Automated Calculation along a Path (ACAP)

Since polymer self-consistent field equations are highly nonlinear, having a good initial guess is very important in practice as it determines not only which final solution (corresponding to a phase in block copolymer self-assembly) can be obtained but also how many iteration steps the solver (*e.g.*, the Anderson mixing) takes to converge these equations. While PSCF includes methods for generating initial guesses for a given ordered phase,[1] ACAP is a simple and robust strategy. Let $\mathbf{f}(\mathbf{x};p)=\mathbf{0}$ be the set of nonlinear equations to be solved at some value of parameter p; the basic idea of ACAP is to use the converged solution $\mathbf{x}^*(p')$ as the initial guess at $p'+\delta p$ and vary the parameter value from p' to p in a stepwise manner (*i.e.*, along a path) by ***automatically adjusting*** δp (depending on whether or not the equations are converged) in each step. While ACAP is similar to the "SWEEP" command (which uses ***fixed*** or ***decreasing*** δp) in PSCF, automatically adjusting δp is the key for ACAP to be successful and efficient. This can be simply done by using a scaling factor $\alpha>1$: if the equations are converged in a step having step size δp, then $\alpha\delta p$ is taken as the step size for the next step; otherwise, one repeats the calculation in this step except with $\delta p/\alpha$ taken as the step size. Of course, one can also limit the largest and smallest absolute value of the step size in ACAP. ACAP works with ***any*** continuous parameter p; note, however, that the block volume fraction cannot be varied continuously, even for continuous Gaussian chain used in the "standard" model due to the numerical integration along the block contour (see `REPS.pdf` for more details).

ACAP described above involves only one (ordered) phase and is suitable for computing, *e.g.*, the curve of the dimensionless Helmholtz free energy density βf of that phase (where $\beta \equiv 1/k_BT$ with k_B denoting the Boltzmann constant and T the thermodynamic temperature of the system). We have also implemented ACAP to efficiently compute the phase boundary between two given phases in PSCF+. For a (nearly) incompressible system of neat block copolymer melts, this requires solving a single equation

$$\beta f_{\mathrm{I}}(x;p) = \beta f_{\mathrm{II}}(x;p) \tag{1}$$

for the two phases (I and II), where, for example, x can be taken as χN and p as the conformational asymmetry between the two blocks in the "standard" model of neat diblock copolymer melts. While the basic idea of ACAP here is the same as described above, some bookkeeping is needed when both I and II are ordered phases; in particular, we solve Eq. (1) with the Ridders' method[2], which requires an estimated interval bracketing the solution of x at given p. This can be compared with the conventional approach of computing the phase boundary, where at each given p-value, βf_{I} and βf_{II} at several ***predetermined*** x-values are calculated and then interpolated to find an ***approximate*** solution (the accuracy of which depends on that of the interpolation, which is often not estimated) to Eq. (1); in contrast, the Ridders' method can quickly solve Eq. (1) to a specified accuracy (comparable to that of βf), and the ACAP here can efficiently trace out the phase boundary $x(p)$ between the two phases, making the construction of phase diagrams in 2D very efficient.

References:

1. Arora, A.; Qin, J.; Morse, D. C.; Delaney, K. T.; Fredrickson, G. H.; Bates, F. S.; Dorfman, K. D., Broadly Accessible Self-Consistent Field Theory for Block Polymer Materials Discovery. *Macromolecules* **2016,** *49* (13), 4675-4690.
2. Press, W. H., Chap. 9.2 in *Numerical recipes in C: The art of scientific computing,* 2nd ed.; Cambridge University Press: Cambridge; New York, 1992.