y^2]} \Big|_{(r_i, \theta_j)}, \end{aligned}$$

where

$$\alpha_1 = \alpha_1(r, \theta) = \frac{\sin^2 \theta}{\Delta r^2} + \frac{\cos^2 \theta}{r^2 \Delta \theta^2},$$

$$\alpha_2 = \alpha_2(r, \theta) = \sin 2\theta \left(\frac{1}{\Delta r^2} - \frac{1}{r^2 \Delta \theta^2} \right),$$

and

$$\alpha_3 = \alpha_3(r, \theta) = \frac{\cos^2 \theta}{\Delta r^2} + \frac{\sin^2 \theta}{r^2 \Delta \theta^2}.$$

We continue to make updates in this way as we repeatedly sweep through the grid points until the solution converges to within a specified tolerance. It should be noted that once ϕ_{ij}^k is updated in the k th sweep, the updated value is used for the remainder of the sweep. Once the prescribed degree of accuracy is achieved, we construct an approximate solution g in the restricted domain,

$$g(x_{ij}, y_{ij}) \approx x_{ij} \log x_{ij} + y_{ij} \log y_{ij} + z_{ij} \log z_{ij} + \tilde{\phi}_{ij},$$

where $\tilde{\phi}_{ij}$ is the approximation of ϕ_{ij} computed in the above iterations. Interpolation can then be used to approximate the free energy at any concentration in the restricted domain.

An example of such a computation is shown in the right panel of Fig. 5. To test the validity of the method, we make use of the regular solution model, in which the excess free energy has the simple form

$$\phi(x, y) = C_{xy}xy + C_{xz}xz + C_{yz}yz,$$

where C_{xy} , C_{xz} , and C_{yz} are prescribed constants. For convenience, we assume that the three dielectric gradients are constant, namely, $\nabla \varepsilon = \langle \sqrt{3}/2, 1/2 \rangle$, $\nabla \delta = \langle \sqrt{3}/(2\sqrt{2}), \sqrt{5}/(2\sqrt{2}) \rangle$, and $\nabla \gamma = \langle 1/2, \sqrt{3}/2 \rangle$. The free energy solution g and the three dielectric gradients are substituted into Eq. (4), to determine the three corresponding Rayleigh ratios, R_1 , R_2 , and R_3 . The chosen dielectric gradients and the corresponding Rayleigh ratios are then used as input in computing the solution ϕ , and consequently, g . Again, we assume that the Rayleigh ratio R_1 , corresponding to the dielectric coefficient ε , is known throughout the restricted domain and its boundary, as well as on the binary

x - and y -axes. In addition, it is assumed that the Rayleigh ratios R_2 and R_3 , corresponding to the dielectric coefficients δ and γ , respectively, are known on the curved portion of the boundary that lies in the interior of the ternary triangle. For the solution shown in Fig. 5 (right), we let $C_{xy} = 1.0$, $C_{xz} = 0.5$, $C_{yz} = 0.25$, and $r_0 = 0.5$. We began with the initial guess function $\phi^1 = 0$ for the relaxation scheme and we iterated until all updates to ϕ_{ij} over a given sweep were less than 10^{-8} .

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