

Supplementary Material on “Polyelectrolyte Complex Coacervation: Effects of Concentration Asymmetry”

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(Dated: April 18, 2018)

I. PHASE DIAGRAM CONSTRUCTION

A. A general method

For an asymmetric mixture of polycation and polyanion solutions, there are four explicit charged components – polycation, polyanion, cation and anion. At a fixed l_B , using the Gibbs phase rule, we have two degrees of freedom for two-phase coexistence – this is reflected by the fact that there are nine independent variables $\rho_{p+}^{I/II}$, $\rho_{p-}^{I/II}$, $\rho_+^{I/II}$, $\rho_-^{I/II}$ and Ψ_G but only seven equations (four for equality of *electrochemical potential* for the four components, one for pressure equality, and two for charge neutrality in the coexisting phases). By virtue of charge neutrality, the concentration of one of the four components can be expressed in terms of the concentrations of the other three components; without loss of generality, here we choose ρ_{p+} , ρ_{p-} and ρ_+ as the three independent variables, and the anion concentration is thus $\rho_- = \rho_{p+} - \rho_{p-} + \rho_+$. The fact that there are two degrees of freedom indicates that, at a given l_B , the coexisting concentrations ($\rho_{p+}^I, \rho_{p-}^I, \rho_+^I$) and ($\rho_{p+}^{II}, \rho_{p-}^{II}, \rho_+^{II}$) form a two-dimensional (2D) binodal *surface* in the three-dimensional (3D) polycation-polyanion-cation concentration ($\rho_{p+}-\rho_{p-}-\rho_+$) phase diagram. The *critical line* (denoted by $\rho_{p+,c}, \rho_{p-,c}, \rho_{+,c}$) is one special curve on the binodal surface and is defined by $\rho_{p+}^I = \rho_{p+}^{II}$, $\rho_{p-}^I = \rho_{p-}^{II}$ and $\rho_+^I = \rho_+^{II}$. Moreover, the Galvani potential Ψ_G remains finite except for the symmetric mixture with $\rho_{p+}^I = \rho_{p-}^I$ and $\rho_{p+}^{II} = \rho_{p-}^{II}$ and the critical line where the coexisting phases merge together.

For given N and l_B , since there are two degrees of freedom, we need to fix two of the nine variables to solve the other seven variables. For convenience, here we fix ρ_{p+}^{II} and ρ_{p-}^{II} and solve the other six concentrations in the coexisting phases $\rho_i^{I/II}$ and the Galvani potential Ψ_G numerically by using the Newton-Raphson method[1] with the residual error in $\max\{|\mu_i^I - \mu_i^{II} + ez_i\Psi_G|, |P^I - P^{II}|, |\sum_i \rho_i^{I/II} z_i|\} < 10^{-12}$. The 2D binodal surface is then constructed by scanning all possible values of ρ_{p+}^{II} and ρ_{p-}^{II} .

B. An alternative method

While the general procedure presented above is convenient to construct the 2D binodal surface in the 3D $\rho_{p+}-\rho_{p-}-\rho_+$ phase diagram for an asymmetric polycation and polyanion mixture, it is different to be implemented numerically to examine the phase-separation evolution (including the volume fraction of the coexisting phase, the concentrations of different components in each phase and the Galvani potential) along some *pre-specified* varying paths in the 3D phase diagram. Here we present an alternative technique for such a purpose.

Supposing that $(\bar{\rho}_{p+}, \bar{\rho}_{p-}, \bar{\rho}_+)$ is a point on the specified varying path and this point is located in the phase-separated region, the single homogeneous mixture will phase-separate into a PE-poor phase and a coexisting PE-rich phase, and the coexisting concentrations $\rho_i^{I/II}$ and the volume fraction of the PE-poor phase x can be determined by the lever rule $\bar{\rho}_i = x\rho_i^I + (1-x)\rho_i^{II}$. Therefore, we have a total of ten variables ($\rho_{p+}^{I/II}, \rho_{p-}^{I/II}, \rho_+^{I/II}, \rho_-^{I/II}, \Psi_D, x$), which can be solved for from ten equations – four for electrochemical potential equality for four all components, one for pressure equality, two for charge neutrality, and three for mass conservation of three components (mass conservation for the fourth component is automatically satisfied because of charge neutrality). Likewise, the ten variables are obtained by numerically solving the ten independent equations via the Newton-Raphson method[1]. The evolution of the phase separation is then constructed by scanning all points on this specified path. We use this procedure to examine the phase-separation evolutions along the asymmetry factor r , the extra-salt concentration $\rho_{s,0}$ and the initial PE concentration $\rho_{p,0}$ for the concentration-asymmetric mixtures.

II. EVOLUTION IN THE CONCENTRATIONS FOR A TITRATING PATH OF SYSTEM 2

While the volume fraction of the PE-poor phase x exhibits two distinct scenarios for different titrating paths (as shown by Fig. 5 in the main text), the concentrations of each component in the coexisting phases show qualitatively similar behaviors. Because of the mixture is

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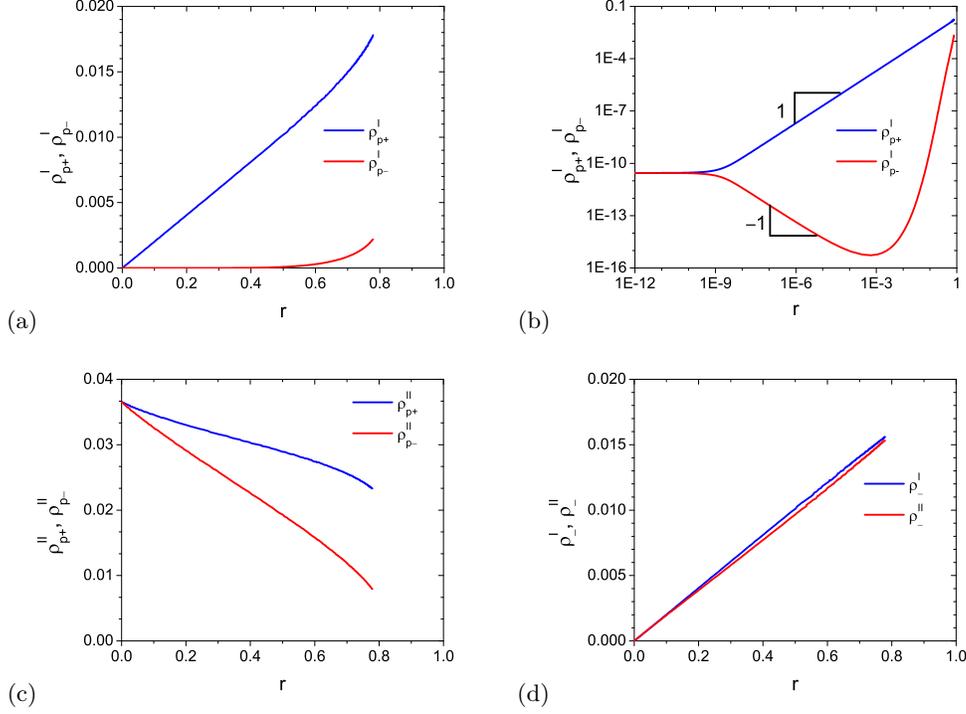


FIG. 1. Polycation and polyanion concentrations in the PE-poor phase, $\rho_{p\pm}^I$, (a) in the linear-linear plot and (b) in the log-log plot respectively. (c) Polycation and polyanion concentrations in the PE-rich phase, $\rho_{p\pm}^{II}$. (d) Concentrations of small cation and small anion in the coexisting phases, $\rho_{\pm}^{I/II}$. $\rho_{p,0} = 0.02$ and $l_B = 0.5$ for all figures.

symmetric with respect to r by exchanging $\rho_{p+} \leftrightarrow \rho_{p-}$ and $\rho_+ \leftrightarrow \rho_-$, hereafter we focus on the $r \geq 0$ region where polycation is the major PE species and anion is the only type of small ions. First, we recall that, the overall concentrations of polycation and anion increase linearly with r , i.e., $\bar{\rho}_{p+} = (1+r)\rho_{p,0}/2$ and $\bar{\rho}_- = r\rho_{p,0}$, and the overall polyanion concentration decreases linearly with r , i.e., $\bar{\rho}_{p-} = (1-r)\rho_{p,0}/2$.

Taking path 1 in Fig. 5 of the main text (i.e., with $\rho_{p,0} = 0.02$) as an example, in Figs. 1(a)-(b) we show both polycation and polyanion concentrations in the PE-poor phase, $\rho_{p\pm}^I$, as functions of r . Fig. 1(a) shows that the polycation concentration $\rho_{p+}^I \propto r$ and the polyanion concentration $\rho_{p-}^I \approx 0$ over a wide range of r except for that close to the phase boundary r^* . The log-log plot in Fig. 1(b) further shows that ρ_{p-}^I actually exhibits a minimum at $r \equiv r_m \approx 10^{-3}$. The region with $r < r_m$ can further be divided into two sub-regions. For very small r , $\rho_{p-}^I \approx c - b_1 r$ with $c \equiv \rho_{p-}^I(r=0)$; this is easy to be understood via the Taylor expansion. For slightly larger r , $\rho_{p-}^I \approx b_2/r$ with b_1 and b_2 are two constants. For $r > r_m$, ρ_{p-}^I starts to increase with r with a larger rate than ρ_{p+}^I . While ρ_{p-}^I is generally very small in magnitude over a wide range of r and is hard to be accurately measured in experiment, it has a direct and experimentally observable consequence – the Galvani potential, as discussed detailedly in the main text (see

Fig. 6(b) of the main text).

In Fig. 1(c), we show both polycation and polyanion concentrations in the PE-rich phase, $\rho_{p\pm}^{II}$, as a function of r . First, both $\rho_{p\pm}^{II}$ decreases monotonically with r , indicating the PE-rich phase become less concentrated with increasing asymmetry. The polyanion concentration ρ_{p-}^{II} decreases faster than ρ_{p+}^{II} . By noticing the lever rule $\bar{\rho}_i = x\rho_i^I + (1-x)\rho_i^{II}$ and the behaviors of x and $\rho_{p\pm}^I$ discussed above, we see the decrease of the polyanion concentration ρ_{p-}^{II} is mainly because of the decrease of $\bar{\rho}_{p-}$ with r . The decrease of ρ_{p+}^{II} is mainly because a substantial amount of added polycations are partitioned into the PE-poor phase.

Since anion is the only type of small ions for $r > 0$, in Fig. 1(d) we show the anion concentration in the PE-poor phase ρ_-^I and in the PE-rich phases ρ_-^{II} . Because the overall anion concentration $\bar{\rho}_-$ increases linearly with r , i.e., $\bar{\rho}_- = r\rho_{p,0}$, the anion concentrations in both phases $\rho_-^{I/II}$ likewise increase approximately linearly with r in the entire phase-separated region. Further, for the sake of the translational entropy, the anion concentrations in the coexisting phases are approximately equal, i.e., $\rho_-^I \approx \rho_-^{II}$. Finally, in the PE-poor phase, because the polyanion concentration is generally very close to 0, the polycation concentration is approximately equal to the small anion concentration over a large range of r , i.e., $\rho_{p+}^I \approx \rho_-^I$.

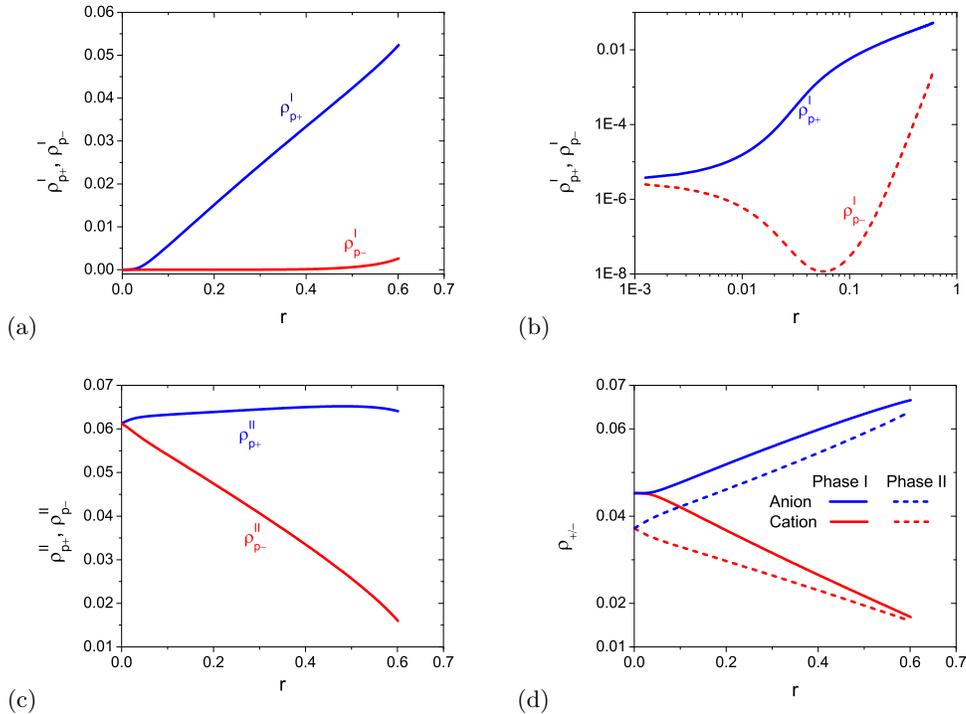


FIG. 2. Polycation and polyanion concentrations in the PE-poor phase, $\rho_{p\pm}^I$, (a) in the linear-linear plot and (b) in the log-log plot. (c) Polycation and polyanion concentrations in the PE-rich phase $\rho_{p\pm}^{II}$. (d) Concentrations of small cation and small anion in the coexisting phases $\rho_{\pm}^{I/II}$. $\rho_{p,0} = 0.08$ and $\rho_{s,0} = 0$ for all figures.

III. EFFECT OF r FOR MIXTURE WITHOUT EXTRA SALT AT LARGE $\rho_{p,0}$

As shown in Fig. 7(a) of the main text, for mixtures without extra salt, the volume fraction of the PE-poor phase x exhibits qualitatively different behavior for mixtures at small $\rho_{p,0}$ and at large $\rho_{p,0}$, it is thus interesting to examine how different are the concentrations of each component in the coexisting phases. Since the small $\rho_{p,0}$ case has been detailedly studied in the main text, here we restrict to the large $\rho_{p,0}$ case and highlight the major similarities and differences, taking the mixture with $\rho_{p,0} = 0.08$ as an example.

In Figs. 2(a)-(b), we show both PE concentrations in the PE-poor phase $\rho_{p\pm}^I$ as a function of the asymmetry factor r in a linear-linear plot and in a log-log plot respectively. Similar to the $\rho_{p,0} = 0.006$ case (see Fig. 8(a) in the main text), for $r \lesssim 0.02$, ρ_{p+}^I remains close 0 and depends weakly on r . For $r \gtrsim 0.02$, ρ_{p+}^I starts to increase approximately linearly with r . On the other hand, the polyanion concentration ρ_{p-}^I remains close to 0 over a wide r regime except for that close to the boundary r^* . The log-log plot of Fig. 2(b) shows that ρ_{p-}^{II} exhibits a minimum at some r ; this is similar to the system studied in the previous section and the asymmetric case with $\rho_{p,0} = 0.006$ and $\rho_{s,0} = 0$ in the main text.

Next, Fig. 2(c) shows both PE concentrations in the

PE-rich phase $\rho_{p\pm}^{II}$ as a function of r . The polycation concentration ρ_{p+}^{II} increases slightly with r for small and intermediate r and decreases slightly when r is close to r^* ; the magnitude of the variation, however, is very small. While the variation trend of ρ_{p+}^{II} seems to be somewhat different for this case and the case in the main text (see Fig. 8(b) there), we notice the common feature of both systems, i.e., ρ_{p+}^{II} is weakly dependent on r . On the other hand, the minor PE concentration ρ_{p-}^{II} decreases approximately linearly with r ; this is qualitatively similar to the case with $\rho_{p,0} = 0.006$ over a wide range of r .

Finally, in Fig. 2(d), we show both small ion concentrations in the coexisting phases $\rho_{\pm}^{I/II}$ as a function of r . We see that the distinction of the two r regimes in $\rho_{\pm}^{I/II}$ becomes less clear comparing with the $\rho_{p,0} = 0.006$ case (see Fig. 8(c) in the main text). Moreover, the cation concentration in the PE-poor phase is always higher than that in the PE-rich phase, i.e., $\rho_{+}^I > \rho_{+}^{II}$; this is qualitatively consistent to the $\rho_{p,0} = 0.006$ case. The anion concentration in the PE-poor phase is also higher than that in the PE-rich phase, i.e., $\rho_{-}^I > \rho_{-}^{II}$; this is in opposite to the $\rho_{p,0} = 0.006$ case for most r .

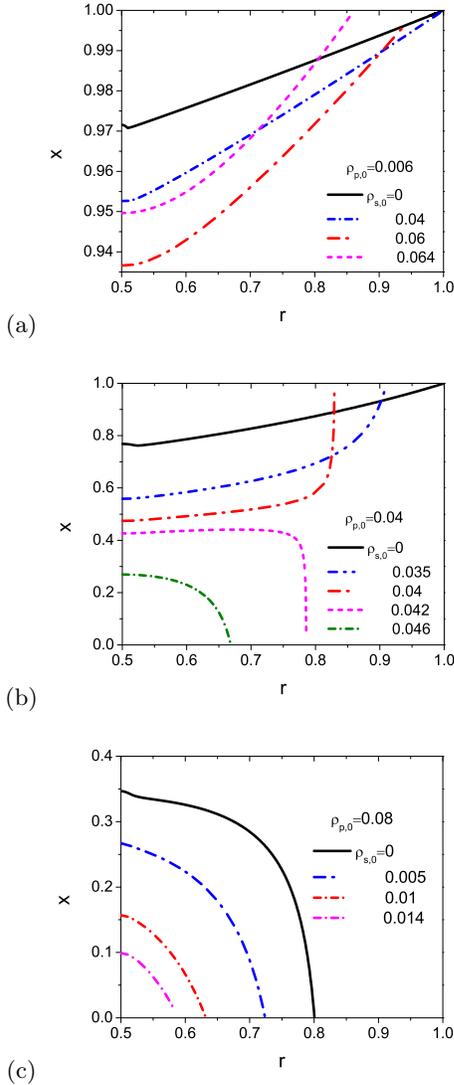


FIG. 3. Volume fraction of the PE-poor phase x vs. the asymmetry factor r for mixtures with finite extra-salt concentrations $\rho_{s,0}$ at (a) $\rho_{p,0} = 0.006$, (b) 0.04 and (c) 0.08 respectively.

IV. EFFECT OF r FOR MIXTURES WITH FINITE $\rho_{s,0}$

Here we examine how the asymmetry factor r affect the phase behavior for the polycation and polyanion mixtures with *finite* extra-salt, i.e., $\rho_{s,0} > 0$. In Figs. 3(a), (b) and (c), we show the volume fraction of the PE-poor phase x vs. r for mixtures with various $\rho_{s,0}$ at fixed $\rho_{p,0} = 0.006$, 0.04 and 0.08, respectively. First, for all three $\rho_{p,0}$, the boundary asymmetry factor r^* where the mixture enters into a single-phase is always smaller for mixtures with larger $\rho_{s,0}$. Second, for all mixtures at small $\rho_{p,0} = 0.006$ (see Fig. 3(a)), x is 1 at r^* , indicating that it is the *PE-rich* phase that vanishes at r^* . For all mixtures at large $\rho_{p,0} = 0.08$ (see Fig. 3(c)), $x = 0$ at r^* and thus it is

always the *PE-poor* phase that vanishes herein. Finally, for the intermediate $\rho_{p,0} = 0.04$ (see Fig. 3(b)), while at small $\rho_{s,0}$ it is the PE-poor phase that vanishes at r^* , for large $\rho_{s,0}$ it is the PE-rich phase that vanishes. In addition, the slope of r close to r^* becomes very sharp when $\rho_{s,0}$ is close to the critical line (see the red and magenta curves in Fig. 3(b)).

We thus construct the r^* - $\rho_{p,0}$ phase diagram for mixtures at finite $\rho_{s,0} = 0.01$ and 0.04, respectively, as shown by the blue and red curves in Fig. 7(b) of the main text. We see that mixtures with larger $\rho_{s,0}$ exhibits a narrower phase-separated window along r .

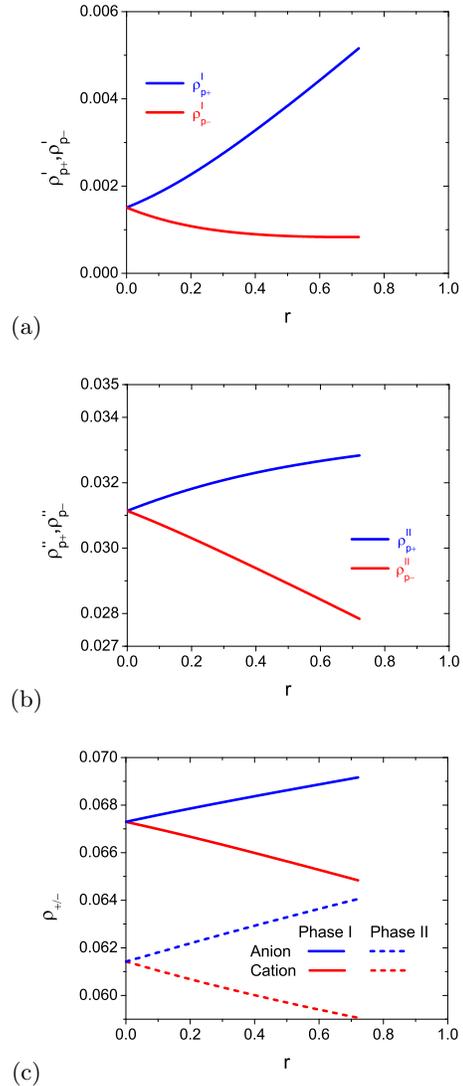


FIG. 4. Polycation and polyanion concentrations (a) in the PE-poor phase, $\rho_{p\pm}^I$, and (b) in the PE-rich phase, $\rho_{p\pm}^{II}$, for the mixtures with $\rho_{p,0} = 0.006$ at a large extra-salt concentration $\rho_{s,0} = 0.064$. (c) Concentrations of both small cation and small anions in the coexisting phases, $\rho_{\pm}^{I/II}$.

Next, we examine how the concentrations of each component, $\rho_i^{I/II}$, vary with r for mixtures at *finite* extra-salt

concentration $\rho_{s,0}$. When $\rho_{s,0}$ is small, the dependence of $\rho_i^{I/II}$ on the asymmetry factor r is qualitatively similar to the mixture without extra-salt at the same $\rho_{p,0}$ and we thus do not show the data here. On the other hand, for mixtures with a *large* amount of extra-salt, the PE concentrations in the PE-poor phase $\rho_{p\pm}^I$ take reasonably finite values for the symmetric mixture, different from the mixture without extra salt, in which there are very few PEs in the PE-poor phase. We thus expect the concentrations of each component for the asymmetric mixtures at large $\rho_{s,0}$ to be different from that in the extra-salt-free mixture.

Taking the case with $\rho_{p,0} = 0.006$ and $\rho_{s,0} = 0.064$ as an example, in Figs. 4(a) and (b), we show both PE concentrations in the PE-poor phase $\rho_{p\pm}^I$ and that in the PE-rich phase $\rho_{p\pm}^{II}$ as the red curves, respectively. Different from the extra-salt-free mixture, we do not observe the two distinct r regimes. Instead, we find that,

in the PE-poor phase, ρ_{p-}^I decreases slightly with r while ρ_{p+}^I increases approximately linearly. On the other hand, in the PE-rich phase, ρ_{p+}^{II} increases slightly with r but ρ_{p-}^{II} decreases approximately linearly; this is qualitatively consistent with the mixture without extra-salt or with a small amount of extra salts.

In Fig. 4(c), we show the concentrations of small cation and small anion in the coexisting phases $\rho_{\pm}^{I/II}$, for the mixture with $\rho_{p,0} = 0.006$ and $\rho_{s,0} = 0.064$. Likewise, we do not observe the two r -regimes in which small ions partition differently. Instead, we find that both ρ_{\pm}^I and ρ_{\pm}^{II} follow approximately linearly with $\bar{\rho}_{\pm}$ in the entire phase-separated region. Furthermore, the concentrations of both small cation and small anion are always higher in the PE-poor phase than in PE-rich phase, i.e., $\rho_{+}^I > \rho_{+}^{II}$ and $\rho_{-}^I > \rho_{-}^{II}$ for all r values.

[1] W. H. Press, S. A. Teukolsky, W. T. Vetterling and B. P. Flannery, *Numerical Recipes: The Art of Scientific Com-*

puting, 3rd ed.(Cambridge University Press, New York, 2007) p470.