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Elongational Deformation by Shear Flow of Flexible Polymers Adsorbed in Porous Media

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ABSTRACT: We have studied the influence of a shear flow on the configuration of flexible polymers adsorbed in porous media. High molecular weight fractions of polyacrylamide and polystyrene were adsorbed from solution onto commerical filters of different nature and structure and the thickness of the adsorbed layers was studied by using a hydrodynamic method based on Poiseuille's law. An abrupt coil-stretch transition was observed when the velocity of the solvent flowing through the pores was increased. The observed hydrodynamic thickness increased by a factor of 3–6, depending on the molecular weight of the adsorbed polymers. We have deduced that the number of trains in contact with the surface is very low, about 3 or 4, leading to a model of spotwise adsorption with a low surface attraction, and that a net circulation of solvent exists in the layer. By studying the influence of the pore size, we have shown that the parameter governing the stretching is not the transverse velocity gradient but the average velocity of the solvent into the pores. We conclude that the acting velocity gradient is in the axial direction and results from the nonuniform structure of the adsorbed layer which can be viewed as a monolayer stacking of semipermeable prolate spheroids.

The increasing amount of work on the adsorption of macromolecules from solution onto solid surfaces can be well understood, considering the theoretical and practical interest of the subject. One of the most spectacular effects of such adsorption is the restriction of flow in capillaries due to the effective decrease in size. Such an effect influences many processes, such as filtration, ultrafiltration, liquid chromatography, and, more recently, oil recovery by injection of a polymer into the oil-bearing rock. On the other hand, this phenomenon is the basis of an interesting method with which to study the thickness of the adsorbed layer.[1-5] This method has been developed in our laboratory and leads to very interesting results based upon the iteraction of the flowing phase with the adsorbed polymer. Due to the tendency for a flexible macromolecule to adsorb with free loops of segments extended out into the solution phase, one can foresee that strong interaction with the flow can lead to a deformation of the adsorbed layer. Very little has been published on this subject. In 1978, Varoqui et al.[4] detected no effect of the applied pressure on the thickness of the adsorbed layers of polystyrene. However, their results are limited to the cases of intermediate molecular weights and a rather low pressure difference. Silberberg[6] observed a tremendous reduction of throughput at high applied pressure gradient for polyacrylamide gels coated on tubes.

The purpose of this paper is to present evidence of such deformation and to study the different parameters governing this phenomenon.

The basic experimental method used has already been described.[2] The permeability of a porous medium is measured before and after adsorption by solvent flow. If ϕ_0 and ϕ are the flow rates due to a given pressure drop, measured before and after adsorption, the permeability reduction is given by $R_k = \phi_0/\phi$. In the case where the size of the pores is known, the use of Poiseuille's law leads to the value L_H for the hydrodynamic thickness of the adsorbed layer

$$L_H = \bar{r}[1 - (\phi/\phi_0)^{1/4}]$$

where $\bar{r}$ is the radius of the pores or an appropriate average in case of a pore-size heterogeneity. The commercial filters used as porous media in this study present a nonnegligible pore-size heterogeneity and a complete analysis of this influence on the value of L_H demands an extensive characterization of the filters, but this is beyond the scope of this paper where we are mainly interested in the relative variations of L_H. However, a quick analysis of this problem[3] shows that the error becomes negligible for small values of $L_H/\bar{r}$ corresponding to $\phi/\phi_0 < 0.5$.

Experimental Section

Porous Media. Three different types of commerical filters have been used as porous media. Their characteristics are presented in Table I. Millipore filters are made of a mixture of cellulose esters, Sartorius filters are made of cellulose nitrate, and Nuclepore filters consist of polycarbonate. In contrast with the first two types, which have a spongy structure, Nuclepore filters offer nice cylindrical pores. All the filters were repeatedly washed

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Table I
Characteristics of the Filters Used as Porous Media

type[a]	pore radius,[b] μm	thickness, μm	specific area[c] BET, m²/g	porosity, % vol
MF SS3	1.5 (0.45)	150	4.0	82
MF SM5	2.5 (0.75)	130	3.7	84
MF SC8	4 (0.7)	130	3.9	84
SM 12500	6	200	2.2	85
N 500	2.25 (0.25)	10	0.24	8

[a] MF, Millipore; SM, Sartorius; N, Nuclepore. Diameter 47 mm. [b] The values in parentheses are the standard deviations given by the manufacturer. [c] Determined with Kr.

Table II
Characteristics of the Polymers Studied

type	$\overline{M}_w \times 10^{-6}$	$\overline{R}_g$, Å	$\overline{M}_w/\overline{M}_n$
HPAM 0%[a]			
$f_{8.2}$	8.2	2000	1.15
$f_{2.9}$	2.9	1030	1.4
$f_{0.92}$	0.92	490	1.35
$f_{0.32}$	0.32	200	1.2
HPAM 15%[a]			
$f_{2.2}$	2.2	1200	1.36
HPAM 35%[a]			
$f_{2.1}$	2.1	1730	
PS			
$f_{8.2}$	8.2	2000	1.8
$f_{2.4}$	2.4	980	

[a] Percent hydrolysis, respectively, measured according to ref 7: <0.3, 21, 38.

before using; they were treated under vacuum in order to remove any trapped gas and then saturated by introducing the outgassed solvent used for the adsorption study.

Polymers. Most of the experiments have been carried out with fractions of commerical polyacrylamides (Calgon) with various degrees of hydrolysis (HPAM α%). They have been obtained from François,[7] who characterized the samples by viscometry, light scattering, and GPC in water (0.1 M NaCl). In addition, two fractions of polystyrene (PS) have been studied. Characteristics of all the samples are given in Table II.

Preparation of Solutions. The solutions of commerical polyacrylamide are often difficult to solubilize; fractionated samples are much easier to solubilize and very stable solutions can be obtained if the solutions are prepared in absence of oxygen and divalent and trivalent cations.[7] In addition, too vigorous stirring must be avoided in order to prevent possible shear degradation. It has been shown that with such care, polyacrylamide solutions do not contain aggregates if the concentration is lower than 10^{-3} g/cm³.

All solutions were carefully prepared in the absence of oxygen, using deionized water of 12 μΩ cm^{-1} purified by a Millipore device (Millipore Super-Quality). They were stored for 24 h before used in closed polyethylene vessels. Analytical grade NaCl was added in order to minimize polyelectrolyte effects.

Polystyrene solutions were prepared with freshly distilled toluene, stored for 24 h, and then slowly filtered on 0.45-μm Millipore filters.

Adsorption Measurements. The water- or toluene-soaked filter was placed into the cell described below and the volume flow ϕ_0 was measured. Then it was placed in a closed polyethylene vessel containing 100 mL of polymer solution. After a predetermined time the filter was removed, washed with pure solvent, and placed again into the cell. The volume flow ϕ was measured.

For high shear rates ($200 < \dot{\gamma} < 2000$ s^{-1}) a simple glass filtration cell (Selectron) was used, and the flow rate was determined by recording directly the weight of liquid flowing through the filter as a function of time. This was performed with a Mettler P1200 balance coupled to a rapid recorder. The pressure difference applied, ΔP, was varied by changing the height of the liquid in the cell. In order to increase the range of ΔP we used two upper cylindrical containers (17- or 34-cm high) with a diameter large enough to allow any small change in the height of the solvent during the measurement to be negligible. Under these conditions Poiseuille's law is followed with the filters used in all ranges of ΔP studied. Measurements were made at a controlled room temperature (25 °C).

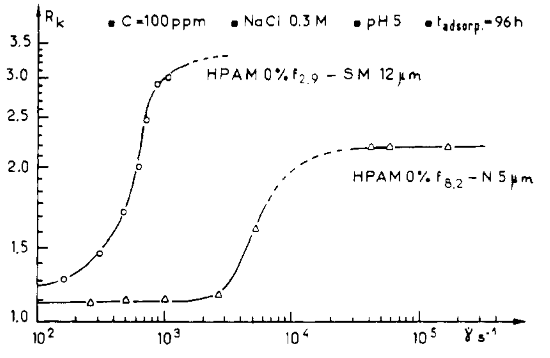

Figure 1. Variation of the permeability reduction $R_k = \phi_0/\phi$ with the applied velocity gradient.

For low shear rates ($10 < \dot{\gamma} < 200$ s^{-1}) we used an apparatus especially conceived by Chauveteau.[8] In this case the loss of pressure produced by a series of filters when solvent is flowing through at a constant rate is measured. The arrangement includes a constant-flow pump, four filtration units placed in series in a constant-temperature bath, and a water–oil manometer measuring the ΔP between the first and fourth filtration unit. Each filitration unit includes three filters and the additivity of the loss of pressure with the number of filters was checked before the measurements were performed.

A preliminary calibration of the loss of pressure due to the empty filtration units was made in order to correct the obtained values. With Nuclepore filters, which present a low porosity, nylon grids of 50-μm hole diameters were put between each filter in order to obtain a homogeneous flow.

In both types of measurement, repeated determinations were made. The value of the shear rate $\dot{\gamma}$ is calculated from Poiseuille's law, taking into account the reduction of the diameter of the pores due to the adsorbed layer

$$\dot{\gamma} = 4\phi/(\bar{r} - L_H)S$$

where S is the open area of the filter.

Results

As is generally observed, all the adsorbed layers studied here were found to be very stable, and significant desorption in the presence of pure solvent was never observed during the measurements. The observed quasi-irreversibility was confirmed by two types of experiment.

In the first type, the permeability of a filter containing an adsorbed layer was measured after a significant quantity of solvent had passed through. Even though 10 L of solvent had passed, no significant change in ϕ was observed.

In the second type of experiment, the filter, after adsorption was complete, was washed and immersed in 1 L of pure solvent and its permeability was measured periodically. After 144 h of immersion, a slight decrease of ϕ was observed, corresponding to a decrease in L_H of 10%.

This quasi-irreversibility permits cyclic experiments where the pressure difference applied is changed from low to high values and then reversed.

Influence of the Nature of Porous Media. Figure 1 presents the results obtained with two different porous media. The polymers tested were two polyacrylamide fractions with high molecular weights adsorbed from water solutions. Although the structure of both filters is quite

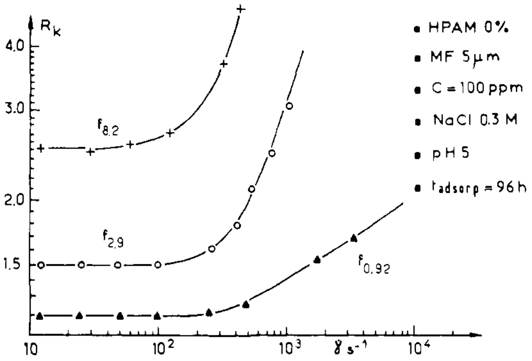

Figure 2. Influence of the molecular weight on the permeability reduction.

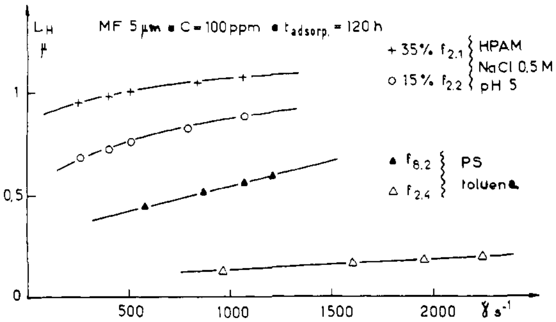

Figure 3. Variation of the hydrodynamic thickness as a function of the velocity gradient for different polymers.

different, the same type of dependence as a function of the applied velocity gradient is observed. Nuclepore filters show a hydrophobic character and cylindrical, well-defined pores, in contrast with Sartorius filters, which have a more polar chemical nature and a spongy porous structure. We observed that in both cases the permeability decreased strongly from a definite value of the gradient up to a value where a plateau is attained. A clear and reversible transition appears, indicating a reversible dilatation of the adsorbed layer.

Influence of the Molecular Weight. Figure 2 presents the behavior of three polyacrylamides with the same degree of hydrolysis and different molecular weights. They were adsorbed onto a 5-μm-diameter filter. We note that, as molecular weight is increased, the dilatation increases and, conversely, the critical value of $\dot{\gamma}$ for the inception of the deformation drops off with increased molecular weight.

Influence of the Nature of the Polymers. Although most of this work has been done with polyacrylamides of 0% hydrolysis, Figure 3 shows the behavior of two high molecular weight polystyrenes in toluene together with two polyacrylamides of different degrees of hydrolysis. In each case an increase of the adsorbed thickness is observed. Compared with a polyacrylamide of the same molecular weight, the dilatation for the polystyrene seems much lower particularly for $f_{2.4}$. However, it must be considered first that the observed thickness for PS is much smaller than for HPAM and second that, considering the difference of molecular weight of the monomers (72 for HPAM and 104 for PS), the total length of the PS chains is much lower than for HPAM chains. If we consider the adsorbed chains formed of loops and trains, the previous consideration demonstrated that the PS loops must be shorter than the HPAM loops. Evidently such comparison is only valid if the mode of adsorption is the same for the two polymers. Anyway the observed behavior proves that the dilatation of the adsorbed layer under the influence of ΔP is not particular to HPAM polymers and it should be very interesting to verify if this behavior is typical of flexible polymers.

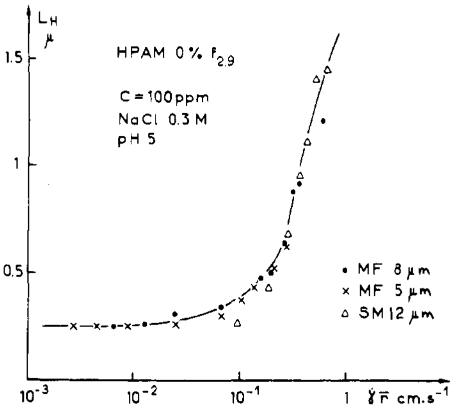

Figure 4. Variation of the hydrodynamic thickness as a function of the average velocity of the solvent for pores with different radii for HPAM 0% $f_{2.9}$.

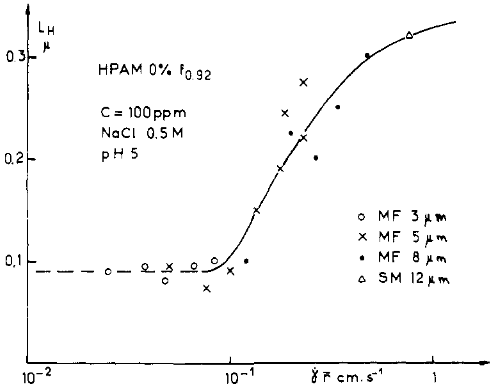

Figure 5. Variation of the hydrodynamic thickness as a function of the average velocity of the solvent for pores with different radii for HPAM 0% $f_{0.92}$.

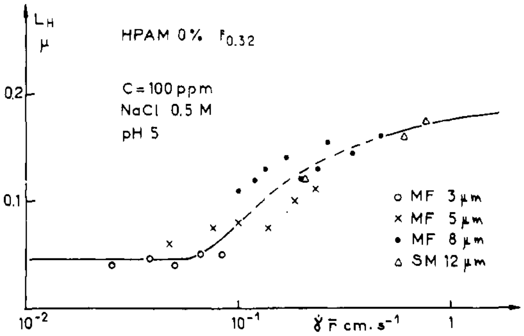

Figure 6. Variation of the hydrodynamic thickness as a function of the average velocity of the solvent for pores with different radii for HPAM 0% $f_{0.32}$.

Influence of the Flow Velocity. Up to now we have considered the transverse velocity gradient of the fluid in the pores as a parameter of deformation; however, the experiments show that the observed dilatation of the adsorbed layer increases with the radius of the pores increases. This dependence vanishes if we plot the thickness not as a function of $\dot{\gamma}$ but as a function of $\dot{\gamma}\bar{r}$, which is proportional to the average velocity of the solvent ($\dot{\gamma}\bar{r} = 4\bar{v}$). In Figure 4 such a plot is made for three sizes of pores: a universal curve representative of all the collected data is obtained. In Figures 5 and 6 the same plots are presented for two lower molecular weights. Taking into account that the precision of the measurements is lower when

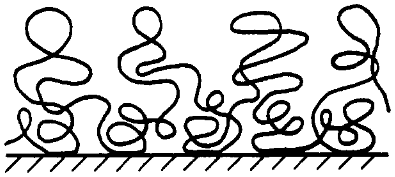

Figure 7. Classical representation of the polymer chains weakly adsorbed on a flat surface at high coverage ratio.

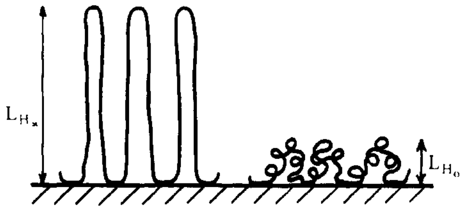

Figure 8. Schematic representation used for the calculation of the number of trains.

the thickness of the absorbed layer is small compared with the size of the pores, a remarkable correlation is obtained, indicating that the parameter governing the deformation is the velocity of the fluid through the pores.

Discussion

The experimental results presented clearly show that strong interactions exist between the flow and the adsorbed polymers leading to a reversible deformation of the layer. This behavior seems to be quite general for weak-adsorption cases (high L_H values) and was observed with different types of flexible macromolecules adsorbed into porous media of different nature and structure. In addition, similar effects have been observed on shaly sands.[9]

While the deformation of macromolecules in solution under the influence of hydrodynamic forces is now well documented,[10] the problem of hydrodynamic interactions between the flow and the adsorbed macromolecules is quite new; a very limited approach has been recently published[11] in the case of one-point-attached polymer. A complete solution of this problem presents many difficulties, one of which is a precise description of the structure of the adsorbed layer. In an important contribution, the relationships between the dimensions of the adsorbed layers and the corresponding hydrodynamic thickness has recently been discussed[4] but no attempt has been made to include large hydrodynamic interactions leading to a deformation of the layer.

In an attempt to explain the effect observed and to propose a possible model we will first try to envisage what kind of change of structure of the adsorbed layer is induced by the flow of solvent and secondly the hydrodynamic origin of this dilatation. In order to discuss the first point it is necessary to recall some facts concerning the structure of the adsorbed layer. Excellent reviews have already treated this problem in detail[12] and only the main conclusions relative to our extensive work on polyacrylamide adsorption[3,13] are recalled. According to our experimental conditions, all the results discussed here correspond to the plateau in the adsorption isotherm at high surface coverage. The chains are very long and the solvent is quite good so that excluded-volume effects can be important. The thickness L_H for the adsorption layers are very large (higher than $2\bar{R}$), indicating that we have a case of weak adsorption. The overall attraction resulting from the balance between attractive forces toward the surface and repulsive forces due to monomer interaction is very small. Measurements of the adsorbed quantities show that this parameter becomes independent of the molecular weight for molecular weights higher than 10^6. Combined with L_H, which is function of the molecular weight, high values are obtained for the average density of the adsorbed layer. In addition this density decreases with the molecular weight and tends to the mean density of a Gaussian coil in solution for very high molecular weight.

According to the classical representation in Figure 7, the chains are divided into trains tightly anchored to the surface and in loops or tails extending more or less into the liquid phase. The relative sizes of the loops, trains, or tails depend on the length and flexibility of the chain, and the repartition of the segments in the planes parallel to the surface is uniform. Among the various profiles proposed for the segment density distribution along a perpendicular to the surface, the most likely is an exponential decrease from the surface, but to date there is no experimental confirmation. To complete this picture, the facts that L_H increases more rapidly than $2\bar{R}$ with $\bar{M}_w$ and that the adsorbed quantity shows no dependence on $\bar{M}_w$ can be interpreted in terms of a decrease of the fraction of segments anchored to the surface with $\bar{M}_w$. Such behavior has recently been observed with PS adsorbed on silica,[14] leading to a limiting value of 0.20–0.25. This value depends on the surface structure[15] and can be very low. We will see that a crude estimation of the number of trains shows that the HPAM chains also have low number of attached segments. Considering this picture, the main question now is to know what is the change of structure of the layer induced by the flow of solvent and leading to such an increase of L_H. One can suppose that under the influence of a certain hydrodynamic strength—that we will try to describe later—the number of segments directly attached to the surface decreases, leading to a progressive increase in the size of the loops. Two remarks prompt us to reject this picture. First we observe a reversible transition curve of the deformation with the appearance of a constant thickness after a definite value of the solvent velocity has been attained. If we suppose that the frictional forces are able to break some contact points between the segments and the surface, there is no reason that the same forces could not remove all the polymer from the surface. All experimental attempts to produce a complete desorption by increasing the flow rate and the duration of the deformation have failed. Secondly, we observe a very rapid reversibility of the phenomena: a partial desorption of the molecules would lead, in the absence of strain, to a rearrangement, which, as demonstrated by all the adsorption kinetics, is a very slow process. Another model which is much more likely is that under the influence of the flow forces the loops become stretched and unwind in the radial direction up to the maximum possible elongation. This behavior is expected in the case of solution of flexible polymers under high velocity gradients,[16-18] where abrupt stretching can occur when a critical value of the velocity gradient is reached. Under these conditions the maximum increase of L_H is governed by the number of attached segments. This last parameter is one of the most difficult to measure experimentally but the hydrodynamic stretching which is observed can lead to some indication of this number. Taking 2.52 Å for the distance between three carbon atoms in the polymeric chain, one can compare the total length l of a completely stretched coil with the observed maximum values of L_H ($L_{H\infty}$, maximum thickness observed under stretching). According to the diagram in Figure 8, $^1/_2 L_{H\infty}$ gives the number of loops and $^1/_2 L_{H\infty} + 1$ gives the number of trains. This rough calculation for the case of HPAM 0% $f_{2.9}$, $f_{0.92}$, and $f_{0.32}$ gives a value of three or four trains. This low value is not inconsistent with the quasi-irreversibility of the

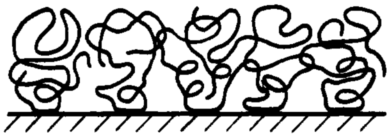

Figure 9. Model proposed for the structure of the adsorbed layer of high molecular weight HPAM-spotwise adsorption.

adsorption if we consider that a train can be formed from a significant number of attached segments. Such a calculation is based on the direct identity between L_H and the geometric length of the chain, which is a very crude approximation because L_H is an hydrodynamic average resulting from the interactions between the segments and the flow.

Now the question is to understand the origin of this stretching. We are at present so far removed from the solution of this problem that only very qualitative pictures can be proposed. First of all it is clear that a net circulation of solvent must exist through the adsorbed layer. This is well understood both for the case of a macromolecule in solution as well as for an isolated adsorbed molecule. For high ratios of surface coverage with a uniform density of segments in the planes of the surface as depicted in Figure 7, it is difficult to suppose that the solvent can easily flow near the surface. In addition, the effect of the flow on such a layer can only be a flattening of the layer. The dilatation observed, together with the discussed structure of the layer lead us to propose the model in Figure 9 in which considerable circulation of solvent can exist as a consequence of a nonuniform distribution of segments near the surface. We suppose a discrete segment density along the surface corresponding to a spotwise adsorption. The layer must be viewed as a monolayer stacking of semipermeable prolate spheroids in which a tortuous circulation of solvent takes place. As the velocity of this circulation increases, the solvent is forced to penetrate more and more into the coils and the flow is diverted toward the center of the pores. The polymer swells more and more and expands in the axial direction, the only possible direction. The rheological property controlling this deformation is the elongational viscosity more than the shear viscosity. Interest in elongational flow behavior of polymer fluids has increased rapidly in recent years[19] but much more research into this area is needed in order to understand the behavior of the adsorbed polymer layers.

One consequence of the proposed model is the presence of a large number of unoccupied surface sites. This is in agreement with the results of Thies[20] and Steinberg[21] showing that polymer chains can be overadsorbed in a surface already covered to saturation by another polymer. We have obtained similar results[3] with two fractions of HPAM with different molecular weights; the final adsorbed quantity corresponds to the sum of the quantities obtained for each polymer alone and the hydrodynamic thickness corresponds to that of the higher molecular weight alone. However, we think that this behavior can only be understood by considering that the real equilibrium was not attained even after some days.

Conclusion

In spite of considerable efforts, both experimental and theoretical, to clarify the problem of the adsorption of polymers on solid surfaces, the observation of dilatation of the adsorbed layer under the effect of flow forces indicates that the current understanding is not complete and that further theoretical effort is required. This phenomenon has significant practical consequences, as it can perturb various processes and lead to incorrect interpretations. From a fundamental point of view this effect requires us to take into account an additional parameter in the description of the adsorbed macromolecules. Once more, one can note the interest of the hydrodynamic method used, which, considering its simplicity, leads to numerous experimental results which are inaccessible by other methods.

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