

Fractionation of polymers using supercritical fluid extraction

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Abstract

The supercritical fluid extraction (SFE) of polymers has been modelled both at constant density and with a linear density programme with time. The oligomers are seen to emerge in succession and the data are then used to calculate the number-averaged molar mass and polydispersity as a function of time. SFE of polyisobutene and polydimethylsiloxane was carried out experimentally using linear density programmes and the results are found to have the same qualitative behaviour as the predictions. © 1997 Elsevier Science B.V.

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1. Introduction

Fractionation of polymers using supercritical fluid extraction (SFE) has been carried out for a number of years and this work has been recently reviewed comprehensively by McHugh and Krukoni [1]. These processes have been based on considerations of phase behaviour and solubility. In the method that is closest to the process discussed in the present study, the polymer is extracted for a number of successive periods of time. In each period, the pressure is constant and higher than that in the previous period. Extraction is continued in each period until very little polymer is being extracted at that pressure. As pointed out in the review cited [1], this an arbitrary criterion, as in principle all the polymer will be eventually extracted if the process is continued for a sufficient length of time. Using this method as an example, polyethylene has been separated into narrow fractions using supercritical carbon dioxide [2].

Time is thus an important parameter in the ex-

traction of a polymer by a supercritical fluid, and in the present study the process has been modelled as a function of time. From the modelling studies, a method of polymer fractionation by pressure (or density) programming was then developed, which was then tested by experiment.

2. Modelling of polymer fractionation at constant pressure

Each step of the process described above is carried out at constant pressure. SFE of a simple model polymer was therefore first carried out at constant pressure as a function of time. A number of assumptions were made to simplify the model used, as described below. These assumptions are not unrealistic and do not affect the qualitative behaviour predicted. Firstly, the characteristic time for (a) diffusion out of the polymer films and (b) the residence time of the fluid in the extraction cell is assumed to be small enough that it has little effect on the polydispersity of the polymer being extracted at any time. This assumption can be made realistic in

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practice by choice of experimental conditions and, for example supporting the polymer on sand so that the liquid film is thin. Secondly, the fluid substance does not dissolve in the polymer film and the concentrations of oligomers in the fluid are negligible. These second assumptions will be approximately true at lower pressures, but may have to be rethought at higher pressures. Thirdly, it is assumed that the polymer behaves as an ideal mixture of oligomers and that there is a relationship $y_i/x_i=S_i$ between the mole fraction of the i th oligomer in the polymer, x_i and that in the fluid, y_i , with S_i being a solubility, which is constant at constant pressure and temperature.

The polymer is considered to contain n_i moles of the i th oligomer with n moles in total, with initial values of n_i^0 and n^0 . F is the flow-rate of fluid in moles per unit time through the extraction cell and a parameter a_i is defined by $a_i=FS_i$. The rate of removal of each oligomer will be equal to the flow-rate times the mole fraction of the oligomer in the fluid, thus

$$dn_i/dt = -Fy_i = -FS_ix_i = -a_in_i/n. \quad (1)$$

Therefore

$$d \ln n_i = -(a_i/n)dt, \quad (2)$$

which on integration becomes

$$\ln n_i = -a_i \int_0^t (du/n) + C, \quad (3)$$

where u is a dummy variable and C an integration constant. At $t=0$, $n_i=n_i^0$ and thus $C=\ln n_i^0$ and Eq. (3) becomes

$$\ln n_i = \ln n_i^0 - a_i \int_0^t (du/n). \quad (4)$$

This equation gives the variation of n_i with t . However, calculations cannot be easily carried out with this equation and it is better to define a quantity

$$x = \int_0^t (du/n) \quad (5)$$

and to calculate both t and mole fraction variation

from x . Calculation of mole fraction from x can be carried out using the following equation

$$n_i = n_i^0 \exp(-a_ix), \quad (6)$$

which is obtained by substituting x from Eq. (5) into Eq. (4) and taking exponentials. To obtain the equation for the calculation of t in terms of x Eq. (6) is summed over all oligomers and then divided by n to obtain

$$1 = \sum_i n_i^0/n \exp \left[-a_i \int_0^t (du/n) \right]. \quad (7)$$

Multiplying both sides by du and integrating between 0 and t gives

$$t = -\sum_i \left(n_i^0/a_i \exp \left[-a_i \int_0^t (du/n) \right] \right) + D. \quad (8)$$

At $t=0$, we find $D=\sum_i (n_i^0/a_i)$ and thus

$$t = \sum_i (n_i^0/a_i)[1 - \exp(-a_ix)]. \quad (9)$$

Thus Eqs. (6) and (9) enable n_i and t to be calculated from a variable x allowing n_i to be obtained indirectly as a function of t . Calculation were carried out for a simplified model polymer of ten oligomers of equal amounts, i.e. $n_i^0=1$ for all i and $n=10$. It was assumed that $a_i=1/2^{i-1}$, assuming an exponential fall-off of solubility with i , which is consistent with the more complex solubility behaviour assumed later in the density programming calculation and introduced by Fjeldsted et al. [3]. The calculations have been presented below in the form of the plots of the mole fraction of oligomer i in the polymer being extracted, z_i , the number-averaged molar mass, $\langle M \rangle_n$, and the polydispersity, P , of the polymer being extracted at a particular time, t . The mole fraction of polymer (not including the fluid) being extracted at any time can be calculated from Eq. (1) to be

$$z_i = (dn_i/dt)/(dn/dt) = a_in_i/\sum_i a_in_i. \quad (10)$$

Plots for i from 1 to 6 are shown below for the model polymer in Fig. 1. Note that the mole fraction of each oligomer peaks successively and that these peaks are progressively spread out with time as the oligomers become less soluble.

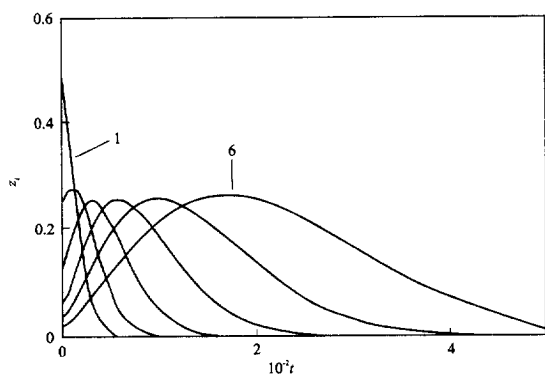


Fig. 1. Plots of the mole fraction of oligomer i in the polymer being extracted, z_i , using constant pressure at time t for i equal to 1 to 6, with oligomers 1 and 6 labelled. The simple model polymer consists of equal amounts of ten oligomers and the solubility is assumed to behave such that $a_i = 1/2^{i-1}$.

The number-averaged molar mass can be written as $(1/n) \sum_i n_i i m$, where m is the mass of the monomer unit. The average molar mass emerging at any particular time is thus given by $\langle M \rangle_n = [1 / (dn/dt)] \sum_i (dn_i/dt) i m$. From Eq. (1) this becomes after cancellation of n

$$\langle M \rangle_n / m = \frac{\sum_i a_i n_i i}{\sum_i a_i n_i} \quad (11)$$

Calculations of $\langle M \rangle_n / m$, using the same simplified model data as before are plotted in Fig. 2. The number averaged molar mass rises with time as the lower oligomers are exhausted, but this rise slows, due to the low solubility of the higher oligomers.

The polydispersity is defined in general as the

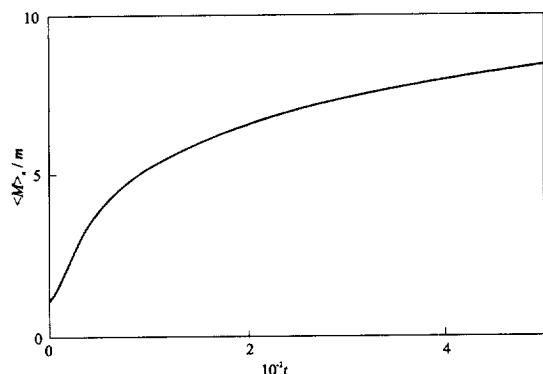


Fig. 2. Plot of $\langle M \rangle_n / m$, the number-averaged molar mass, versus time, t , using the same artificial data as in Fig. 1.

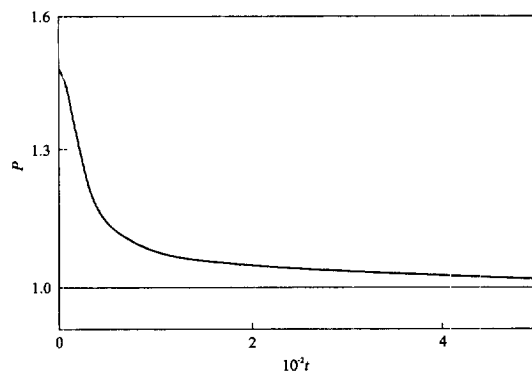


Fig. 3. Plot of the polydispersity obtained, P , versus time, t , using the same artificial data as in Fig. 1.

ratio of the weight-averaged molar mass divided by the number-averaged molar mass and can be represented in terms of the variable used here as $n \sum_i n_i i^2 / (\sum_i n_i i)^2$. The polydispersity of the extracted polymer emerging at any particular time is therefore given by $P = [\sum_i (dn_i/dt) i^2] / [\sum_i (dn_i/dt) i]^2$. From Eq. (1) this becomes after cancellation of n

$$P = \frac{\left[\sum_i a_i n_i i^2 \right]}{\left[\sum_i a_i n_i i \right]^2} \quad (12)$$

A plot of P calculated from the simplified model system is given in Fig. 3. The polydispersity is seen to fall with time, as the higher less soluble oligomers are being extracted slowly.

3. Modelling of polymer fractionation with a density gradient

For SFE at constant pressure, excessively long times are needed towards the end of the separation, as can be seen from Fig. 1 where successive peaks emerge more slowly. In existing methods [1,2], the pressure is increased in steps each time the extraction slows to obtain a fraction of higher average molar mass. The aim of this study was to include time in the modelling of polymer fractionation and so the pressure changes need to be described as a function of time, i.e. be carried out according to a programme. This approach has been used in supercritical fluid chromatography (SFC) to obtain chromatograms

with suitably distributed peaks. For the chromatography of polymers, for example, it is desirable to have the oligomer peaks equally spaced with respect to time and for this an asymptotic density programme was developed [3]. In the case of polymer fractionation by SFE, the requirements may be different and a likely situation is that constant polydispersity is required. At constant polydispersity, a greater range of oligomers are present at higher average molar masses. Thus for constant polydispersity, successive peaks needs to emerge more rapidly as the process continues. This effect occurs in SFC with a linear density gradient [3] and so this was the starting point for the study of density programming. As will be seen a linear density programme was found to give approximately constant polydispersity and so this was the only type of programme studied.

The solubility behaviour used by Fjeldsted et al. [3], which was successful for developing density programming for SFC, is used here. They assumed that the solubility of oligomers is given by

$$S_i = b_1 \exp[-(b_2 - b_3\rho)i] \quad (13)$$

where b_i are constants for a particular polymer and fluid. If a linear density program of $\rho = b_4 + b_5t$ is applied, where b_4 and b_5 are similar constants, the parameter a_i defined earlier, is given by

$$\begin{aligned} a_i &= Fb_1 \exp[-(b_2 - b_3b_4 - b_3b_5t)i] \\ &\equiv c_1 \exp[-c_2(1 - c_3t)i], \end{aligned} \quad (14)$$

where the c_i are constants for a particular polymer, fluid and density programme. The solubility behaviour used in the last section was a simple example of Eq. (14), with $c_1 = 2$, $c_2 = 0.693$ and $c_3 = 0$.

Now that a_i is a function of t , the algebraic analysis used earlier, in particular the integration of Eq. (2) to give Eq. (3), is no longer valid. The calculations are therefore carried out numerically. A more realistic model of a low polymer is now used in which there are 100 oligomers with amounts distributed according to a Gaussian distribution of $n_i^0 = \exp[-(i-50)^2/1250]$. a_i was taken to be given by Eq. (14) with $c_1 = 2$, $c_2 = 0.693$ and $c_3 = 10^{-5}$. Fig. 4 shows the quantity z_i , the mole fraction of a particular oligomer in the extract, for oligomers 10–15 and thereafter every tenth oligomer. As can be seen,

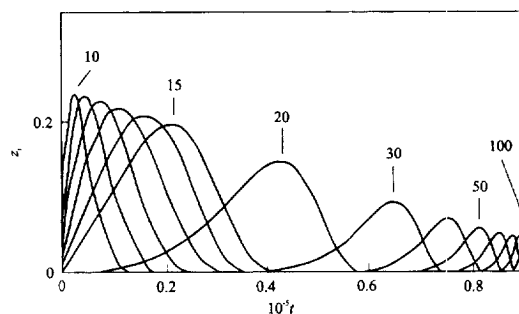


Fig. 4. Plots of the mole fraction of oligomer i in a polymer being extracted, z_i , using linear density programming at time t for oligomers 10–15 and then every tenth oligomer, with some oligomers labelled. The model polymer consists of 100 oligomers with a Gaussian distribution such that $n_i^0 = \exp[-(i-50)^2/1250]$ with solubility behaviour and density programme such that $a_i = 2 \exp[-0.693(1 - 10^{-5}t)i]$.

the oligomers emerge in sequence, but more and more rapidly with time, in contrast to the situation illustrated by Fig. 1.

The number-averaged molar mass and polydispersity from the same model polymer and density programme were also calculated. The solid line in Fig. 5 shows the natural logarithm of the average molar mass, which can be seen to be roughly linear, with a slight 'S' shape visible at the ends, where little material is being extracted. The solid line in Fig. 6 shows the polydispersity, which is approximately constant over most of the range, although it

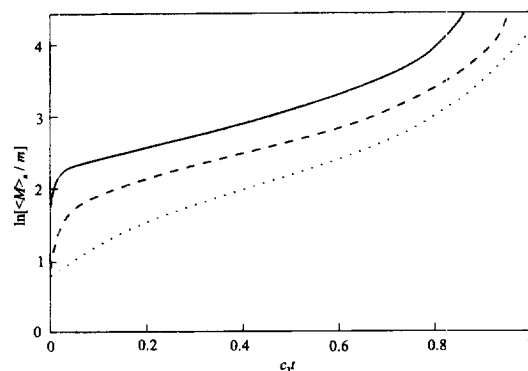


Fig. 5. Plots of the natural logarithm of $\langle M \rangle_n/m$, the number average molecular weight, versus time, t , for various density programmes, using the same model polymer as in Fig. 4, with solubility behaviour and density programme such that $a_i = 2 \exp[-0.693(1 - c_3t)i]$ and $c_3 = 10^{-5}$ (solid line); $c_3 = 10^{-4}$ (dashed line); $c_3 = 10^{-3}$ (dotted line).

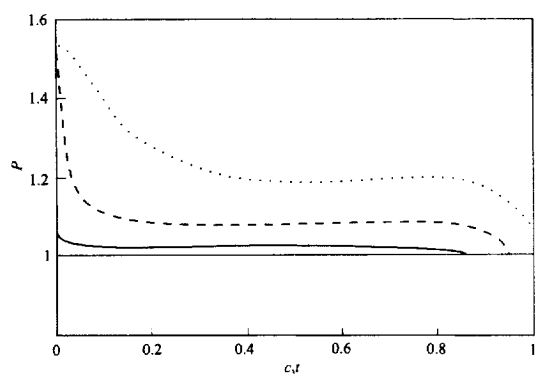


Fig. 6. Plots of the polydispersities, P , versus time, t , for various density programmes, using the same model polymer as in Fig. 4, with solubility behaviour and density programme such that $a_1 = 2 \exp[-0.693(1 - c_3 t)]$ and $c_3 = 10^{-5}$ (solid line); $c_3 = 10^{-4}$ (dashed line); $c_3 = 10^{-3}$ (dotted line).

peaks slightly in the middle and falls at both ends. Calculations were also carried out for the same model polymer, but with more rapid density programmes in which c_1 and c_2 were given the same values as before, but in which $c_3 = 10^{-4}$ and 10^{-3} . More rapid density programmes are seen to give similar shaped curves, but with a lower molar mass curve and a higher polydispersity.

4. Experimental

The SFE experiments were carried out using a Spe-ed SFE (Applied Separations, Allentown, PA, USA). This apparatus satisfied the requirements of the study, which were manual and separate control of pressure and flow-rate and a pressure rating up to 680 bar. A weighed amount of the polymer was thoroughly mixed with fine sand with a loading of 2.5% w/w. The polymers used were polyisobutene, supplied as Hyvis 10 (BP, Grangemouth, UK), and polydimethylsiloxane supplied as silicone oil (Hopkins and Williams, Chadwell Heath, UK). A 3.5-ml extraction cell was used. All experiments were conducted with carbon dioxide as the fluid, which was SFC/SFE grade with helium overpressure (Air Products, Crewe, UK). As a result extraction could not be carried out below 130 bar. The extracts were collected in High Purity Reagent grade tetrahydrofuran (THF) (Fisher Scientific, Loughborough, UK)

and the collection vial was exchanged after a pre-determined time interval, thus producing a series of fractions. For each density programme a table was prepared of pressure versus time at 1-min intervals using a recently published equation of state for carbon dioxide [4].

The weight-averaged molar mass and polydispersity of the fractions were determined by gel permeation chromatography (GPC). The analytical system consisted of a Model 422 liquid pump (Kontron, Watford, UK), a Rheodyne injection valve (Jones Chromatography, Hengoed, UK), a guard column and a 60-cm, 100 Å, 10 μm PLGEL column (Polymer Labs, Shropshire, UK) and a mass detector (Varex, MD, USA). The solvent used was THF, supplied as above and the flow-rate was 1 ml/min. The method was calibrated using polystyrene standards (Polymer Labs, Shropshire, UK). Calibration with polystyrene is known to give errors when used to analyse other polymers. For example, number-averaged molar masses of polyisobutene, obtained using polystyrene can be 10% below their true value. However, this procedure is adequate for the present study, where comparisons between the fractions and also with the starting material are what is required and qualitative behaviour was being investigated.

5. Fractionation of polyisobutene

Polyisobutene is not very soluble in carbon dioxide and only low oligomers can be extracted. However, this also means that high polydispersities can be obtained. The starting material was in fact a polymer of a mixture of butenes, predominantly isobutene. It had a number-averaged molar mass, measured by the procedures described above, of 1274 and a polydispersity of 1.54. A preliminary extraction was carried out at 50°C and 636 kg m⁻³ (the minimum 130 bar) for 10 min to remove the tail at low molar masses and to produce the first fraction. Extraction was then carried out at 50°C with a linear density programme rising from 656 kg m⁻³ to 1011 kg m⁻³ at a rate of 6.32 kg m⁻³/min. The flow-rate of carbon dioxide, calculated as liquid carbon dioxide at the pump, was 10 ml/min. Eight further fractions were collected at equal density intervals of

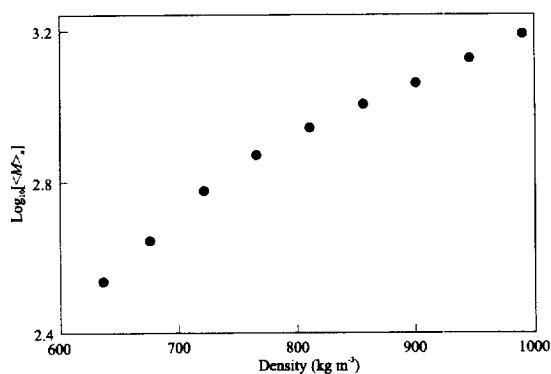


Fig. 7. SFE of polyisobutene using a linear density programme, showing the logarithm of the number-averaged molar masses of the fractions versus density.

45 kg m⁻³. 52% by weight of the polymer was extracted. The number-averaged molar masses of the fractions were between 342 and 1528 and are plotted as logarithms in Fig. 7 against density, which is equivalent to time as the density programme is linear. The shape of the curve is similar to the first part of the curves in Fig. 5, bearing in mind that only half of the polymer was extracted. The polydispersity, shown in Fig. 8, falls and then rises slightly, as in the first part of the theoretical curves of Fig. 6. These results show agreement between experiment and prediction and also that, with the right density programme low and approximately constant polydispersities can be obtained, except at the beginning.

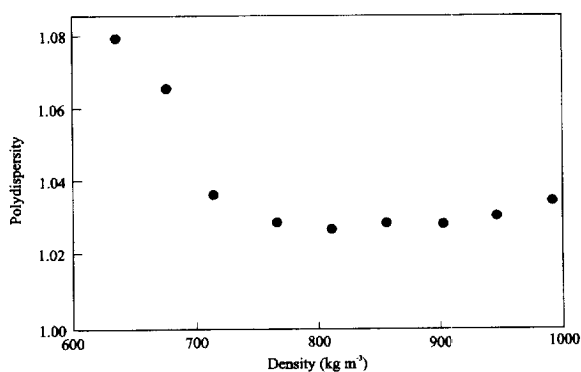


Fig. 8. SFE of polyisobutene using a linear density programme, showing the polydispersity of the fractions versus density.

6. Fractionation of polydimethylsiloxane

The purpose of these experiments was to demonstrate that the effect of density ramp speed on the molar mass and polydispersity agrees with the theoretical predictions of Figs. 5 and 6. The large changes in the rate of rise of density, possible in calculations, are impracticable and a ratio of about 2 was used. Polydimethylsiloxane is much more soluble in carbon dioxide than polyisobutene and the fractions obtained had higher polydispersities. The starting material had a number-averaged molar mass, measured by the procedures described above, of 127 682 and a polydispersity of 1.32. Both extractions described were carried out at 40°C and with a flow-rate of carbon dioxide, calculated as liquid carbon dioxide at the pump, of 6.5 ml/min. In each case a preliminary extraction was carried out at low densities to remove the tail at low molar masses, and were discarded. Two linear density programmes are reported, different in the rate of rise of density by a factor of 2.13. For the lower speed ramp (filled circles in Figs. 9 and 10) the density rose from 889 kg m⁻³ to 1014 kg m⁻³ at a rate of 0.94 kg m⁻³/min and seven fractions were collected at equal density intervals of 18 kg m⁻³. For the higher speed ramp (open circles in Figs. 9 and 10) the density rose from 912 kg m⁻³ to 1022 kg m⁻³ at a rate of 2.00 kg m⁻³/min and seven fractions were collected at equal density intervals of 16 kg m⁻³. 86% and 84%

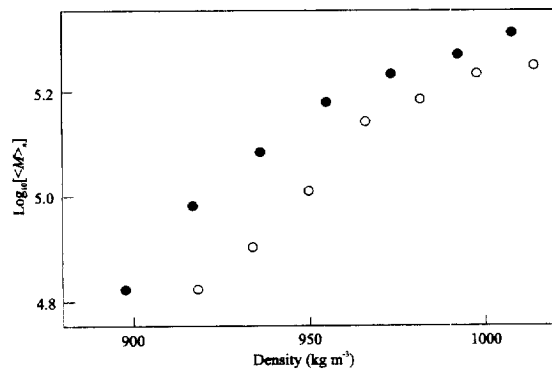


Fig. 9. SFE of polydimethylsiloxane using a linear density programme, showing the logarithm of the number-averaged molar masses of the fractions versus density with filled circles for a lower rate of density rise and open circles for a higher rate.

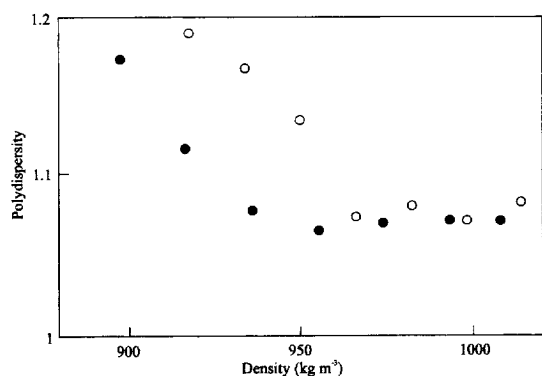


Fig. 10. SFE of polydimethylsiloxane using a linear density programme, showing the polydispersity of the fractions versus density with filled circles for a lower rate of density rise and open circles for a higher rate.

by weight of the polymer was extracted in the two experiments, respectively. The number-averaged molar masses of the fractions for both runs are plotted as logarithms in Fig. 9 against density, which is equivalent to time as the density programme is linear. The filled circles for the lower speed ramp lie above those for the higher speed ramp, as predicted

in Fig. 5. The polydispersities, shown in Fig. 10, have the filled circles for the lower speed ramp below those of the higher speed ramp, as predicted by Fig. 6. Thus the effect of ramp speed has the same qualitative effect on the experimental results as it does on the theoretical predictions.

Acknowledgments

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