Pis'ma v ZhETF, vol. 114, iss. 6, pp. 400 – 401

A statistical model for short-wavelength collective chain fluctuations in a lipid bilayer under a high external electric field

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Submitted 8 August 2021
Resubmitted 14 August 2021
Accepted 20 August 2021

DOI: 10.31857/S1234567821180105

We develop a statistical model of short-wavelength number density fluctuations in the hydrophobic region of a lipid bilayer, composed of hydrocarbon lipid chains, under a high ($\sim 1\,\mathrm{V/nm}$) quasistatic uniform external electric field. The wave vector $\mathbf{k}$ of the number density fluctuations is assumed to be in the plane of the bilayer. We consider wave numbers k up to approximately the position of the peak of the density-density static structure factor $k_{\max} \sim 14\,\mathrm{nm}^{-1}$.

The hydrophobic region of a lipid bilayer is represented as a classical system of particles. The microscopic particle density is represented as $\rho_{\mathrm{micro}}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)$, where $\mathbf{r}_1, \ldots, \mathbf{r}_N$ are the positions of the particles (their centers of mass). The bound charges form localized groups that belong to individual particles. Using a dipole approximation for these groups of charge, we get for the microscopic charge density $\rho^{(q)}_{\mathrm{micro}}(\mathbf{r}) = -\sum_{i=1}^{N} \mathbf{d}(\mathbf{r}_i) \cdot \nabla\delta(\mathbf{r} - \mathbf{r}_i)$, where $\mathbf{d}(\mathbf{r}_i)$ is the electric dipole moment of the particle i, induced by the external field (it is assumed that there are no free electric charges).

Under the external uniform electric field $\mathbf{E}^{(\mathrm{ext})}$, the system remains homogeneous. To derive the static structure factor of the system, we consider an external nonuniform perturbation $\phi(\mathbf{r})$ coupled to the microscopic particle density. The Hamiltonian of the system is given by

$$H(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N) = K(\mathbf{p}_1, \ldots, \mathbf{p}_N) + \\ + W(\mathbf{r}_1, \ldots, \mathbf{r}_N) - \sum_{i=1}^{N} \mathbf{d}(\mathbf{r}_i) \cdot \mathbf{E}^{(\mathrm{ext})} + \sum_{i=1}^{N} \phi(\mathbf{r}_i),$$

where $\mathbf{p}_1, \ldots, \mathbf{p}_N$ are the momenta of the particles, K is the kinetic energy, W is the interparticle potential energy, and $\sum_{i=1}^{N} \phi(\mathbf{r}_i) = \int \rho_{\mathrm{micro}}(\mathbf{r})\phi(\mathbf{r})d\mathbf{r}$ is the potential energy due to the interaction of the particles with $\phi(\mathbf{r})$.

The average number density is defined as $\rho(\mathbf{r}) = \langle \rho_{\mathrm{micro}}(\mathbf{r}) \rangle$, where the bracket denotes an average over a grand canonical ensemble. The grand partition function has the form

$$\Xi = \sum_{N=0}^{\infty} \frac{(2\pi m k_B T)^{3N/2}}{h^{3N} N!} \int \exp\Bigg\{ -\frac{1}{k_B T} \times \\ \times \Bigg[W - \mu N + \sum_{i=1}^{N} [\phi(\mathbf{r}_i) - \mathbf{d}(\mathbf{r}_i) \cdot \mathbf{E}^{(\mathrm{ext})}] \Bigg] \Bigg\} d\mathbf{r}_1 \ldots d\mathbf{r}_N,$$

where T is the temperature, μ is the chemical potential in electric field, m is the mass of the particle, k_B is the Boltzmann constant and h is the Planck constant. The average charge density is defined as the ensemble average of the microscopic charge density [1]

$$\rho^{(q)}(\mathbf{r}) = \langle \rho^{(q)}_{\mathrm{micro}}(\mathbf{r}) \rangle. \quad (1)$$

In the quasielectrostatic approximation, the average value of the internal electric field $\mathbf{E}(\mathbf{r})$ in the medium can be defined by the relation [1]

$$\mathrm{div}(\mathbf{E} - \mathbf{E}^{(\mathrm{ext})}) = 4\pi\rho^{(q)} \quad (2)$$

The averaging (1) implies that we deal with the averaged in the same sense values of $\mathbf{E}$ through Eq. (2) [1].

The nonpolar lipid chains exhibit a frequency-independent, approximately isotropic, low-value permittivity with a magnitude ~ 2, which corresponds to their electronic polarization [2]. Since the dominant mechanism of polarization of lipid chains is the electronic polarization, the characteristic distance λ of the decay of the correlations of polarization fluctuations is determined by the length scale of the overlap of electron wave functions $\sim 0.05\,\mathrm{nm}$ [1]. Therefore we assume that for

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wave numbers $k \le k_{\max} \approx 14\,\mathrm{nm}^{-1}$, that are smaller than $\lambda^{-1} \sim 20\,\mathrm{nm}^{-1}$, the average electric field in the medium $\mathbf{E}$ can be represented as a sum of its mean value $\mathbf{E}_0 = \mathrm{const}$ and fluctuation $\delta\mathbf{E}$, and one can use the linear approximation in $\delta\mathbf{E}$. We consider the characteristic case $\mathbf{k}\cdot\mathbf{E}_0 = 0$. We show that under the conditions imposed, rapidly varying in space fields, which cause the nonlocal character of the relation between $\mathbf{D}$ and $\mathbf{E}$, are decoupled from the number density fluctuations.

An expansion of the free energy

$$F(\rho, T, \mathbf{E}) = \langle H\rangle - TS - \frac{1}{4\pi}\int \mathbf{D}\cdot\mathbf{E}d\mathbf{r} -$$

$$- \int \rho(\mathbf{r})\phi(\mathbf{r})d\mathbf{r} + (E^{(\mathrm{ext})})^2/8\pi,$$

where S is the entropy, in terms of number density fluctuations may be written in the form

$$\Delta F = \frac{1}{2}\iint \theta(\mathbf{r}-\mathbf{r}')\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')d\mathbf{r}'d\mathbf{r}.$$

We show that under the imposed restrictions, $\theta(k)$ ($\theta(\mathbf{k}) = \int \theta(\mathbf{r})\exp(-i\mathbf{k}\cdot\mathbf{r})d\mathbf{r}$) can be approximated as

$$\theta(k) \approx \theta^{(0)}(k) - \left(\frac{\partial^2\varepsilon(\rho_0)}{\partial\rho^2}\right)_T \frac{E_0^2}{8\pi}, \qquad (3)$$

where $\varepsilon = \varepsilon(k=0)$ is the permittivity of the medium, $\rho = \rho_0$ is the equilibrium number density, and $\theta^{(0)}(k)$ is determined from the static structure factor of the system in the absence of an external electric field. Using the technique given, e.g., in [3], we obtain for the static structure factor

$$S(k, E_0) \approx \frac{k_B T}{\rho_0\theta^{(0)}(k) - \mathrm{H}}, \qquad (4)$$

where $\mathrm{H} = \rho_0\left(\partial^2\varepsilon(\rho_0)/\partial\rho^2\right)_T E_0^2/8\pi$.

On the basis of the developed statistical model, we derive the Brillouin components of the dynamic structure factor of the system from first principles, i.e., from the Liouville equation, in the framework of the Zwanzig–Mori projection operator formalism.

We compare the results of the developed theory with new results of MD simulations on the initiation of lipid bilayer electropores [4] to show a nearly perfect agreement. Thus, on the microscopic level, the model explains the effect revealed in [5].

In order to assess the robustness of the analysis, we set $\theta(k) = \theta^{(0)}(k) + \theta^{(e)}(k)$ instead of Eq. (3) and expand $\theta^{(e)}(k)$ in $(\lambda k)^2$ to obtain

$$S(k, E_0) \approx \frac{k_B T}{\rho_0\theta^{(0)}(k) - \mathrm{H}(1-\lambda^2k^2)}. \qquad (5)$$

Comparison of the static structure factor given by Eq. (5) with $\lambda = 0.05\,\mathrm{nm}$ with $S(k, E_0)$ given by Eq. (4) indicates the robustness of our analysis. Thus, one may expect that the presented statistical model could be applied to handle analogous problems for a range of similar soft matter systems such as hydrophobic, low permittivity interior of globular proteins and DNA molecules, as well as nonpolar dielectric fluids.

This work was supported by Russian Foundation for Basic Research, the Government of the Krasnoyarsk Territory, and the Krasnoyarsk Regional Fund of Science (project # 19-41-240003).

This is an excerpt of the article "A statistical model for short-wavelength collective chain fluctuations in a lipid bilayer under a high external electric field". Full text of the paper is published in JETP Letters journal. DOI: 10.1134/S002136402118003X

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