

**THEORY AND SIMULATION OF POLYMER
LIQUIDS UNDER EXTENSIONAL AND
SHEAR FLOWS**

by

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ABSTRACT

We examine several aspects of the dynamics of linear polymers under shear and extensional flows. We use nonequilibrium molecular dynamics (NEMD) to simulate systems under planar Couette flow (PCF) and planar extensional flow (PEF). In addition we look at several kinetic models of polymer melts, in particular the Curtiss-Bird model, for which we calculate the predictions of steady-state viscosity under PEF. To the best of our knowledge this is the first time that these results have been presented for this kinetic model. Our simulations under PEF are enabled by the use of Kraynik-Reinelt periodic boundary conditions (pbcs). We include here our observation that these pbcs are closely related to the Arnold cat map, a simple example of a dynamical map with chaotic properties. This observation enhances our understanding of this simulation technique.

We compare directly under flow for the first time two commonly used coarse grained models of linear polymers. The first, a bead-spring model which uses the flexible *finitely extensible nonlinear elastic* potential (FENE) to bond adjacent beads. The second, a bead-rod model which uses a constraint force algorithm to fix the bond length. For this model we use the name *freely jointed chain* (FJC). The comparison is based on viscometric, structural and dynamical properties. We find that results for FENE and FJC systems are almost identical. Comparing results with predictions of the Curtiss-Bird model under PEF we find that values for the parameters of the Curtiss-Bird model required for a fit with the simulation data fall outside the range allowed by the Curtiss-Bird model and we conclude that assumptions of the Curtiss-Bird model deviate from dynamics observed in liquids under extensional flow.

We then focus on the self-diffusion of molecules under PEF and PCF, calculating elements of the diffusion tensor using appropriate mean-squared displacement formulae. Our interpretation of these results incorporate properties from the FENE and FJC comparison and results for the velocity autocorrelation function in these systems. We find anisotropy of diffusion more significant under PEF than under PCF. We conclude that this arises due to the significant enhancement of alignment under PEF. Our simulations represent the widest range of molecular systems under shear flow for which self-diffusion has been calculated. Results for PEF represent the first examination of self-diffusion for molecular systems under an extensional flow.

DECLARATION

I hereby declare that the thesis entitled “Theory and Simulation of Polymer Liquids under Extensional and Shear Flows”, and submitted in fulfillment of the requirements for the Degree of Doctor of Philosophy in the Faculty of Information and Communication Technologies of Swinburne University of Technology, is my own work and that it contains no material which has been accepted for the award of any other candidate of any other degree or diploma, except where due reference is made in the text of the thesis. To the best of my knowledge and belief, it contains no material previously published or written by another person except where due reference is made in the text of the thesis.

Thomas A. Hunt

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Preface

During the course of this project, a number of publications and presentations have been made which are based on the work presented in this thesis. We also have some publications which we intend to write based on work in this thesis. We have listed them here for reference.

REFEREED JOURNAL PUBLICATIONS

- T A Hunt and B D Todd. On the Arnold cat map and periodic boundary conditions for planar elongational flow. *Molecular Physics*, vol. 101, no. 23-24, pp. 3445-3454, 2003.

PUBLICATIONS IN PREPARATION

- T A Hunt and B D Todd. Diffusive properties of polymer melts undergoing planar shear and extensional flows.
- T A Hunt and B D Todd. Comparison between FENE and FJC simulations of chain molecules under flow.

CONFERENCE PROCEEDINGS

- T A Hunt and B D Todd. On maps, cats, and how to simulate indefinite elongational flow by molecular dynamics. *3rd International Conference "Computational Modelling and Simulation of Materials" & "Modelling*

and Simulating Materials Nanoworld", Acireale, Sicily, Italy, 30 May
- 4 June 2004.

CONFERENCE ABSTRACTS

- Thomas A Hunt and B D Todd. A comparison of the Doi-Edwards model with non-equilibrium molecular dynamics simulations of chain molecules. *3rd Pacific rim conference on rheology*, Vancouver, BC, Canada, 8 July - 12 July 2001.

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Notation

Scalars, Vectors and Tensors:

- All scalars use a plain font.
- In the Latin alphabet bold font is used to denote vectors, while sans serif font is used to denote tensors.
- In the Greek alphabet bold font is used to denote tensors.
- The Greek alphabet is used for vectors only in exceptional cases.
- Components of a vectors and tensors use a plain font and are indexed.

List of Acronyms:

BEF Biaxial extensional flow.

CB-model Model of Curtiss and Bird.

DE-model Model of Doi and Edwards.

FENE Finitely extensible nonlinear elastic spring potential.

FJC Freely jointed chain model.

MD Molecular dynamics.

MIC Minimum image convention.

NEMD Nonequilibrium molecular dynamics.

pbcs Periodic boundary conditions.

PCF Planar Couette flow.

PEF Planar extensional flow.

RIS Rotational isomeric state model.
RME Retarded motion expansion.
UEF Uniaxial extensional flow.
VACF Velocity autocorrelation function.

Greek pronumerals:

β	Scaling exponent for the Curtiss-Bird model.
$\dot{\gamma}$	Strain-rate.
$\dot{\gamma}(\mathbf{r}, t)$	Strain-rate tensor.
$\gamma^{[0]}(t, t')$	Finite strain tensor.
ϵ	Link-tension coefficient, for the Curtiss-Bird model.
ϵ'	Reptation coefficient for the Curtiss-Bird model.
$\dot{\epsilon}$	Extensional strain-rate.
ϵ_{LJ}	Well depth of the Lennard-Jones potential.
ζ	Friction coefficient for the Rouse model
ζ_A	Atomic thermostat multiplier.
ζ_M	Molecular thermostat multiplier.
η	Shear viscosity.
$[\eta]$	Intrinsic steady-state viscosity
$\bar{\eta}$	Planar extensional viscosity.
$\bar{\eta}_\infty$	Plateau planar extensional viscosity.
η_0	Zero strain-rate viscosity.
η_1	First extensional viscosity.
η_2	Second extensional viscosity.
$\eta_1^+(t)$	Transient first extensional viscosity.
$\eta_2^+(t)$	Transient second extensional viscosity.
η_p	The Hencky strain.
η_s	Solute viscosity
η_V	Bulk viscosity.
$\eta_M(t)$	Maxwell memory function
$\eta^+(t)$	Transient shear viscosity.
θ	Orientation angle for spatially and temporally periodic boundary conditions.
$\Theta_2(z \tau)$	Jacobi Theta function.
λ	Time constant in Curtiss-Bird model.
λ_1, λ_2	Eigenvalues of the Kraynik-Reinelt maps.
$\mu(t)$	Memory function in the Curtiss-Bird model.
$\nu(t)$	Memory function in the Curtiss-Bird model.
$\rho(\mathbf{r}, t)$	Density of a fluid.
$\boldsymbol{\sigma}(\mathbf{r}, t)$	Stress-tensor.
σ_{LJ}	Effective diameter of the Lennard-Jones potential.

τ_d	Disengagement time of the primitive chain in the Doi Edwards model.
τ_i	Relaxation coefficients for the generalised Maxwell model.
τ_p	Relaxation coefficients for the Rouse model.
τ_p	Period of temporally-periodic, periodic boundary conditions.
τ_R	The Rouse time.
χ	Alignment angle of molecules also known as the birefringence extinction angle.
$\psi(t)$	Memory function for the Doi and Edwards model; The fraction of a molecule still in the initial tube after a time t .
Ψ_1	First normal stress coefficient for shear flow.
Ψ_2	Second normal stress coefficient for shear flow.
$\Psi_1^+(t)$	Transient first normal stress coefficient for shear flow.
$\Psi_2^+(t)$	Transient second normal stress coefficient for shear flow.
ω	Molecular spin angular velocity.
ω_z	Molecular spin angular velocity about the z -axis.

Latin pronumerals:

a	Step-length of the primitive chain.
a'	Rod length of the Kramers Bead-rod chain model used in the Curtiss-Bird model.
$a(\mathbf{r}, t)$	An arbitrary scalar field.
a_i	Coefficients for the generalised Maxwell model.
$A(t, t')$	Second-order tensor function for the Curtiss-Bird model.
b_0	Bond length in a molecular model.
b	Average bond length of the Rouse model.
b_K	Kuhn length.
b_{mol}	Bond length of a molecule.
$\mathbf{B}(t, t')$	Second-order tensor function for the Curtiss-Bird model.
c	Monomer concentration, number of monomers per unit volume.
c_v	Heat capacity at constant volume.
$C_{\alpha\beta}(t)$	Velocity auto/correlation function $\langle v_\alpha(t)v_\beta(0) \rangle$.
$Cov(x, y)$	Covariance between the variables x and y .
D	Self diffusion coefficient.
\mathbf{D}	Self diffusion tensor.
D_G	Centre of mass diffusion coefficient for the Rouse model.
$e(\mathbf{r}, t)$	Energy density.
$\mathbf{e}_1, \mathbf{e}_2$	Eigenvectors of the Kraynik-Reinelt maps.
$\mathbf{E}(t, t')$	Deformation gradient.
f	Number of degrees of freedom lost through constraint.
$\mathbf{f}(\mathbf{r}, t)$	Body force per unit density exerted on a fluid.

\mathbf{F}_i	Force on particle i .
$\mathbf{F}_{i\alpha j\beta}$	Force on site α of molecule i due to site β of molecule j .
$\mathbf{F}_{i\alpha}^C$	Force on site α of molecule i due to the constraint.
$\mathbf{F}_{i\alpha}^{FENE}$	Force on site α of molecule i due to the FENE potential.
$\mathbf{F}_{i\alpha}^{LJ}$	Force on site α of molecule i due to the Lennard-Jones potential.
G_e	The plateau modulus
$G(\mathbf{q}, t)$	Tracer density.
$H(t)$	Heaviside step function.
\mathbf{l}	Unit tensor.
\mathbf{l}_m	Moment of inertia tensor for a molecule.
II	Second scalar invariant. $\mathit{II} = 8\epsilon^2$ for PEF and $\mathit{II} = 2\dot{\gamma}^2$ for PCF.
$\mathbf{j}(\mathbf{r}, t)$	Mass flux vector.
\mathbf{j}_s	Streaming flux.
$\mathbf{j}_Q(\mathbf{r}, t)$	Heat flux vector.
\mathbf{J}_D	Tracer flux density.
k	Force constant for the FENE potential.
k	Hooke's force constant for the Rouse model.
k_B	Boltzmann constant.
k_T	Coefficient of thermal conductivity.
L	Length of the primitive chain.
L	Side length of a cubic simulation cell.
\mathbf{L}	Angular momentum of a molecule.
\mathbf{L}_i	Lattice vectors.
m	Extensional flow parameter.
m_1, m_2, m_3 and m_4	Elements of an integer matrix.
m_i	Mass of particle i .
$m_{i\alpha}$	Mass of site α on molecule i .
M	Molecular weight.
\mathbf{M}	A mapping. For example, the Kraynik-Reinelt map.
M_i	Mass of molecule i .
n	Polymer concentration, number of polymers per unit volume.
$\hat{\mathbf{n}}_x, \hat{\mathbf{n}}_y, \hat{\mathbf{n}}_z$	Unit vectors parallel to the x, y and z axes respectively.
N	Number of beads per molecule in a model.
\mathbf{N}	An integer matrix.
N_A	Avogadro's number.
N_M	Number of molecules in a simulation.
N_s	Number of sites in a molecule.
p	Isotropic pressure.
\mathbf{p}_i	Peculiar momentum of particle i .
\mathbf{p}_i	Centre of mass momentum of molecule i for molecular simulations.

$\mathbf{p}_{i\alpha}$	Momentum of site α on molecule i .
$\mathbf{P}_{i\alpha}$	Cartesian component α of centre of mass momentum of particle i .
\mathbf{P}	Pressure tensor.
\mathbf{P}_A	Atomic pressure tensor.
\mathbf{P}_M	Molecular pressure tensor.
$\mathbf{q}(t)$	An arbitrary path.
$\mathbf{q}_i(t)$	Lagrangian coordinate of particle i , integral of the peculiar momentum \mathbf{p}_i .
$\mathbf{q}_{i\alpha}(t)$	Cartesian component α of the Lagrangian coordinate of particle i .
$\mathbf{Q}^{(IA)}$	Order tensor for the Doi and Edwards model in the independent alignment approximation.
\mathbf{r}	Position vector.
\mathbf{r}_i	Position of atom i for atomic simulations.
\mathbf{r}_i	Centre of mass of molecule i for molecular simulations.
$\mathbf{r}_{i\alpha}$	Position of site α on molecule i .
$\mathbf{r}_{i\alpha j\beta}$	Vector from site α of molecule i to site β of molecule j .
$\hat{\mathbf{r}}_i$	Unit vector in the direction of the i^{th} bond of a molecule.
r_{ij}	Distance between atoms i and j .
R_0	Maximum extension of the FENE potential.
\mathbf{R}_{e-e}	End-to-end vector of a linear molecule.
R_g	Radius of gyration.
\mathbf{R}_g^2	Tensor of gyration.
$\mathbf{R}(s, t)$	Position of primitive chain at contour coordinate s at time t .
\mathbf{S}	Order tensor.
S	Order parameter.
s, s'	Contour coordinate along the primitive chain.
s, t, t'	Time.
$T(\mathbf{r}, t)$	Temperature field.
T_A	Kinetic temperature.
T_α	Temperature due to component α of molecular momenta.
$\mathbf{u}(\mathbf{r}, t)$	Streaming velocity of a fluid.
$\nabla\mathbf{u}(\mathbf{r}, t)$	Velocity gradient tensor.
$\hat{\mathbf{u}}$	Unit vector used as an independent variable.
$\mathbf{r}_{i\alpha j\beta}$	Potential of site β on molecule j due to site α on molecule i .
U	Total internal energy of a system.
U_{ij}^{FENE}	The FENE potential between atoms i and j .
U_{ij}^{LJ}	Lennard-Jones potential between atoms i and j .
U_{ij}^{WCA}	Weeks-Chandler-Anderson potential between atoms i and j .
V	Volume of a simulation cell.