

The "Sandwich" Model of the Amorphous Material in Semicrystalline Polymers, Block Copolymers and Filled or Reinforced Elastomers

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Summary

A theoretical model of the amorphous material in semicrystalline polymers, block copolymers and filled or reinforced elastomers is presented. The model consists of a dense system of bridges, loops, cilia and floating chains 'sandwiched' between a pair of parallel walls. A prescription is given for determining the total free energy of the model.

Introduction

Each amorphous region in a semicrystalline polymer, block copolymer or filled or reinforced elastomer is made up of a dense system of polymer chains trapped between impenetrable surfaces. Each of these confined chains has none (floating chain), one (cilium) or both (loop or bridge) of its ends permanently attached to the confining surfaces. We seek a method by which we can determine the free energy of each of the chains in the amorphous region, as well as the total free energy of the amorphous region.

The 'Sandwich' Model

The theoretical model consists of a dense system of cilia, loops, bridges and floating chains confined between a pair of infinite parallel walls separated by a distance, d . The quantities which are a priori specified for the model are:

- (1) the numbers of each type of chain.
- (2) the contour length of each chain.
- (3) the overall segment density profile between the walls.

The specification of these quantities is made so as to represent the particular bulk of polymeric system being modeled.

The partition function of a polymer chain, consisting of N segments of length b and having its ends fixed at r, r' , under an external potential $U(r)$ satisfies the equations (deGENNES 1979)

$$[\partial/\partial N - (b^2/6)\nabla^2 + (U(r)/kT)] G_N(r, r') = 0$$

$$G_0(r, r') = \delta(r-r')$$

In applying the above equations to the 'sandwich' model, we make use of the fact that in a dense system of chains confined between walls, the potential exerted on each segment of a chain must be infinite at the walls and constant between the walls, except in proximity to the walls. This fact permits us to replace the external potential with mixed boundary condition equation at each wall (deGENNES 1979). Thus the partition function of a chain in the 'sandwich' model is given by the solution to the equations:

$$[\partial/\partial N - (b^2/2)\partial^2/\partial x^2] G_N(x, x') = 0$$

$$G_0(x, x') = \delta(x-x')$$

$$\partial \ln G_N(x, x') / \partial x \big|_{x=0} = \sigma$$

$$\partial \ln G_N(x, x') / \partial x \big|_{x=d} = -\sigma$$

The value of σ in the above equations indicates the amount of short range attraction between a wall and a chain segment; e.g., $\sigma = \infty$ corresponds to no attraction while $\sigma = -\infty$ corresponds to infinite attraction.

Using the solution to the above set of equations (KIM and GAYLORD 1981) and the mathematical procedures previously developed (GAYLORD et al 1980), we can calculate both the partition function, G , and the segment density function, ρ , of each chain in the 'sandwich' model. The total free energy of the model is given, to within an additive constant (DiMARZIO and GUTTMAN 1980), by

$$A_T = -kT \sum_{\text{chains}} \ln G$$

and the total segment density profile of the model is given by

$$\rho_T = \sum_{\text{chains}} \rho$$

It remains to determine the value of σ for each chain in the model.

It is reasonable to assume, initially, that the potential exerted on each chain in the model is the same, thereby resulting in a common value of σ for every chain. If this is true, then the value of σ is determined by requiring that the a priori specified overall segment density profile of the model, ρ_{exp} , agrees with ρ_T .

If it is found that the above assumption does not work, then it can logically be assumed that each type of chain in the model is subjected to a different potential field in the vicinity of the walls. Therefore, a different value of σ is designated for each chain type; σ_L for a loop, σ_B for a bridge, σ_C for a cilium and σ_F for a floating chain. These σ values are determined by minimizing the total free energy of the model with respect to each σ , subject to the constraint that ρ_{exp} equals ρ_T ; i.e., by solving the set of equations

$$\partial[A_T + \lambda(\rho_{\text{exp}} - \rho_T)]/\partial\sigma_j = 0 \quad \text{for all } j$$

$$\partial[A_T + \lambda(\rho_{\text{exp}} - \rho_T)]/\partial\lambda = 0$$

where $j = C, L, F, B$ denotes the chain type and λ is a Lagrange multiplier.

Conclusion

The model which has been presented herein, differs from previously

developed models of the amorphous region of various bulk polymeric systems in that, rather than arbitrarily assuming a specific value of σ , we have allowed σ to adjust itself so as to satisfy a segment density requirement. It should be emphasized, however, that the unspecified nature of the boundary condition arises, not from the desire to have an adjustable parameter with which to force the model to 'work', but from the unknown nature of the short range interaction between a chain segment and the impenetrable surface in the various bulk polymeric systems being modelled.

Once, the total free energy of the 'sandwich' model is determined for a particular bulk polymeric system, we can calculate the deformation properties of the model. If we have information about the relative arrangement of the amorphous regions within the bulk polymeric system, then we can use the model to calculate the contribution of the amorphous material to the overall deformation behavior of the bulk polymer.

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