A THE 27-POINT ISOTROPIC STENCIL OPERATORS

In this appendix we briefly discuss the values for the weights $d_{\alpha}$ in a 27-point isotropic stencil. In Fourier space the discrete half point derivative operator $\hat{D}_{\alpha}$ in direction $\alpha$ is

$$\hat{D}_{\alpha} = \frac{2i}{|r_{\alpha}|} \sin 2\mathbf{q} \cdot \mathbf{r}_{\alpha}$$  \hspace{1cm} (A.1)

where $\mathbf{r}_{\alpha}$ is a lattice direction in positive half-space:

$$\mathbf{r}_{\alpha} = \left\{ \begin{array}{c}
(1, 0, 0) \\
(0, 1, 0) \\
(0, 0, 1) \\
(1, 1, 0) \\
(1, -1, 0) \\
(1, 0, 1) \\
(1, 0, -1) \\
(0, 1, 1) \\
(0, 1, -1) \\
(1, 1, 1) \\
(1, 1, -1) \\
(1, -1, 1) \\
(1, -1, -1) \\
\end{array} \right\} d_{100}$$

$$\mathbf{r}_{\alpha} = \left\{ \begin{array}{c}
(1, 1, 0) \\
(1, -1, 0) \\
(1, 0, 1) \\
(1, 0, -1) \\
(0, 1, 1) \\
(0, 1, -1) \\
\end{array} \right\} d_{110}$$

$$\mathbf{r}_{\alpha} = \left\{ \begin{array}{c}
(1, 1, 1) \\
(1, 1, -1) \\
(1, -1, 1) \\
(1, -1, -1) \\
\end{array} \right\} d_{111}$$  \hspace{1cm} (A.2)

In Fourier space, $\nabla^2$ is $-\mathbf{q} \cdot \mathbf{q}$, with the corresponding discrete $S(\mathbf{q})$:

$$-q^2 \to S(\mathbf{q}) = \sum_{\alpha} d_{\alpha} \hat{D}_{\alpha} \hat{D}_{\alpha}$$  \hspace{1cm} (A.3)

The values for the weights $d_{\alpha}$ are found by invoking three conditions:

$$\frac{\partial^2 S}{\partial q^2_{x_i}} = -2 \quad x_i = x, y, z \quad \text{(Scaling condition)}$$

$$S(\pi, 0, 0) = S \left( \frac{\pi}{\sqrt{2}}, \frac{\pi}{\sqrt{2}}, 0 \right) = S \left( \frac{\pi}{\sqrt{3}}, \frac{\pi}{\sqrt{3}}, \frac{\pi}{\sqrt{3}} \right) \quad \text{(Isotropy)}$$
which results in

\[ d_{100} = 0.294726 \]
\[ d_{110} = 0.235425 \]
\[ d_{111} = 0.175818 \]

The root mean square deviation from isotropy with these conditions at \(|q| = \pi\) is less than 1\%.
B THE EXPANSION IN THE EXTERNAL FIELD

We define two different Hamiltonians $H$ and $H'$. The densities and external potentials corresponding with $H'$ are marked with a $'$. Using the bijectivity of the density functional and demanding that

$$\theta_I = \theta'_I$$

for all $I$, where $\theta_I = \nu_I \rho_I$ is the volume fraction, we can write the set of external potentials $U'_I$ as an exact functional Taylor series of the fields $U_I$, by definition:

$$U_I(q) = \sum_J k_{IJ}^{(2)}(q) U_J'(q) + \frac{1}{2} \sum_{JK} \int k_{IJK}^{(3)}(q, q_1) U'_J(q - q_1) U'_K(q_1) dq_1 + \cdots$$

Expressions for the expansion kernels can be found by first inserting the expansion for $U$ in the density, followed by the expansion of the density in $U'$. This results in

$$k_{IJ}^{(2)}(q_1) = \sum_K I_K(q_1) \frac{\nu'_K}{\nu_K} G^{(2)}_{KJ}(q_1)$$

$$k_{IJK}^{(3)}(q_1, q_2) = \sum_L I_L(q_1 + q_2) \frac{\nu'_L}{\nu_L} G^{(3)}_{LJK}(q_1, q_2) + \sum_{LM} I_{LM} G^{(3)}_{LMJK}(q_1, q_2) \frac{\nu'_M}{\nu_M} G^{(2)}_{MK}(q_2)$$

where

$$,_{I,J,...,M}^{(n)} \equiv \frac{\delta^{n-1} U_I}{\delta \rho_J \ldots \delta \rho_M} \bigg|_{\rho=\rho'}$$

$$G^{(n)}_{I,J,...,M} \equiv \frac{\delta^{n-1} \rho'_I}{\delta U'_J \ldots \delta U'_M} \bigg|_{U'=0}$$

$\nu$ and $\nu'$ are the particle volumes in the two descriptions. Notice, that all $'$, and $G'$ functions are evaluated when the external fields are zero.
C CHAIN MODELS WITH SEPARABLE CONFIGURATIONAL ENERGIES

Figure C.1 Cartesian reference frames for the bond rotations.

The characteristic ratio of a chain with $n$ backbone-bonds is defined as

$$C_n = \frac{\langle r^2 \rangle}{\sum_i l_i^2}$$

(C.1)

where $l_i^2$ is the square of bondlength $i$ and $r^2 = \sum_{i,j} l_i \cdot 1_j$.

We define the orthogonal transformation matrices $T_{i,j}$ which transform an arbitrary vector $v$ in reference frame $j$ to $v'$ in reference frame $i$. For two consecutive bonds with reference frames as drawn in figure C.1 we obtain

$$T_{i,i+1} = \begin{pmatrix} -\cos \theta_i & \sin \theta_i & 0 \\ -\sin \theta_i \cos \phi_i & \cos \theta_i \cos \phi_i & \sin \phi_i \\ -\sin \theta_i \sin \phi_i & \cos \theta_i \sin \phi_i & -\cos \phi_i \end{pmatrix}$$

(C.2)

Then for $j > i$,

$$\langle l_i \cdot 1_j \rangle = l_i l_j \langle (T_{i,i+1}...T_{j-1,j})_{11} \rangle$$

(C.3)

where the $X_{11}$ denotes the upper left element of the matrix $X$. In order to calculate $\langle r^2 \rangle$ we assume separable configurational energies,\(^{91,112}\) so that $\langle T_{i,i+1}...T_{j-1,j} \rangle \equiv \langle T_{i,i+1} \rangle...\langle T_{j-1,j} \rangle$ and

$$\langle T_{i,i+1} \rangle = \mathcal{N} \int d\phi_i T_{i,i+1} \exp -\beta E_{i,i+1}(\phi_i)$$

(C.4)
where $E_{i,i+1}$ is the dihedral energy of bond $i$ and $N$ is a normalization constant.

For chains with a repeating unit, it is convenient to index the transformation matrices with the bondtypes instead of the bond number. For an ethylene oxide chain or a propylene oxide chain, we obtain three different matrices $T_{cco}$, $T_{cc}$, and $T_{occ}$, which transform the reference frame of a $C-O$ bond into the preceding $C-C$ bond, a $O-C$ bond into the preceding $C-O$ bond and a $C-C$ bond into a preceding $O-C$ bond. Then the expression for $\langle r^2 \rangle$ for a chain of $N$ EO monomers is

$$\langle r^2 \rangle = \langle \left(-N l_{cc}^2 + (2N - 1) l_{co}^2 \right) I + 2N l_{co} l_{cc} T_{cco} +$$
$$2l_{cc} \left(N \left(I - T_{EO} \right)^{-1} - T_{EO} \cdot (I - T_{EO}^N) \cdot (I - T_{EO})^{-2} \right) \cdot$$
$$(I_{cc} + T_{cco} l_{co} + T_{cco} T_{cco} l_{co}) +$ 
$$2l_{cc} (T_{occ} + T_{cocl} T_{cocl}) \left(N \left(I - T_{EO} \right)^{-1} - (I - T_{EO}^N) \cdot (I - T_{EO})^{-2} \right) \cdot$$
$$(I_{cc} + T_{cco} l_{co} + T_{cco} T_{cco} l_{co}) \rangle_{11}$$

where $I$ is the unity matrix, $l_{cc}$ is the carbon-carbon bondlength, $l_{co} = l_{oc}$ is the oxygen carbon bondlength and $T_{EO} = T_{cco} T_{cocl} T_{cco}$.

The characteristic ratio is given by

$$C_{\infty} = \lim_{N \to \infty} \frac{\langle r^2 \rangle_{11}}{N \left(l_{cc}^2 + 2l_{co}^2 \right)}$$

$$= \left(2l_{cc}^2 \left(1 + \langle T_{cco} \rangle_{11} \right) - l_{co}^2 \right) \left(l_{cc}^2 + 2l_{co}^2 \right)^{-1} +$$
$$2 \left\langle \left(I_{cc} + T_{cco} l_{co} + T_{cco} T_{cco} l_{co} \right) \cdot$$
$$(I - T_{EO})^{-1} \right\rangle \cdot$$
$$\langle I_{cc} + T_{cco} l_{co} + T_{cco} T_{cco} l_{co} \rangle_{11} \left(l_{cc}^2 + 2l_{co}^2 \right)^{-1}$$

The results are similar for PO monomers.
We consider an homogeneous melt of $n$ molecules with non-Gaussian intra-molecular Hamiltonian $H$. All inter-chain interactions are neglected. In order to determine the linear response of the system, we apply the following method:

We consider an weak external field $U$ which is isotropic around the origin

\[ U_I(r) = A \delta_{I,J} \frac{\sin q \cdot r}{q \cdot r} \]  

where $q$ and $A$ are parameters. The response of the system is calculated by Metropolis Monte Carlo, according to

\[ \rho_I(r) = \mathcal{N} \sum_C \sum_s \delta_I \delta_I(r - r_s) \exp -\beta \left[ H + \sum_{s'} U_{s'}(r_{s'}) \right] \]  

where $\sum_C$ denotes a sum over all generated conformations, $\mathcal{N}$ is a normalization constant and $H$ is the intra-chain Hamiltonian. In the calculations we used the force-field from reference 92, with fixed bond lengths and bond angles. In order to prevent collapse of the chain, only the repulsive Lennard Jones terms were taken into account.

For small values of the external field amplitude $A$, the response is linear. In the weak segregation limit, the density deviations $\hat{\rho}_I = \rho_I - \rho_0^I$, where $\rho_0^I$ is the average density, are given by

\[ \hat{\rho}_I(r) = \frac{A}{4\pi} \int q_1^{-2} \exp[iq_1 \cdot r] \delta (|q - q_1|) \tilde{G}_{IK}^{(2)} (|q_1|) \, dq_1 \]

\[ = \frac{A}{4\pi} \int q^{-2} \exp[iq \cdot r \cos \theta] q^2 \sin \theta \delta (q - q_1) \tilde{G}_{IK}^{(2)} (q_1) \, d\phi d\theta dq \]

\[ = \frac{A}{2} \int \exp[iqr \cos \theta] \sin \theta \tilde{G}_{IK}^{(2)} (q) \, d\theta \]

\[ = A \frac{\sin qr}{qr} \tilde{X}_{IK}^{(2)} (q) \]

where $\tilde{X}$ denotes the Fourier transform of $X$.

The response functions can therefore be determined from

\[ \tilde{G}_{IJ}^{(2)} (q) = A^{-1} \hat{\rho}_I (0) \]
After calculating the $G$ functions, the $\lambda$ functions are obtained through a matrix inversion

$$\lambda_{ij}^{[2]}(q) = \left(G_{ij}^{[2]}(q)\right)^{-1}$$

where $G_{ij}^{[2]}$ is a matrix with elements $G_{ij}^{[2]}$.

In order to calculate higher order $G$ and $\lambda$ functions, the same derivation can be repeated, taking into account the bi-linear expansion term and using two non-zero external fields.