NonEquilibrium Thermodynamics of Flowing Systems: 4

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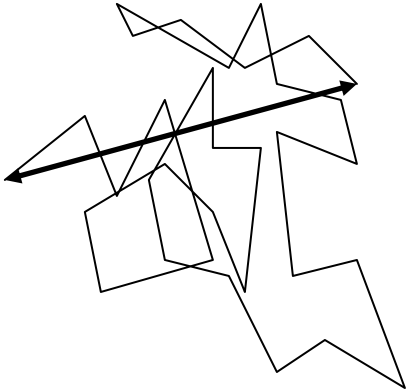
Schedule:

1. **4/13/07, 9:30 am Introduction. One mode viscoelasticity.**
2. **4/13/07, 10:15 am Coupled transport: Two-fluid model.**
3. **4/14/07, 2:00 pm Modeling under constraints: Liquid crystals.**
4. **4/14/07, 3:00 am Non-homogeneous systems: Surface effects*.**

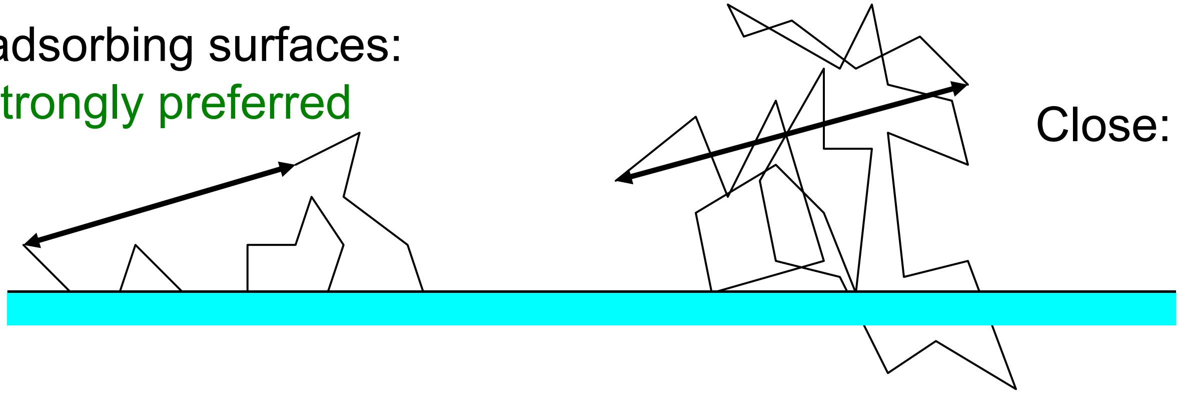
*Following the development in “Mavrantzas and Beris, 1999, JCP 110:616-627,628-638”

Chain Conformations Close to a Surface



Far away: allowed

For polymers, the bulk internal thermodynamic state is entropy driven. The more the allowed configurations, the higher the entropy and the Lower the free energy---Inversely, the higher the restrictions, the less the entropy and the higher the free energy. Approach to a surface lowers the number of possible internal configurations; alternatively, it may add enthalpic contributions.



For adsorbing surfaces:
strongly preferred

Close: not allowed

Surface

Chain Conformations and Rheology of a Polymer Solution Close to a Surface: Challenges

- The presence of a surface brings inhomogeneity into a problem due to the potential for long range surface interactions over a characteristic length L_s (for polymers this coincides with the radius of guration, R_G)
- Especially when a polymer medium is involved, the presence of a surface changes also the local structure in an nonlocal way: the polymer conformation problem cannot any longer be dealt only macroscopically---a multiscale analysis is warranted
- The flow problem becomes coupled with both the direct and indirect (through changes in the polymer conformation) surface-induced changes
- The Hamiltonian formalism can accommodate inhomogeneities (direct dependencies on spatial location) and multiscale phenomena both at equilibrium and in the presence of flow
- Next: We develop the general equations and present applications involving a non-interacting (neutral) surface, both under equilibrium and under flow

General Equations: Variables

- We assume an incompressible (constant total mass density, ρ_0 ($n_0=N_A\rho_0/MW_0$ being the number density), inhomogeneous (variable polymer concentration, n=chain number density is variable) system on top of an interacting surface. Thus, we have:
  - ρ_1, the polymer density ($n_1=N_A\rho_1/MW_1$, assuming $MW_1=N\ MW_0$)
  - **v**, the velocity (**M** = ρ_0**v** = momentum density)
  - s, the entropy density (alternatively, T, temperature)
  - **C**, the conformation tensor where
    - **C** = <**RR**> (second moment of the end-to-end distribution function) = $n_1\mathbf{c}$
- At equilibrium, $c=k_BT/K$ where K is the equilibrium equivalent entropic elastic energy constant of the polymer chain

Dynamic Equations: Two-Fluid Dilute+Non-Homogeneous System

$$\frac{\mathrm{D}}{\mathrm{Dt}}\rho_1 = -\nabla_\alpha \left(D \left(\nabla_\alpha \Pi + \frac{\partial h}{\partial r_\alpha} - \nabla_\gamma T_{\alpha\gamma} \right) \right)$$

$$\rho_0 \frac{\mathrm{D}}{\mathrm{Dt}} v_a = -\nabla_\alpha p + \nabla_\beta T_{\alpha\beta} - \frac{\partial h}{\partial r_\alpha} + \nabla_\beta \left(\eta_s \left(\nabla_\beta v_\alpha + \nabla_\alpha v_\beta \right) \right)$$

$$\frac{\mathrm{D}}{\mathrm{Dt}} c_{\alpha\beta} - \nabla_\gamma v_\alpha c_{\gamma\beta} - c_{\alpha\gamma} \nabla_\gamma v_\beta = -\Lambda_{\alpha\beta\gamma\varepsilon} \frac{\delta H}{\delta c_{\gamma\varepsilon}}$$

$$\mathbf{T}^T = 2\mathbf{C} \cdot \frac{\partial a_e}{\partial \mathbf{C}}$$

Hamiltonian

- The Hamiltonian (extended Helmholtz free energy of the system) is assumed to have the form:

$$A = \int_{\mathrm{V}} \left(\tfrac{1}{2} \rho v^2 + a_e + a_m + a_s \right) \mathrm{dV}$$

where a_e, a_m and a_s represent the contrbutions to the free energy density corresponding to elasticity, mixing and enthalpic surface interactions, respectively.

Of those free energy contributions the most straightforward is the last one which has the form (under the assumption that only the environment at the surface is affected):

$$a_s = n_0 (u_s - \varphi_s \chi_s) \delta\left(y / \ell \right)$$

where u_s is energy of adsorption for the solvent molecules, φ_s is the surface polymer volume fraction, χ_s is the Flory χ parameter at the surface, $\chi=-(u_p - u_s)$, ℓ is a characteristic molecular unit length of the solvent molecules and the segment polymer chain (assumed to be the same) and the surface is assumed to be perpendicular to the y axis at $y=0$

The Mixing Contribution

- The mixing contribution to the free energy is provided by an extension of the Flory-Huggins expression:

$$a_m = k_B T\left(n_1 \log\left(\frac{n_1 N}{n_0 Z(N-1)}\right) + n_0(1-\varphi)\log(1-\varphi)\right) + n_0 \chi \varphi (1-\varphi)$$

where φ is the polymer volume fraction and *Z*(*N*-1) is an *N*-long chain relative partition function (defined later) representing the relative number of chains (with respect to the bulk) that can develop freely at a particular location without hitting the surface.

At homogeneous equilibrium and in the bulk, we have a homogeneous distribution of the polymer chain segments with the solvent molecules (assumed here of the same volume)

$$\varphi = {(n_1 N)}\big/{n_0}$$

However, in a inhomogeneous medium, the connection between the local polymer chain segment volume fraction and the number density of the polymer chains is more complicated: In order to describe it we need detailed knowledge of the polymer chain conformation. This is achieved through knowledge of the propagator, $G(y,n;y_0)$

The Propagator $G(\mathbf{r},n;\mathbf{r}_0)$

- It is defined so that $G(\mathbf{r},n;\mathbf{r}_0)\,\mathrm{d}^3\mathbf{r}$ is proportional to the number fraction of the n-member multisegment chains that starting at distance $\mathbf{r}_0$ they end within $\mathrm{d}^3\mathbf{r}$ of $\mathbf{r}$.
- If no excluded volume effects are considered, $G(\mathbf{r},n;\mathbf{r}_0)$ satisfies a diffusion equation describing a random polymer chain conformation:

$$\frac{\partial}{\partial n}G(\mathbf{r},n;\mathbf{r}_0)=\frac{\ell^2}{6}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)G(\mathbf{r},n;\mathbf{r}_0)$$

with initial condition

$$G(\mathbf{r},0;\mathbf{r}_0)=\delta(x-x_0)\delta(y-y_0)\delta(z-z_0)$$

and boundary conditions dictated by the specification of the problem; in the above equation ℓ is the chain segment length. Then, the relative chain partition function, $Z(n,\mathbf{r}_0)$ is defined by the integral of the propagator $G(\mathbf{r},n;\mathbf{r}_0)$ as

$$Z(n,\mathbf{r}_0)\equiv\int_{\mathrm{V}}G(\mathbf{r},n;\mathbf{r}_0)\,\mathrm{d}^3\mathbf{r}$$

Note that from the initial conditions of the propagator $Z(0,\mathbf{r}_0) = 1$

The Relationship of φ(y) with n_1

- First we need to be specific on what we count by n_1: let us assume, chain segment ends. Also, we limit our discussion to problems symmetric on *x*,*z*.
- The expression for φ can then be obtained by summing up all contributions of all chains, over all possible number of chain segments from the origin, *k*=0, 1, 2, … *N*-1 (for an *N*-bead chain).
- Each such contribution needs to take into account all possible chain end positions, y_0, thus involving an integration over that variable.
- The weight in such integration needs to take into account the conditional probability P(*y*,*k*;y_0,*N*) that a *N*-bead chain starting from y_0 has its *k*-th segment at the desired location y. The final expression thus is:

$$n_0\varphi(y) = \sum_{k=0}^{N-1}\int_0^\infty \tfrac{1}{2} n_1(y_0) P(y,k;y_0,N)\,dy_0$$

with the factor ½ used to take into account the double counting of the chains (two ends)

Then, taking into account the definition of the propagator *G*(*y*,*n*;y_0) and the relative chain partition function, Z(n,y_0), the conditional probability P(*y*,*k*;y_0,*N*) is defined as

$$P(y,k;y_0,N) = G(y,k;y_0)\frac{Z(N-1-k,y)}{Z(N-1,y)}$$

The Elastic Contribution

- In general this would have been provided directly in terms of the conformation tensor **C** as:

$$a_e = \tfrac{1}{2}\left(K\,\mathrm{tr}\,\mathbf{C} - nk_BT\log\left(\det\left({(K\mathbf{C})}\Big/{(nk_BT)}\right)\right)\right)$$

- However, this does not provide a segment length resolution! An alternative expression is needed.
- To evaluate the alternative definition we go back to Flory's original definition of chain elasticity based on an expression for the entropy loss as a result of the flow deformation (which was derived for simple deformations*) and to generalize it for an arbitrary flow deformation

*P.J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1953)

Generalized Flory's Expression for the Entropy

- First, we need to connect the conformation tensor **c** to that of a general deformation field tensor **α**. This is done based on elasticity theory through the relationship

$$\mathbf{c} = \boldsymbol{\alpha} \cdot \mathbf{c}_0 \cdot \boldsymbol{\alpha}^T$$

where $\mathbf{c}_0$ represents the chain conformation before the application of the flow deformation

- Then, we evaluate the entropy changes using a Boltzmann expression based on the changes in the propagator from *G* to *G'* induced by the deformation field **α**

$$a_e = k_B T n_1(y) \int_0^\infty \frac{G(\mathbf{r}', N-1; \mathbf{r})}{Z(N-1, \mathbf{r})}$$

$$\times \log\left[\frac{G'(\mathbf{r}', N-1; \mathbf{r}, \boldsymbol{\alpha})}{G(\mathbf{r}', N-1; \mathbf{r})} \frac{Z(N-1, \mathbf{r})}{Z'(N-1, \mathbf{r}; \boldsymbol{\alpha})} \right] \mathrm{d}^3 \mathbf{r}'$$

The Modified Propagator $G'(\mathbf{r},n;\mathbf{r}_0,\alpha)$

- If no excluded volume effects are considered, $G'(\mathbf{r},n;\mathbf{r}_0,\alpha)$ satisfies a modified diffusion equation describing a biased random polymer chain conformation along preferential directions, ξ, η, and ζ:

$$\frac{\partial}{\partial n}G'(\mathbf{r},n;\mathbf{r}_0,\boldsymbol{\alpha}) = \left(D_1\frac{\partial^2}{\partial\xi^2} + D_2\frac{\partial^2}{\partial\eta^2} + D_3\frac{\partial^2}{\partial\zeta^2}\right)G'(\mathbf{r},n;\mathbf{r}_0,\boldsymbol{\alpha})$$

with initial condition

$$G'(\mathbf{r},0;\mathbf{r}_0,\boldsymbol{\alpha}) = \delta(x-x_0)\delta(y-y_0)\delta(z-z_0)$$

and boundary conditions dictated by the specification of the problem. In the above equation D1, D2 and D3 are proportional to the squares of the eigenvalues of the matrix α with the new coordinates ξ, η, and ζ along the direction of the corresponding eigenvectors

It can be shown, that for a homogeneous system, the new approach leads exactly to the same expressions for the elastic component of the free energy as before

Application to a Neutral Surface*

- Key: The propagator equation can be solved exactly with the proper boundary conditions (zero probability on the surface)
- The solution is also factorized in the three directions, $G=G_xG_yG_z$ with
  - G_x and G_z represented by Gaussian functions (like in the bulk)
  - G_y represented by the subtraction of two Gaussian terms at (y-y0) and (y+y0)
- This solution leads to equilibrium profiles represented by the error function for both the partition function and the chain number density in agreement to previous work
- In the presence of flow, G' can also be solved analytically; however the full solution to the problem requires a numerical solution to a system of 1-d ODEs

* Mavrantzas and Beris, 1999, JCP 110:628-638

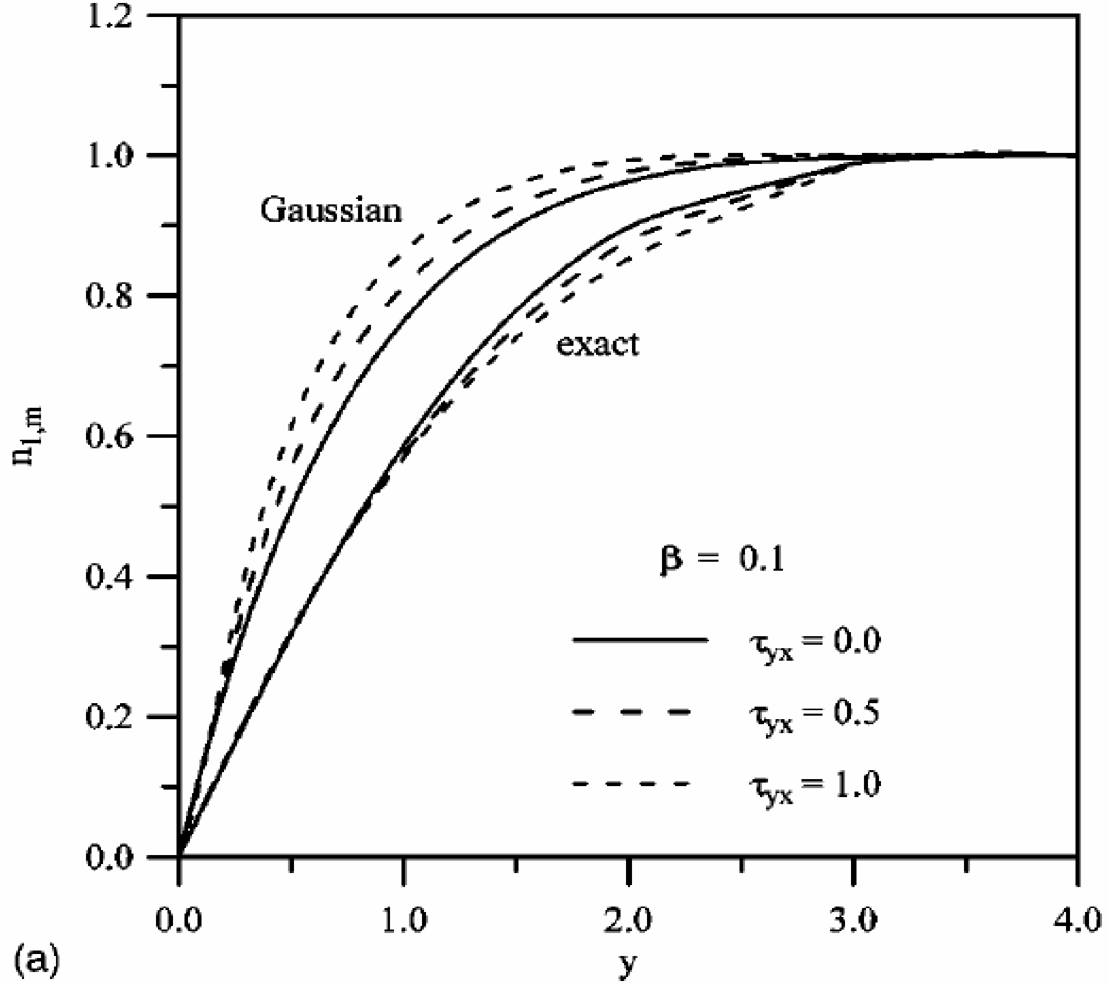


FIG. 3. The density of chain middle points $n_{1,m}$ as a function of the distance y from the wall for various shear stresses τ_{yx} and for two values of the viscosity parameter β, $\beta = 0.1$ (a) and $\beta = 0.5$ (b), respectively. The distance y is scaled with the root-mean-square equilibrium end-to-end distance in the bulk R_0. The upper set of curves corresponds to the ''fully Gaussian approximation'' whereas the lower set to the ''exact'' form for the distribution function near the wall.

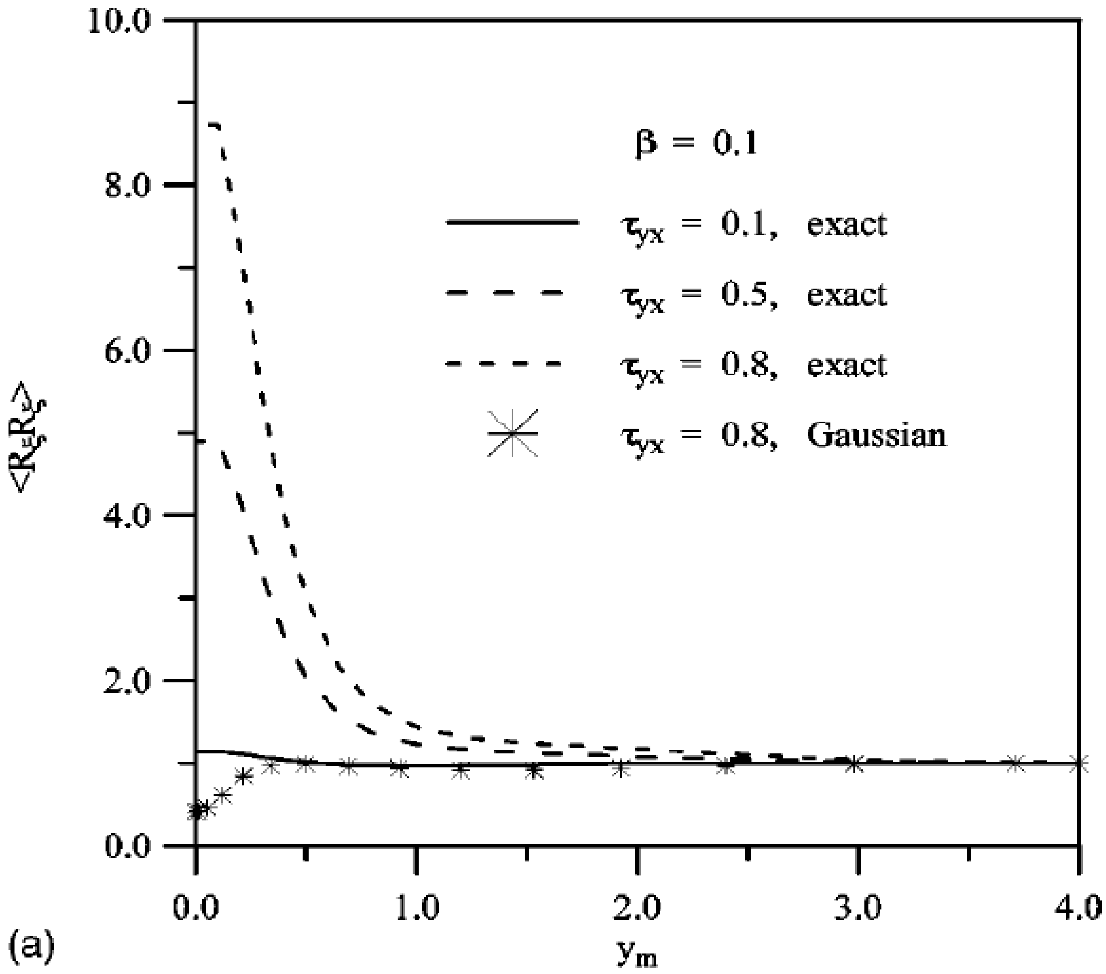


FIG. 4. The component $\langle R_\xi R_\xi \rangle$ (a), the component $\langle R_\eta R_\eta \rangle$ (b) of the second moment of the distribution function perpendicular to the wall, and the tan(α) (c), as a function of the distance from the surface of the middle point of the chain for various shear stresses τ_{yx}. For the highest value of the shear stress ($\tau_{yx}=0.80$), the corresponding results obtained with the use of the Gaussian assumption are also indicated. Also $\beta=0.1$. In all cases, distances from the wall are scaled with the root-mean-square equilibrium end-to-end distance in the bulk R_0.

finite value. This is the first instance where the apparent character of the slip phenomena has directly been verified experimentally. Quantitative comparison of their results with our model predictions, however, is not feasible at the present time, because additional electrostatic interactions between the charged PMA molecules and an electric double layer at the wall existed in the experiments for which the present model cannot account. A rough comparison has nevertheless been attempted where the parameters (data) entering into our model have been taken from the experimental work of Mueller-Moehnssen *et al.*[19] For the lowest polymer concentration (0.005% wt.) examined in the experiments, the experimentally measured slip coefficient k was found to be 4 $\times 10^{-3}$ cm^3/dyn/s whereas the model prediction is $(0.8 \pm 0.1) \times 10^{-3}$ cm^3/dyn/s. It is seen, therefore, that by simply accounting for conformational changes near the wall, is enough to capture the correct order of magnitude of the slip phenomena. Moreover, the model prediction is lower than the experimentally measured value, which is quite pleasing, because the additional electrostatic repulsions for which the model cannot presently account are expected to enhance the depletion and slip phenomena in the interfacial area. For a

Conclusions

- Complex, multiscale problems can also be handled using the Hamiltonian formalism
- Care needs to be exercised in formulating the free energy
- It is possible to involve microscopic information that requires the solution of microscopic governing equations subject to parameters coupled with respect to the macroscopic problem
- In this way the resolution of the approach can be significantly enhanced: For polymer flows, details down to chain segment length scale can be resolved
- Remaining challenges: Introduction of more faithful dissipation characteristics of the deformation field: Recent work* suggests that they also need to be position-dependent

* Jendrejack, Schwartz, de Pablo and Graham, 2004, JCP 120:2513-2529