Slow plasmon modes in polymeric salt solutions

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The dynamics of polymeric salt solutions are presented. The salt consists of chains A and B, which are chemically different and interact with a Flory-interaction parameter $\chi$, the A chain ends carry a positive charge whereas the B chain ends are modified by negative charges. The static structure factor shows a peak corresponding to a micro phase separation. At low momentum transfer, the interdiffusion mode is driven by electrostatics and is of the plasmon-type, but with an unusually low frequency, easily accessible by experiments. This is due to the polymer connectivity that introduces high friction and amplifies the charge scattering thus allowing for low charge densities. The interdiffusion mode shows a minimum (critical slowing down) at finite $k$ when the interaction parameter increases we find then a low $k$ frequency quasi-plateau.

Scattering methods are a powerful tool to study the structure and phase behavior of multicomponent polymer mixtures and were the subject of intensive investigations. In general, polymer blends are characterized by a low entropy of mixing and relatively high enthalpic interactions and polymers are thus to a large extend immiscible. An effective way to enhance the compatibility of polymer blends, consists to introduce long range Coulomb forces between particles by adding electrostatic charges.

Quasi elastic scattering experiments allow, in principle, to measure the decay of various concentration fluctuations in the solution. The fastest relaxation mode is usually the plasmon mode related to the relaxation of charge fluctuations. In the macroscopic limit ($k \rightarrow 0$) for small ions, the plasmon frequency is proportional to the inverse friction coefficient $\zeta$, and to the Debye-Hückel screening parameter $\kappa_2$, i.e., $\Gamma \propto k_B T \kappa_2^2 \zeta^{-1}$. Although it is possible to detect the plasmon by spin echo techniques it remains very difficult to measure, because of low contrast. Then other processes such as water binding - unbinding perturbate a clear detection of the plasmon. To find experimentally accessible plasmon modes in reasonable time scales larger friction coefficients, low charge densities, and higher contrast are required. We suggest to use polymeric salts, where anions and cations are linked to the end of two chemically different polymeric backbones. To be more precise, chains A and B interact by a Flory - $\chi$ parameter, which allows for composition fluctuations. Many hydrophilic polymers involve hydrogen bonding and may exhibit a more complex behavior. These effects can be limited by an appropriate choice of temperature and polymers, e.g., end-modified POE at room temperature. The chain friction is a power of $N$ larger than the monomer friction of the order of $\zeta$ introduced above.

To benefit from the polymeric effects small ions should be absent, which is possible in a one to one A-B mixture, this point will be discussed later. Electroneutrality forbids macrophase separation as $\chi$ increases and microphase separation at a finite wave vector $k^*$ is anticipated. Large scale composition fluctuations violate electroneutrality and their relaxation is primarily driven by electrostatics. We will indeed show that at low wave vector the relaxation of composition fluctuations is of the plasmon type but at an unusually slow time scale. Though critical slowing down
closer to the microphase separation is interesting, we will mainly concentrate on systems far from the transition where excluded volume effects do not interfere with the plasmon effects. For the weakly charged chains we have in mind that the value for $\kappa$ is small. On the other hand the polymer concentration is high and high contrast in scattering experiments can be achieved. Symmetric polymer salt solutions with moderately incompatible backbones (e.g., hydrogenated and deuterated) are thus good candidates to detect slow plasmon modes.

The static properties of the polymeric salts in equilibrium are well described by the random phase approximation, since we assume a sufficiently large overall concentration. The chains are assumed to be of Gaussian connectivity, the monomers interact with an excluded volume interaction of a strength given by $V_{ij}$, and the electrostatic interaction between the ionic groups. In the latter the strength of the Coulomb potential is expressed in term of the Bjerrum length: $l_B = \beta e^2/4\pi\epsilon$, where $e$ and $\epsilon$ are respectively the electric unit charge and the dielectric constant. The different chemical nature of the chains is commonly expressed by a Flory $\chi$ - parameter, $V_{AB} = V + \chi$. For the purpose here it turns out convenient to use linear combinations of the collective variables to study the usual plasmon (total charges) modes and the interdiffusion (relative A and B fluctuations). It is straightforward to calculate the corresponding static structure factor matrix $S(k)$ which is expressed as a function of the bare structure matrix $S_0(k)$, corresponding to the single chain conformations in the mixture, and the interaction matrix $U_{int}(k)$ in the form

$$S(k)^{-1} = S_0(k)^{-1} + U_{int}(k).$$

The interaction matrix $U_{int}(k)$ contains short (excluded volume) and long (electrostatic) range interactions. The elements of the first matrix are the usual parameters $V_{ij}$. The relevant structure factors are $S^{00}(k)$ (charge/charge structure factor), $S^{11}(k)$ (ionic strength/ionic strength structure factor), $S^{00}(k)$ (concentration/concentration structure factor), $S^{xx}(k)$ (composition/composition structure factor), $S^{11}(k)$ (ionic strength/concentration structure factor), $S^{xx}(k)$ (charge/composition structure factor). In the case of the symmetric salt where chains A are charged positively and B charged negatively, $S^{xx}(k)$, $S^{11}(k)$ and $S^{xx}(k)$ have a peak which increases as the value of the Flory parameter $\chi$ increases. In this case we find a microphase instability with a characteristic finite wavevector $k^*$. The microphase separation at non-avoiding vector $k^*$ occurs for a sufficiently strong incompatibility. For $\chi = 0$ or $\chi$ finite but sufficiently small, entropy effects are dominant and favor mixing.

In light or neutron scattering experiments, one can measure directly the matrix of dynamical functions $S_{ij}(k, t)$. To compute the relevant elements of the dynamic structure factor matrix we start from the generalized Langevin equation, which describes the (short) time evolution of $S(k, t)$ and, neglecting memory effects, lead us to a single exponential decay of $S(k, t)$, $S(k, t) = e^{-\Omega(k)t}S(k)$. The decay rate, which is experimentally available is given by the first cumulant matrix $\Omega(k)$ which is related to different correlation functions. Hydrodynamic interactions between monomers are taken into account in the Oseen level.

$$\Omega(k) = k_B T \int \frac{dq}{(2\pi)^3} S(k+q) \frac{k^2 - (q \cdot k / q)^2}{\eta q^2} S^{-1}(k)$$

The eigenvalues of $\Omega(k)$ lead us to the decay rates of thermal fluctuations in the solution. In a first step the eigenvalues of the frequency matrix eq.2 have been computed numerically.

Let us first concentrate on the fast (usual) plasmon mode, which corresponds to the relaxation of charge fluctuations. At high wavevector limit, the relaxation is diffusive as for a monomeric salt and the electrostatic interactions are irrelevant. In the low $k$ limit, the symmetric salt behaves as an usual monomeric salt. The relaxation of charge fluctuations of size larger than $\kappa^{-1}$ is driven by electrostatics. Since the chain ends are different from the rest of the chain monomers, an additional relaxation mode is expected. At high wave vectors, the relaxation is diffusive and at larger length scales, the relaxation is rather driven by chain elasticity. The lowest mode corresponds to the relaxation of monomer concentration fluctuations and is similar to the mode observed in binary polymer-solvent solutions. This mode is independent of the strength of the electrostatic interaction and, depends mainly on the excluded volume $V$. It is insensitive to the Flory parameter $\chi$. At small length scales, the relevant friction is proportional to the probed length scale $1/k$ and in the limit of the large length scales, the relevant friction is proportional to the correlation length $\xi$.

Let us now turn to the interdiffusion mode. If the charges were absent the interdiffusion would show the classical critical slowing down of the composition fluctuations close to the macro phase separation. Charges stabilize the solution against macrophase separation and the relaxation of composition fluctuations at low $k$ is dominated by electrostatics: the relaxation frequency has a finite value in the macroscopic limit. This behavior is characteristic for plasmon modes. As can be seen on the Fig. 2 below the frequency is very low (of the order of $10^4$Hz, for the typical values shown). At wavevector zero a weak (not visible at the scales of Fig. 2) splitting occurs, due to the dependence of the mobility on the Flory-$\chi$ parameter. The behavior found here is somewhat similar to block copolymers. The usually observed critical slowing down is shifted to the local scale $k^*$. Thus the corresponding relaxation frequency shows a minimum for high enough values (higher than chosen in the figure) of the interaction parameter $\kappa$.
FIG. 2. Variations of interdiffusive mode versus the wave vector \( k \). Dashed curves correspond to system (2\times2). Continuous curves correspond to system (4\times4) for different values of \( \chi \) (0, 0.1 and 0.24), \( N = 10^4 \), \( b = l_B = 710^{-8} \text{cm} \), \( \phi a^3/N = 3.6710^{-6} \).

The analytical calculation of the full 4\times4 system involves tedious algebra and produces long and non-transparent formulae. In the low wavevector limit the precise position of the charges is not of specific interest. Therefore it is convenient to smear out the charges. Thus it is possible to replace the system described above by an effective two chain model with a charge \( f = 2/N \) per monomer. The static composition structure factor \( S_{xx} \) can then be represented as

\[
S_{xx} = \frac{\phi N}{2} \left\{ \frac{1}{(2 - \chi \phi N) + k^2 R_g^2 + 4\kappa^2/k^2} \right\},
\]

where \( \kappa^2 = 4\pi l_B(2\phi)/N \). If the chains are uncharged, the classical case of a binary polymer blend is recovered. The term proportional to \( 1/k^2 \) stems from the bare Coulomb interaction between the charges. \( S_{xx} \) diverges then at \( k = 0 \) and \( \chi \phi N = 2 \). The charges themselves enhance compatibility and yield a microphase separation transition at \( \chi \phi N = 2 + 4\kappa R_g \). The structure factor \( S_{xx} \) shows a characteristic peak at a finite wavevector \( k^* \) where \( k^*2 = 2\kappa/R_g \).

For understanding the dynamical results obtained by numerical computation of the full four component system it is further convenient to rewrite the structure factor to

\[
S_{xx} = \frac{\phi N}{2} \sqrt{\Delta} \left\{ \frac{1}{1 + k^2 \xi_1^2} - \frac{1}{1 + k^2 \xi_2^2} \right\},
\]

where we have defined the discriminant \( \Delta = (2 - \chi \phi N)^2 - (4\kappa R_g)^2 \). In this representation two important length scales show up, i.e., \( \xi_{1,2}^2 = (2R_g^2)/(2 - \chi \phi N \pm \sqrt{\Delta}) \). It is immediately seen that \( \xi_1 \xi_2 = k^{*-2} \). For weak incompatibility, i.e., \( \chi \phi N \leq 2 - 4\kappa R_g \), the correlation function in real space consists of two exponential decaying functions \( \exp(-r/\xi_{1,2}) \), see eq (3). Closer to the microphase instability, \( 2 - 4\kappa R_g < \chi \phi N < 2 + 4\kappa R_g \), the real space structure factor contains decaying oscillatory parts. In the latter regime the plasmon behavior of the composition mode at low \( k \) will turn out to be hidden by the composition fluctuations. Moreover renormalization theories beyond the RPA are required.

The dynamics can be understood within the same framework. The relaxation frequencies can be computed along the lines discussed above. It is sufficient to understand the behavior of the relaxation frequencies from figure (1) at low values for the wavevector. Most interesting is the limit at zero wavevectors

\[
\Omega_{xx}(k = 0) = \frac{k_B T}{6\pi\eta} k^{*4} \left( \frac{1}{\xi_1} + \frac{1}{\xi_2} \right)^{-1},
\]

which has to be discussed in several limits. The first is the limit of \( \chi = 0 \), i.e., no composition fluctuations and therefore no coupling between thermodynamic and electrostatic interactions. For this case we find the simple result

\[
\Omega_{xx}(\chi = 0) = \frac{k_B T}{6\pi\eta} \frac{4\kappa^2}{R_g \sqrt{2}}.
\]

\(^1\)This statement is less obvious for the mobility integral occurring in eq.(4). However it can be checked afterwards that the integral is not dominated by the large \( k \) range.
where $\kappa R_g << 1$ was taken into account. The physical interpretation here is indeed simple: The relaxation frequency corresponds to a plasmon mode of $\phi/N$ macroions carrying two elementary charges each, whose hydrodynamic interaction is of the range of the radius of gyration $R_g$ (corresponding to the Oseen - tensor $1/r$). Composition fluctuations do not couple in this limit, thus the non appearance of any wavevector $k^*$ is natural, in contrast to the upper boundary $\chi \phi N = 2 - 4 \kappa R_g$. There the first sign of the microstructure shows up in terms of $k^*$. Indeed we find

$$\Omega_{xx}(\chi \phi N = 2 - 4 \kappa R_g) = \frac{k_B T}{6 \pi \eta} (k^*)^3 / 2 \quad (7)$$

In this regime of the interaction parameter the dynamics is ruled by the intrinsic length scale $k^*$ of the microphase separation transition. The plasmon character of the composition mode is reflected by eq. (4). For its observation a weak incompatibility like between deuterated and hydrogenated polymers is necessary. In the other limit which is given by eq. (6) the plasmon character is already blurred by the microphase separation. The slow plasmon mode is predicted in a range accessible by quasi elastic light scattering and spin echo techniques. The dynamical study has been limited to short time scales where the decays are exponential. Entanglements have been ignored completely. With respect to our studies, they will only further slow down all polymeric modes. The measurements are carried out in aqueous solution, and small amount of salt and ions could destroy this behavior. We carried out a model calculation, which involves these ions as individual component in the Langevin dynamics. The small ions couple to the electric charges bound at the chains, via a Coulomb potential. The dynamics of these ions with respect to all polymer modes involving the composition and concentration is a power of $N$ faster, $N$ being the chain length. Therefore the fast small ions produce a screened electrostatic potential of the Debye - Hückel type, where the screening constant is determined by the concentration of the remaining small ions. The relevant concentration in water is often of order $10^{-6}$, slightly higher than imposed by self-dissociation, and the corresponding wave vector is about $k = 10^4$ cm$^{-1}$. Thus we expect that at larger wave vectors the slow plasmon mode can be observed.

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