Polymers in Solution

Their Modelling and Structure

J. DES CLOIZEAUX

and

G. JANNINK

Polymers in Solution

Their Modelling and Structure

Jacques des Cloizeaux   and   Gérard Jannink
Service de Physique Théorique   *Laboratoire Léon Brillouin*
du Centre d'Etudes Nucléaires   *au Centre d'Etudes Nucléaires*
de Saclay   *de Saclay*

Translated from the original French text
by J. des Cloizeaux
with the collaboration of G. Jannink

CLARENDON PRESS · OXFORD
1990

Polymers in Solution
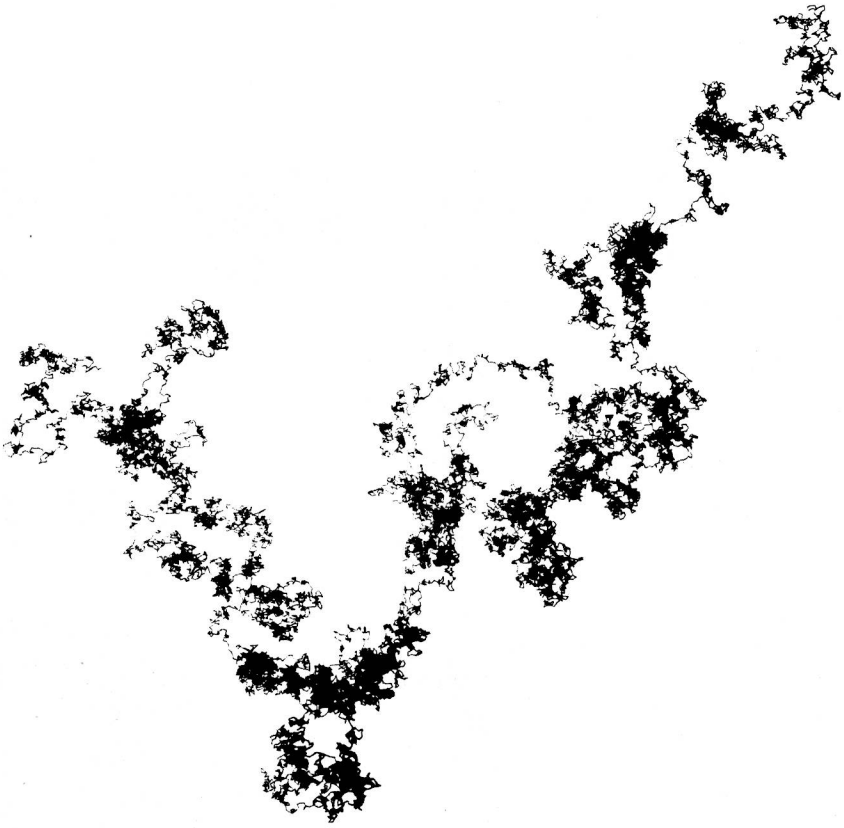
A Brownian chain (random walk) of 2×10^5 steps (from B. Duplantier and J.M. Luck, 1987)
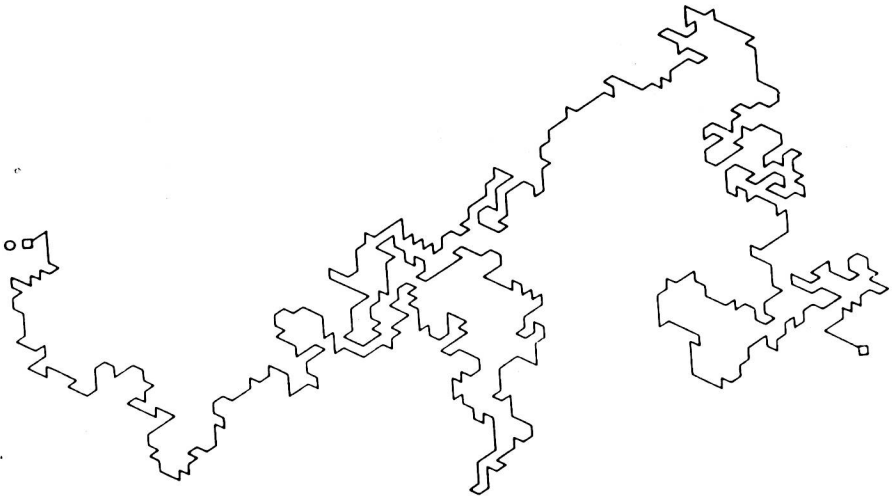
A self-avoiding chain (self-avoiding walk) drawn on a triangular lattice (from J.F. Renardy, 1971). The starting point of this chain is at O.
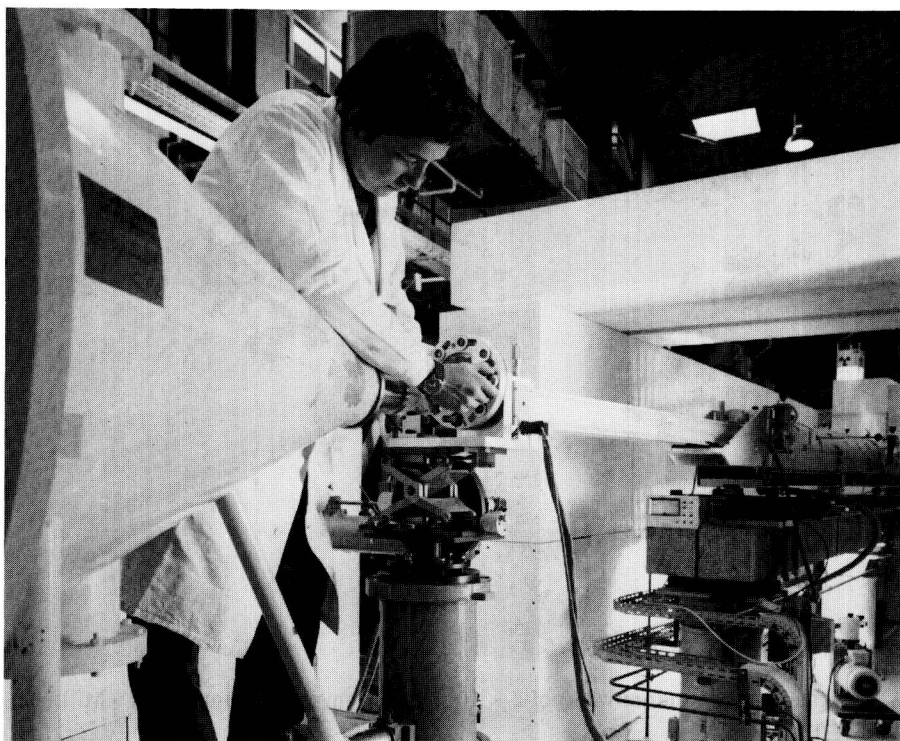
Preparation of a small-angle scattering experiment using neutrons: view of instruments at the Laboratoire Léon Brillouin in Saclay. Incident neutrons coming from the Orphéc source are guided in the tube seen on the right hand side of the figure. A sample holder stands at the tube end. The operator is setting a sample of a polymer solution in place. The cone seen on the left side is the front part of the void duct in which the scattered beam propagates; intensity is recorded on a detector placed at the rear of the duct.

PREFACE TO THE ENGLISH EDITION

The authors are pleased to present an English version of their book *Polymères en solution: leur modélisation et leur structure* to the scientific public. The text is practically the same, but a few recent results and references have been added; moreover, misprints, errors, and obscurities have been corrected. Since 1987, no great progress has been made in the field, except in two dimensions. The authors hope that the book will be useful to the community.

Saclay   J.C.
23 December 1988   G.J.

PREFACE

This book is dedicated to the study of the static properties of flexible polymers in solution; its aim is to present the vast progress made by both theory and experiment over the last fifteen years. It might be asked why this question has aroused such lively interest and why great effort has been expended in this domain. What has progressively appeared is that long polymer chains, despite the variety in their chemical composition and physical properties, behave in a universal manner when in solution. Recognition of this fact is on a par with the formulation of the critical system concept of which the polymer in solution is a very good example.

At the same time, the use of new means of observation by diffraction of neutrons and photons has led to a better experimental knowledge of the critical behaviour. Finally, at the juncture between theory and experiment, the development of computers has, by means of network simulation, enabled interesting results to be obtained.

It should be noted, however, that many researchers in the field of polymers have been unwilling to accept the new principles, thereby minimizing their impact and interest. By stressing the diversity of the components of the different types of polymers, they have continued to use inadequate and superfluous parameters. Thus, the use of a poor notation has often masked the simplicity and beauty of the phenomena. Nevertheless, today there exists a substantial number of results which outstandingly show the validity of the universality hypothesis. Only appearing on a large scale, this universality is, moreover,

compatible with the existence of specific physical properties which can be observed on more reduced scales.

As early as 1980, P.G. de Gennes brilliantly presented the question, in the light of the new principles, in his book *Scaling Concepts in Polymer Physics*, but the authors wanted to study thoroughly the concepts and develop the calculations which led them to treat the various aspects of a more restricted subject.

This work is the fruit of the collaboration of authors who have both worked for a good many years on polymer solutions, but these authors differ profoundly in character, education, and interests. One of them is a pure product of the French University system, the other carried out his studies in Switzerland and the United States: one is a theoretician, the other is more of an experimentalist. This disparity, which has not always facilitated the writing of the various chapters, despite the excellent relationship between the two, has certainly contributed to the value of the book. In this work, the authors have presented all the facets of the question, starting from first principles, and they have striven to extend their explanations as far as they could without entering into horrible complications. Moreover, the confrontation between theoretical and experimental points of view was inevitable; as G. Bachelard said of any scientific activity 'If it reasons, you must experiment; if it experiments, you must reason'. Difficulties nevertheless emerged. First, it is clear that theoretical propositions and experimental facts must be established in an autonomous way. The risk of 'seeing' what is predicted, or, inversely, of 'explaining' what is seen, without a true agreement, is great. Moreover, the fundamental quantities are obviously perceived in different ways by the theoretician and the experimentalist. Thus, to define the size of a polymer, the theoretician naturally uses the end-to-end distance, whereas the experimentalist, equally naturally, uses the radius of gyration. This is only an example; the reader will recognize others which are more serious. These difficulties, however, can be overcome and, on essential points, the views converge. Between theory and experiment, an agreement which is not only qualitative but also quantative will be sought and this is favoured by the universality of the behaviour of long polymers in solutions. Thus, and for more than one good reason, this book is a work of synthesis.

In particular, the authors endeavoured to present old and new results within the same scope thereby extending the work of their predecessors. This book is thus linked to *Polymer Chemistry* by Paul Flory, to *Modern Theory of Polymers* by Hiromi Yamakawa, and naturally to *Scaling Concepts in Polymer Physics* by Pierre Gilles de Gennes.

Despite writing the chapters quite independently, the authors wanted to give a true unity to the book. Thus, throughout the work, they aimed at using coherent notation and reasonable designations. Consequently, logic sometimes forced them to distance themselves somewhat from awkward traditions. Nevertheless, this problem of notation has not always been easy to solve, due to the large number of disciplines concerned by the study of polymers; namely, computer simulation, statistical mechanics and theory of liquids, description of the

polymers themselves, field theory, study of the structure of a system by neutron or photon scattering, principles of renormalization theory and applications. The work thus contains very diverse elements.

The authors, however, had to restrict themselves and thus sacrificed the study of dynamic properties. No doubt it should not be regretted. In fact, these dynamic phenomena are very complex and not as well understood as the static phenomena, and for several reasons. First, we have to take into consideration the special hydrodynamic effects, a difficult task. In addition, it can be shown that the critical asymptotical limits are much more difficult to obtain in dynamics than in statics. In dynamics, we are always in an ill-defined crossover zone which is not easy to study with precision. For all these reasons, the authors considered only the static problem.

Within this framework, the book can be used as a basic manual by the student who wishes to instruct himself in the domain. It can also serve as a reference book, providing material for the experienced researcher. It is aimed, in the first instance, at the physicist, theoretician or experimentalist, as well as the physico-chemist. It may also interest certain mathematicians and chemists.

As with all the sciences, the study of polymers in solution developed in an anarchic fashion, drawing on very diverse disciplines. In order to help the reader to get his bearings, a good number of the chapters begin with a genesis which retraces the evolution of the ideas and techniques as the authors perceived them. These geneses are not historical accounts and do not attempt to be impartial; they simply serve as a guide to the reader. They might also interest the science historian, as the Memoirs of Saint-Simon interest the historian of the reign of Louis XIV.

Glancing through this preface, the reader will have understood that this book can be nothing other than imperfect, and for this, he or she has the authors' apologies, as do all the scientists whose works have been badly quoted or even unjustly forgotten.

The writing was nevertheless improved by the constructive criticisms which were made by certain physicists whom the authors would like to thank.

Saclay   J.C.
18 May 1987   G.J.

ACKNOWLEDGEMENTS

NOTATION AND MAIN SYMBOLS

UNITS

Atomic lengths are expressed in nanometers (1 nm = 10 Å).

CONVENTIONS

(a) As a rule, the symbols concerning the internal structure of polymer chains are printed in italic type; the symbols concerning a set of polymers are printed in bold italic type.

Example: N = number of links of a polymer

$\boldsymbol{N}$ = number of polymers in a set

(b) Sets are characterized by braces.

Example: $\{r\}$ = set of vectors $\vec{r}_j$ or $\vec{r}(s)$.

(c) A Fourier transform is indicated by a tilde.

Example: $\tilde{f}(k) = \displaystyle\int_{-\infty}^{+\infty} dx\, e^{ikx} f(x)$.

(d) When a Fourier transform $\tilde{f}(\vec{k}_1, \ldots, \vec{k}_n)$ is proportional to $\delta(\vec{k}_1 + \ldots + \vec{k}_n)$, we write:

$$\tilde{f}(\vec{k}_1, \ldots, \vec{k}_n) = (2\pi)^d \delta(\vec{k}_1 + \ldots + \vec{k}_n)\, \overline{f}(\vec{k}_1, \ldots, \vec{k}_{n-1}, -\vec{k}_1 - \ldots - \vec{k}_{n-1}).$$

(e) The average of an observable $\mathcal{O}$ over configurations is denoted by $\langle\!\langle \mathcal{O} \rangle\!\rangle$. On the contrary, the average of $\mathcal{O}$ over chain lengths is denoted by $\langle \mathcal{O} \rangle$; moreover, we use the notation

$$\mathcal{O}_n = \langle \mathcal{O} \rangle \qquad \mathcal{O}_w = \langle N\mathcal{O} \rangle / \langle N \rangle \qquad \mathcal{O}_z = \langle N^2 \mathcal{O} \rangle / \langle N^2 \rangle$$

where N is the number of links (or of monomers).

(f) When we put an index 'zero' on the upper left-hand side of a symbol, we refer to an unperturbed system (pure solvent, Brownian chain without interaction). Indices 'one' or 'two' in the same position refer to orders of perturbation

(g) In order to distinguish similar quantities pertaining to the solvent or to the solute, we use the following convention: an index 'zero' on the lower right-hand side of a symbol indicates that the corresponding quantity concerns the solvent; an index 'one' on the lower right-hand side of a symbol indicates that the corresponding quantity concerns the solute.

(h) The universal functions which appear in scaling laws are generally represented by symbols printed in upright type.

MAIN SYMBOLS

a	Constant of the Landau–Ginzburg model (coefficient of $(\vec{\nabla}\phi)^2$)
a_c	Critical value of the constant a for the Landau–Ginzburg model
a_B	Value of the two-leg vertex function for the Landau–Ginzburg model at $\vec{k} = 0$ ($a_B = \Gamma_B(\vec{0}, \vec{0})$)
a_R	Value of the two-leg 'renormalized' vertex function for $\vec{k} = 0$ $[a_R = \Gamma_R(\vec{0}, \vec{0})]$
$a(b)$	The number of a chain (N_a = number of links of the chain a)
$A(B)$	Number of links (A like N) or 'area' of a polymer chain (A like S)
A_2, A_3	Second and third virial coefficient (expansion in ρ) for a monodisperse solute $\left(\Pi/RT = \dfrac{\rho}{M} + A_2\rho^2 + A_3\rho^3 + \ldots \right)$
$A_{2,\Pi}$	Second virial coefficient (expansion in ρ) for a polydisperse solute $\left(\Pi/RT = \dfrac{\rho}{M_n} + A_{2,\Pi}\rho^2 + \ldots \right)$
$A_{2,\sim}$	Mean value of the second virial coefficient, obtained by measuring the osmotic compressibility in a scattering experiment
A_2, A_3	Second and third virial coefficient (expansion in C) for a monodisperse solute ($\Pi\beta = C + A_2 C^2 + A_3 C^3$)
$A(x)$	Generating function for trees
$\mathfrak{T}$	Tree (tree diagram)
$\mathscr{A}(\mathscr{B})$	Subset of molecules ($N_{\mathscr{A}}$ = number of polymer chains of the subset $\mathscr{A}$)
$^0A_0(y), {}^0A_1(y)$	Numerical factors connected with the swelling $^0\mathfrak{X}_0$ in the vicinity of the Flory temperature.
$A_4(y)$	Numerical factor connected with the renormalization factor $^1\mathfrak{X}_4$
$A(B)$	A represents a constant
$\circledA$	Avogadro number ($\circledA = 6.02249 \times 10^{23}$)
b	Two-body interaction
b_c	Two-body interaction at the top of the demixtion curve
b	Scattering length
$\mathrm{b}^{\circ\rightarrow}$	Contrast length (with respect to the solvent)
$B(y)$	Generating function of vertex functions (associated with trees)
$\vec{B}(\vec{r}, t)$	Magnetic field

$B_j(\vec{r})$	Auxiliary field component used in the generating function of the Green's functions
$B(u)$	Borel transform
c	Three-body interaction
c	Velocity of light
C	Monomer concentration or link concentration (number per unit volume)
$C_{\mathscr{A}\alpha}$	Monomer concentration
$C(\vec{r})$	Link concentration at the point of position vector $\vec{r}$
$C^{\mathrm{I}}, C^{\mathrm{II}}$	Link concentrations corresponding to the demixtion points of an isotherm ($C^{\mathrm{II}} > C^{\mathrm{I}}$)
$\boldsymbol{C}$	Chain concentration (Number of polymers per unit volume)
$\boldsymbol{C(S)}$	Concentration of chains of area S
$\boldsymbol{C^*}$	Chain concentration corresponding to the cross-over between dilute and semi-dilute solutions.
$\boldsymbol{C^{**}}$	Chain concentration corresponding, for semi-dilute solutions, to the crossover between good and poor solvents
$\mathscr{C}$	Area concentration (quantity analogous to C); $\mathscr{C}$ is a 'Brownian area' per unit volume: $\mathscr{C} = CS$)
$\mathscr{C}_{\mathrm{k}}$	A concentration analogous to C and to $\mathscr{C}$, but for a Kuhnian chain ($\mathscr{C}_k = CX^{1/\nu}$)
$^{\circ}\mathrm{C}$	Degrees Celsius
$\mathfrak{C}$	Chain
C	Integration path
$\mathcal{C}$	Specific heat
d	Dimension of space
$d_{\mathrm{a}1}, d_{\mathrm{a}2}$	Anomalous dimensions of fields
D	Hausdorff dimension of a fractal object
$\mathfrak{D}$	Diagram
$\mathscr{D}$	Diagram contribution to a partition function
$\mathscr{D}$	Diagram contribution before summation over some internal variables (areas or wave vectors)
e	Electric charge
E	Energy level
$\mathscr{E}$	Set (of molecules for instance)
$\mathbb{E}$	Average energy calculated over a large number of configurations

$\vec{E}$	Electric field
$\mathcal{E}$	Euler's constant
f	Fugacity
$\mathfrak{f}$	Another fugacity (renormalized)
$f(x)$	A function
$f(\vec{x})$	Scaling function for the end-to-end distance of a long polymer in a good solvent
$\boldsymbol{f}$	Free energy per unit volume
$F_0(x, z),\ F(x, g)$	Non-universal functions for the osmotic pressure of a polymer solution
$F(x)$	Scaling function for the osmotic pressure in good solvent ($\Pi\beta = F(CX^d)$)
F_∞	Universal constant concerning the osmotic pressure of semi-dilute solutions in good solvent (for $x \gg 1$, $F(x) \simeq F_\infty x^{-1/(\nu d - 1)}$)
$\mathbb{F}$	Helmholtz free energy of an incompressible system or when the compressibility of the solvent is ignored ($\mathbb{F} = \mathbb{E} - \beta^{-1}\mathbb{S}$)
$\mathscr{F}$	Helmholtz free energy of a compressible system
F	Force
$\mathfrak{g}$	Weight constant
g	Two-body osmotic parameter: a pure number which defines the second virial coefficient when the size of the isolated self-interacting polymer chain is chosen as the scaling length
$g(z)$	The osmotic parameter g as a function of the two-body interaction parameter z
g^*	The value of g in the Kuhnian limit ($g^* = g/(z \to \infty)$)
$g(\vec{r})$	Pair correlation function
$\mathbb{G}$	Gibbs free energy (free enthalpy)
$\mathfrak{G}$	Graph
$G(x)$	Scaling function for the osmotic pressure ($F(CX^d) = G(\rho/\rho_G^*)$)
$G(\ldots)$	Green's function for spins on a lattice
$\mathscr{G}(\ldots)$	Connected Green's functions in continuous space
$\mathscr{G}_G(\ldots)$	Non-connected Green's functions in continuous space (index G for general)
$\mathscr{G}(\vec{r}_1, \ldots, r_{2N};\ a_1, \ldots, a_N)$	Connected Green's function with $2N$ legs in continuous space; this function associated with N fields, characterized by different values for the a_{j_2} is the Laplace transform of the partition function $Z(\vec{r}_1, \ldots, \vec{r}_{2N};\ a_1, \ldots, a_N)$

$\mathscr{G}(k_1, \ldots, k_{2N}; a_1, \ldots, a_N)$ Green's function in reciprocal space; it is the Fourier transform of $\mathscr{G}(\vec{r}_1, \ldots, \vec{r}_{2N}; a_1, \ldots, a_N)$

$\mathbf{G}_G\{B\}$	Generating function of the non-connected Green's functions
$\mathbf{G}\{B\}$	Generating function of the connected Green's functions
h	Column height
$\hbar$	Planck constant
h	Three-body osmotic parameter: a pure number which defines the third virial coefficient when one chooses as a scale, the size of the isolated polymer, in the same solvent and at the same temperature
$h(y)$	Three-body osmotic parameter as a function of the three-body interaction parameter y (for $z = 0$)
$h(x)$	Scaling function related to the form function $H(\vec{q})$ of an isolated chain in good solvent
h_∞	Universal constant associated with the asymptotic behaviour of $h(x)$ (for $x \gg 1$)
$H(\vec{q})$	Form function of a polymer ($\vec{q}$ is the transfer wave vector)
$H(\vec{q})$	Structure function of the solute (polymer)
$H^I(\vec{q})$	Intramolecular structure function of the solute (intrachain)
$H^{II}(\vec{q})$	Intermolecular structure function of the solute (interchain)
$\mathfrak{H}$	Hamiltonian for chains
$^0\mathfrak{H}_N$	Hamiltonian for N non-interacting Brownian chains
$^1\mathfrak{H}_N$	Contribution of the interaction to the Hamiltonian for N chains
$\mathscr{H}$	Hamiltonian for a spin system (or a field)
i	$= \sqrt{-1}$
$|i\}$ $(|j\})$	Spin state
$I(q)$	Intensity of a scattered radiation: it is the number of particles that fall, during a period of time t, on a small detector of which the (angular) position corresponds to the deflection characterized by the transfer wave vector
I	Symbol representing an integral
$\mathfrak{I}$	Integration domain
$j(z)$	A function of the two-body interaction parameter: the product $z j(z)$ is a pure number which defines the second virial coefficient when, the size of the non-interacting polymer chain (Brownian chain) is chosen as the scaling length.

J	Contact energy (on a lattice)
J	Incident particle flux
$J(\vec{r})$	The flux of the particles that are scattered at the point of position vector $\vec{r}$
$\vec{J}$	$\vec{J} = \vec{S} + \vec{s}$: operator for the total spin
$J(x)$	Scaling function associated with the structure function of a semi-dilute solution of polymers in good solvent
$J_c(x)$	Scaling function associated with the structure function of a solution in poor solvent, in the vicinity of the critical demixtion point
$J(\vec{r})$	Source associated with $\mathscr{C}(\vec{r})$ (Edwards's method)
$\vec{k}$	Wave vector (in particular external wave vector on a diagram)
$\hat{k}$	Unit vector along $\vec{k}$ ($\hat{k} = \vec{k}/k$)
$\vec{k}_0$	Wave vector of an incoming radiation
$\vec{k}_f$	Wave vector of a scattered radiation (index f for final)
k_B	Conversion factor called Boltzmann constant $k_B = 1/\beta T = R/ \circledA = 1.380 \times 10^{-23}$ joule K^{-1}
$\mathfrak{k}$	Connectivity of a lattice made of sites and bonds between these sites: number of bonds connecting each site to its neighbours
K	Degrees Kelvin (absolute degrees)
K_A	Experimental proportionality factor for converting the scattered intensity into a cross-section
K	Constant determined by the apparatus and the contrast: this constant makes it possible to convert the scattered intensity into the structure function of the solution
l	Characteristic length of a link ($\langle\!\langle u^2 \rangle\!\rangle = l^2 d$)
l_0	Length of a link
l_p	Persistence length
l_a	Atomic length
L	A length; in particular, the length of a chain of N links: $L = N l_0$
$\mathscr{L}(\vec{r})$	Lagrangian associated with the Landau–Ginzburg model
m	Number of species constituting the solute
m	Molecular mass of a monomer ($m = 104$ for the monomer of polystyrene)
M	Molecular mass of a polymer chain
M_n, M_w, M_Z	Mean molecular masses ($M_n = \langle M \rangle$, $M_w = \langle MN \rangle / \langle N \rangle$, $M_Z = \langle MN^2 \rangle / \langle N^2 \rangle$)
$\mathscr{M}$	A mass

M	Magnetization: variable appearing in the generating function of the vertex functions in field theory
$\boldsymbol{M}$	Number of sites of a lattice
M	Point in real space
n	Number of links of a chain (number of links of a sequence)
n	Index of refraction of a material (optical, neutron)
$\mathfrak{n}$	Number of components of the field (of the order parameter)
N	Number of links of a chain
N	Number of polymers
N_ξ	Number of swollen sequences constituting a polymer chain in a semi-dilute solution for a good solvent; the size of a sequence is, by definition, the Kuhnian overlap length
$\mathcal{N}(N)$	Number of partitions of the integer N
$\mathcal{O}$	An observable; a function or a functional of the vectors defining the configurations of polymers; an operator
$\lvert \mathcal{O} \rangle)\}$	A quantum state associated with a neutron and its target (orbital state of the neutron, orbital state of the target and spin state for the total spin)
p	Number of contacts
p	A probability
p	The polydispersity of a polymer sample is $(1 + p)$ $\left(p = \left\langle \left(\dfrac{N}{\langle N \rangle} - 1 \right)^2 \right\rangle, \; \dfrac{M_W}{M_n} \simeq 1 + p \right)$
$\mathfrak{p}^+, \mathfrak{p}^-$	Projection operators on the states of total spin $S + 1/2$ and $S - 1/2$ (S is the spin of the nucleus and $1/2$ the spin of the neutron)
$\boldsymbol{P}$	Pressure
$\boldsymbol{P}^{\mathrm{I}}, \boldsymbol{P}^{\mathrm{II}}$	Pressure in the cells I and II
$\boldsymbol{P}_{\mathrm{v}}$	Vapour pressure
$\mathscr{P}$	Set of correlation points (on polymer chains)
P_μ	Stokes parameters ($\mu = 1, 2, 3, 4$): $P_\mu = (\varepsilon/\hbar\omega)E^+ \sigma_\mu E^-$
$P(\vec{r})$	Probability distribution associated with the vector joining the origin of a polymer to its extremity (end-to-end vector)
$\wp$	Permutation
$\mathfrak{P}$	A plane
$\vec{q}$	Transfer wave vector: difference between the scattered wave vector and the incident wave vector
$\vec{q}_j$	Internal wave vector in a diagram