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Kinetic Monte Carlo residence time distributions in view of extrusion-based polymer modification and recycling

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S1. Formulation of dimensionless groups and correlations

S1.1. Buckingham's Pi theorem

Buckingham's Pi theorem is an essential theorem in dimensional analysis of certain physical systems. It states that if a physical system requires x variables to be fully defined and contain y primary dimensions (*e.g.* time (T), mass (M) and length (L)), then the equation relating these x variables will have x-y dimensionless groups. These dimensionless groups are called π-groups and the final equation is of the form:

$$\pi_1 = f(\pi_2, \pi_3, ..., \pi_{n-m})$$

Each of the fundamental dimensions must appear in at least one of the *x* variables. If one of the primary dimensions does not appear in any of the x variables, the number of primary dimensions should be decreased.

If the physical system is an extruder, then we can distinguish 8 different defining quantities:

- The residence time inside the plug flow reactors (compartment 1 + 7) t_{plug} (s).
- The forward volumetric flow Q_F (m^3 s^{-1}).
- The actual polymer volume inside the metering section of the extruder $V_{p,tot}$ (m^3) (CSTR part).
- Mass feed rate to the extruder F (kg s^{-1}).
- Screw rotation speed N (s^{-1})
- The polymer density ρ (kg m^{-3}).
- The dynamic polymer viscosity η (Pa s).
- The extruder internal volume V (m^3).

Three primary dimensions (m, kg, and s) result, which means 8 – 3 = 5 dimensionless groups. The next step is to select 3 *recurring variables*, whilst following two rules:

1) None of the recurring variables can be dimensionless.
2) No two recurring variables are allowed to have the same overall dimension.

V, F and N are chosen as recurring variables because they are readily available from the operation parameters provided by Zhang *et al.*[1] In general, the next step is to form the pi terms by multiplying one of the non-recurring variables by the product of the repeating variables, each raised to an exponent that will make the combination dimensionless. In our case, this is executed 5 times to form 5 dimensionless groups using the 3 recurring variables (V, F and N), chosen above. This is shown below:

π_1: $\pi_1 = [V]^a[N]^b[F]^c[\rho]^d \rightarrow [/] = [m^3]^a[s^{-1}]^b[kg\ s^{-1}]^c[kg\ m^{-3}]^d$

$a = 1; b = 1; c = -1; d = 1 \rightarrow \pi_1 = \dfrac{V\ N\ \rho}{F}$

π_2: $\pi_2 = [V]^a[N]^b[F]^c[Q_F]^d \rightarrow [/] = [m^3]^a[s^{-1}]^b[kg\ s^{-1}]^c[\ m^3 s^{-1}\ ]^d$

$a = -1; b = -1; c = 0; d = 1 \rightarrow \pi_2 = \dfrac{Q_F}{V\ N}$

π_3: $\pi_1 = [V]^a[N]^b[F]^c[V_{p,tot}]^d \rightarrow [/] = [m^3]^a[s^{-1}]^b[kg\ s^{-1}]^c[m^3]^d$

$a = 1; b = 1; c = -1; d = 1 \rightarrow \pi_3 = \dfrac{V_{p,tot}}{V}$

π_4: $\pi_4 = [V]^a[N]^b[F]^c[\eta]^d \rightarrow [/] = [m^3]^a[s^{-1}]^b[kg\ s^{-1}]^c[kg\ m^{-1}\ s^{-1}]^d$

$a = \dfrac{1}{3}; b = 0; c = -1; d = 1 \rightarrow \pi_4 = \dfrac{\eta\ V^{1/3}}{F}$

π_5: $\pi_5 = [V]^a[N]^b[F]^c[t_{plug}]^d \rightarrow [/] = [m^3]^a[s^{-1}]^b[kg\ s^{-1}]^c[s]^d$

$a = 0; b = 1; c = 0; d = 1 \rightarrow \pi_5 = t_{plug} N$

Since these 5 dimensionless groups dimensionally characterize the extruder, it is sensible to construct predictive correlations for hard-to-measure extruder properties based on these 5 dimensionless groups. For our model, ideally, we want to predict the dimensionless numerical parameters from the known dimensionless process parameters and physical parameters using a correlation. Making use of the OriginPro 8.5 software, power law correlations are constructed between the operational parameters provided by Zhang *et al.*[1] and our optimized/fitted numerical parameters.

S1.2. Correlations for numerical parameters for experimental RTD prediction

As mentioned in the main text, hand-tuned values were at first used to fit the experimental residence time distributions. These values are shown in table S1 below:

Table S1: the variation of numerical parameters: f_F, f_B and t_{plug} for the simulations shown in Figure 9 in the main text.

simulation	f_F (-)	f_B (-)	t_{plug} (s)	F (kg/h)	N (s^{-1})
Green	0.174	0.0665	92	10.7	1
Dark-blue	0.17	0.0625	77	10.7	1.5
Red	0.15	0.0425	67	10.7	2
Purple	0.12	0.0125	56	10.7	2.5
Orange	0.1775	0.0275	40	17.8	2.5

Also mentioned in the modeling section are the constant values for the polymer density (ρ; kg/m^3), the dynamic polymer viscosity (η; Pa.s) and the extruder internal volume (V; m^3): 1200 kg/m^3, 3000 Pa.s and 400 mL respectively. This dataset was then used to construct three correlations which allow to predict three dimensionless numerical parameters as a function of the five dimensionless groups containing only physical parameters.

Correlation 1:

$$\left(\frac{Q_F}{V \cdot N}\right) = -0.00138 + 1.9258 * \left(\frac{V \cdot N \cdot \rho}{F}\right)^{-1} - 1.50E^{11}\left(\frac{\eta \cdot \sqrt[3]{V^1}}{F}\right)^{-3}$$

Correlation 2:

$$\frac{V_{p,tot}}{V} = 0.4268 - 1.87E^{-6}\left(\frac{\eta \cdot \sqrt[3]{V^1}}{F}\right)$$

The absence of the screw rotation speed N in this correlation is remarkable and is corroborated by our hand-tuned numerical parameters as well: surprisingly, $V_{p,tot}$ does not depend on the screw rotation speed, only dependent on the feed rate. This prediction is difficult to verify experimentally, since the extruder fill rate is not observable during operation.

Correlation 3:

$$\left(t_{plug} \cdot N\right) = 32.560 + 0{,}2012 * \left(\frac{V \cdot N \cdot \rho}{F}\right) + 4.16E^{-4}\left(\frac{\eta \cdot \sqrt[3]{V^1}}{F}\right)$$

All three correlations were obtained using the nonlinear surface fit method provided by OriginPro 8.5.

S2. Benchmarking and model sensitivity sensitivity to the numerical parameters

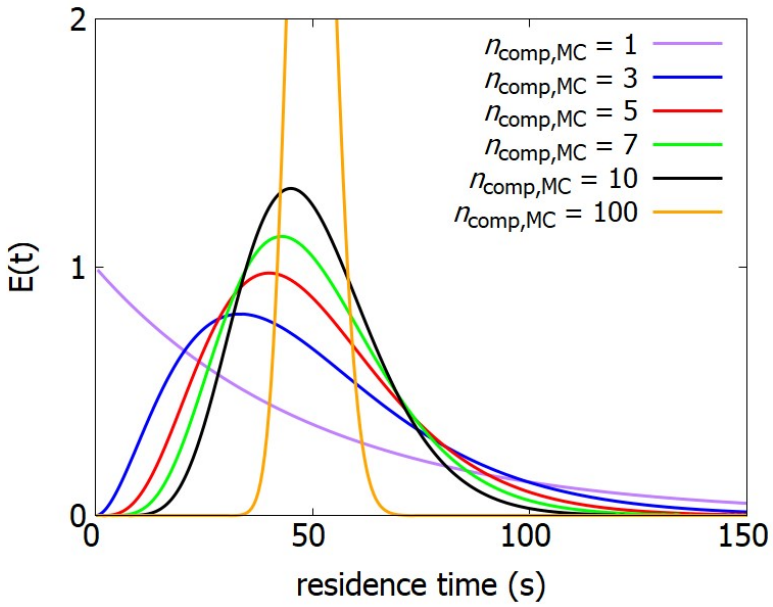

Figure S1: The non-normalized version of subplot b of Figure 6 in the main text. All theoretical RTD's have an average residence time of 50 s.

Figure S1 shows the non-normalized version of the subplot b of Figure 6 in the main text. As the average residence time in subplot a) is close to 50 s, this graph is shown for completeness to indicate the similarities of our micro-macro model and theoretical descriptions on a quantitative instead of qualitative basis.

For completeness, Table S2 shows the explicit values for the numerical parameters regarding the simulations in Figure 6 subplot a) in the main text.

Table S2: the variation of numerical parameters: f_F, f_B for the simulations with varying amount of compartments shown in Figure 6 in the main text. t_{plug} is put to 0 as mentioned in the main text and the MTF_{MC} is taken constant at 1 s^{-1}.

Simulation	$N_{comp,MC}$	Forward mass transfer f_F (-)	backward mass transfer f_B (-)
purple	1	0.02628	0.00478
blue	3	0.07883	0.01430

red	5	0.13139	0.02389
green	7	0.18394	0.03344
black	10	0.26278	0.04778

For completeness, Table S3 shows the explicit values for the numerical parameters regarding the simulations in Figure 7 in the main text.

Table S3: the variation of numerical parameters: f_F, f_B and the net forward mass transfer f_F - f_B for the simulations shown in Figure 7 in the main text. Note that simulations with the same colors have the same net forward mass transfer. t_{plug} is put to 0 as mentioned in the main text and the MTF_{MC} is taken constant at 1 s^{-1}.

Simulation	Forward mass transfer f_F (-)	backward mass transfer f_B (-)	Net forward mass transfer f_F - f_B (-)
Green full	0.80	0.30	0.5
Red full	0.80	0.50	0.3
Blue full	0.80	0.70	0.1
Green dotted	0.6	0.10	0.5
Red dotted	0.4	0.10	0.3
Blue dotted	0.2	0.10	0.1

For completeness, Table S4 shows the explicit values for the numerical parameters regarding the simulations in Figure 8 in the main text.

Table S4: the variation of numerical parameters: f_F, f_B and MTF_{MC} for the simulations shown in Figure 8 in the main text. t_{plug} is put to 0 s.

Simulation	Forward mass transfer f_F (-)	backward mass transfer f_B (-)	MTF_{MC} (s^{-1})
Green	0.40	0.20	0.5
red	0.20	0.10	1
blue	0.10	0.05	2

S3. Convergence check for RTD

Figure S2 shows the RTD for three (Monte Carlo) reaction volumes 10^{-21},10^{-20} and 10^{-19} m^3. It is clear that the general shape of the RTD is already established at 10^{-21} m^3, however, the signal for this lower reaction volume is quite noisy. For all simulations in the main rext a reaction volume of 10^{-19} m^3 is chosen to reach convergence for the polymer properties, as shown in Figure 10 of the main text.

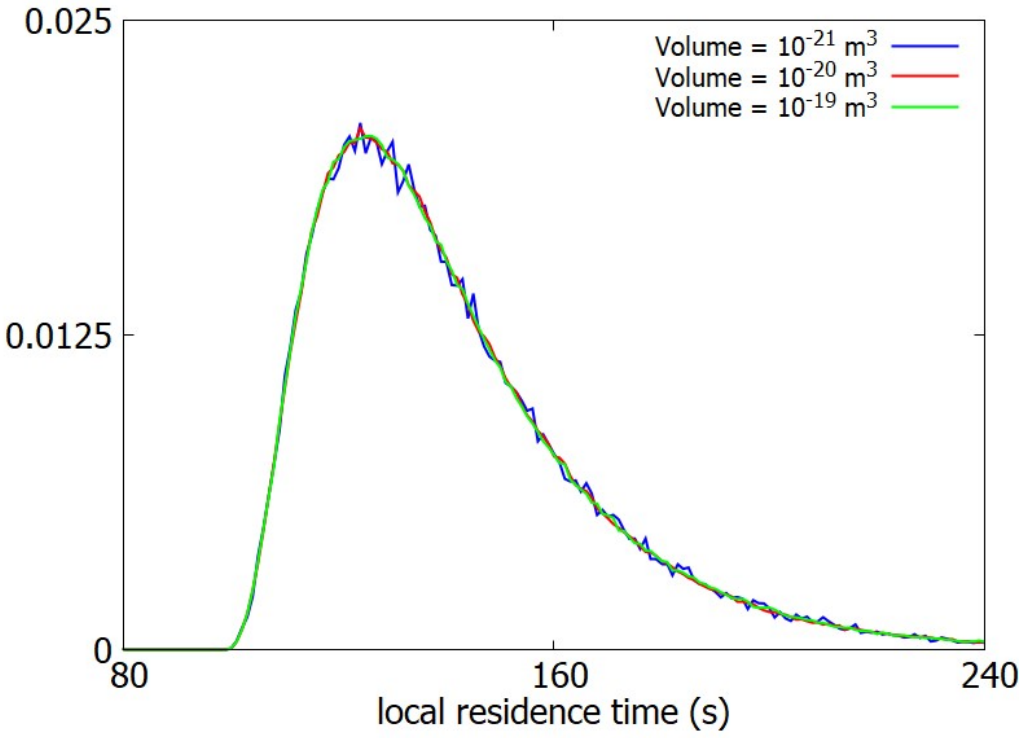

Figure S2: Simulations with different reaction volumes. Blue line: reaction volume of 10^{-21} m^3, red line: reaction volume of 10^{-20} m^3, green line: reaction volume of 10^{-19} m^3.

S4. References

1 X.-M. Zhang, Z.-B. Xu, L.-F. Feng, X.-B. Song and G.-H. Hu, *Polym. Eng. Sci.*, 2006, **46**, 510–519.