

Richardson-Extrapolated Pseudo-Spectral (REPS) Methods

For continuous Gaussian chain (CGC) as used in the “standard” model (see [Models.pdf](#) for details), the chain propagators satisfy the modified diffusion equations. Here we consider as an example the (one-end-integrated) forward propagator $q(\mathbf{r}, s)$ in a block of length N and the statistical segment length b (for CGC, individual values of N and b are not important; strictly speaking, $N \rightarrow \infty$ and $b \rightarrow 0$, and it is \sqrt{Nb} that matters), where $s \in [0, N]$ is the (continuous) variable along the block contour; the modified diffusion equation is then $\frac{\partial q}{\partial s} = \frac{b^2}{6} \nabla^2 q - \omega(\mathbf{r})q$ with given initial condition of $q(\mathbf{r}, s=0)$, where $\omega(\mathbf{r})$ is the conjugate field interacting with segments on the block, and has the formal solution of $q(\mathbf{r}, s + ds) = \exp\left\{\left[\left(b^2/6\right)\nabla^2 - \omega(\mathbf{r})\right]ds\right\} q(\mathbf{r}, s)$. Discretizing the block contour into n steps each of step-size $\Delta s = N/n$, one needs to numerically calculate $q(\mathbf{r}, s + \Delta s)$ from $q(\mathbf{r}, s)$, where $s = j\Delta s$ and $j = 0, \dots, n-1$. For block copolymer self-assembly under the periodic boundary conditions, the 2nd-order pseudo-spectral (PS) method¹ gives $q(\mathbf{r}, s + \Delta s) \approx \exp(-\omega(\mathbf{r})\Delta s/2) \exp\left[\left(b^2/6\right)\Delta s \nabla^2\right] \exp(-\omega(\mathbf{r})\Delta s/2) q(\mathbf{r}, s)$, which has a **global** error of $O(\Delta s^2)$ and can be readily computed using fast Fourier transforms. Morse and co-workers first pointed out that the error of the PS method contains only even powers of Δs and thus proposed a 4th-order method, which is used in PSCF, by linearly extrapolating the two results of $q(\mathbf{r}, s + \Delta s)$ obtained via the PS method with the step-size of Δs and $\Delta s/2$, respectively, to the limit of $\Delta s \rightarrow 0$.² This is similar to the trapezoidal rule for numerical integration, the error of which also contains only even powers of the step-size; the K th-order polynomial extrapolation of the $K+1$ results obtained via the trapezoidal rule with successively halved step-size to the limit of zero step-size then give the commonly used Romberg integration³, with $K=1$ corresponding to the Simpson’s 1/3 rule. We therefore refer to the PS method and that proposed by Morse and co-workers² as the REPS-0 and REPS-1 method, respectively, and have implemented the REPS- K (for $K=0, \dots, 4$) methods in PSCF+; polynomial extrapolation with $K > 4$ is usually unstable.

To be more specific, let q_k ($k=1, \dots, K+1$) be the result of $q(\mathbf{r}, s + \Delta s)$ obtained via the PS method with a step-size of $\Delta s/2^{k-1}$, and q_0 be the extrapolated result given by the REPS- K method; one can then write $q_k = q_0 + \sum_{i=1}^K a_i (\Delta s/2^{k-1})^{2i}$. For given Δs and q_k ’s, solving q_0 and the coefficients a_i ($i=1, \dots, K$) from these $K+1$ equations, we obtain $q_0 = (4q_2 - q_1)/3$ (i.e., Eq. (A6) in Ref. 2) for $K=1$, $q_0 = (64q_3 - 20q_2 + q_1)/45$ for $K=2$, $q_0 = (4096q_4 - 1344q_3 + 84q_2 - q_1)/2835$ for $K=3$, and $q_0 = (1048576q_5 - 348160q_4 + 22848q_3 - 340q_2 + q_1)/722925$ for $K=4$. Note that the REPS- K method has a global error of $O(\Delta s^{2(K+1)})$; this requires the Romberg integration of the same (or higher) order to calculate the integral $\int_0^N ds q(\mathbf{r}, s) q^\dagger(\mathbf{r}, s)$ involved in the volume-fraction field (e.g., the Simpson’s 1/3 rule is used in PSCF to match the REPS-1 method), which in turn requires n be an integer multiple of 2^K (see [RI.pdf](#) for details). We also note that the REPS- K method requires $2^{K+1}-1$ pairs of forward and backward fast Fourier transforms to obtain $q(\mathbf{r}, s + \Delta s)$ from $q(\mathbf{r}, s)$.

References:

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2. Ranjan, A.; Qin, J.; Morse, D. C., Linear response and stability of ordered phases of block copolymer melts. *Macromolecules* **2008**, *41* (3), 942-954.
3. Press, W. H., Chap. 4.3 in *Numerical recipes in C: The art of scientific computing*, 2nd ed.; Cambridge University Press: Cambridge; New York, 1992.