Vol. 29 (1998) *ACTA PHYSICA POLONICA B* No 6

THE DENSITY OF STATES FOR DRUDE–LORENTZ MODEL OF NONPOLAR DIELECTRIC[*]

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(Received April 6, 1998)

The density of states spectrum in the Drude–Lorentz model of nonpolar dielectric is calculated for the face-centered crystal lattice structure. The results are compared with the fluid spectra. In the latter the structure analogous to the transverse and longitudinal polarization modes in solid dielectric is shown to exist.

PACS numbers: 05.90. +m

1. Introduction

Recently there appeared a number of papers (see for example [1–5] and references therein) devoted to analysis of the electrostatic and optical properties of Drude–Lorentz fluid. In particular, the spectral representation of such quantities as electrostatic constant and renormalized polarizability were found.

It seems that many properties of the above-mentioned systems can be better understood by considering their solid counterpart - Drude–Lorentz crystal, which is much simpler and easier to analyze than a fluid. In this paper we investigate the renormalized polarizability of such a system and compare the results with those for the fluid. Because of the periodicity of the crystal structure it is possible to apply reciprocal space techniques, what allows us to find the electrostatic spectrum of renormalized polarizability with high accuracy. At the same time we can apply here the methods used normally in the fluid theory (in particular the continued fraction method) thereby checking their accuracy by comparing their results with those given by the standard solid-state techniques.

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[*] Presented at the Marian Smoluchowski Symposium on Statistical Physics, Zakopane, Poland, September 1–10, 1997.

2. Drude–Lorentz model of a nonpolar dielectric

In the Drude–Lorenz model of a nonpolar dielectric we represent each molecule as a fixed nucleus accompanied by the elastically bounded "dispersion electron" oscillating with the eigenfrequency ω_o. The interaction potential between any two molecules is limited to dipole-dipole terms. The Hamiltonian for such a system reads:

$$H=\sum_i \frac{\boldsymbol{p}_i^2}{2m}+\sum_i \frac{1}{2}m\omega_o^2\boldsymbol{u}_i^2-\frac{1}{2}\mathrm{e}^2\sum_{i,j}\boldsymbol{u}_i\cdot\hat{T}_{ij}\cdot\boldsymbol{u}_j\,, \tag{1}$$

where $\boldsymbol{u}_i$ is the deviation of the i-th electron from its equilibrium position, $\boldsymbol{p}_i$ – its momentum. $\hat{T}_{ij}$ is the dipol–dipol interaction tensor:

$$\hat{T}_{ij}=\hat{T}(\boldsymbol{r}_i-\boldsymbol{r}_j)\,,\quad \text{where}\quad \hat{T}(\boldsymbol{r})=\frac{-\hat{I}+3\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}}{r^3}\,. \tag{2}$$

We consider the dielectric with face-centered crystal structure. We restrict ourselves to the cubic structure only for mathematical simplicity — our calculations are automatically applicable to any other lattice structure.

Let us rewrite now the Hamiltonian (1) in the reciprocal space variables:

$$\boldsymbol{u}(\boldsymbol{k})=\sqrt{\frac{\upsilon}{(2\pi)^3}}\sum_i \boldsymbol{u}_i\mathrm{e}^{-i\boldsymbol{k}\cdot\boldsymbol{r}_i}\,, \tag{3}$$

$$\boldsymbol{p}(\boldsymbol{k})=\sqrt{\frac{\upsilon}{(2\pi)^3}}\sum_i \boldsymbol{p}_i\mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{r}_i}\,, \tag{4}$$

where the summation is over the lattice points and υ is the elementary cell volume.

In terms of these variables, the Hamiltonian reads:

$$\begin{aligned}H\;=\;&\int\limits_{\mathrm{BZ}}\frac{\boldsymbol{p}^\star(\boldsymbol{k})\cdot\boldsymbol{p}(\boldsymbol{k})}{2m}\mathrm{d}\boldsymbol{k}+\int\limits_{\mathrm{BZ}}\frac{1}{2}m\omega_o^2\boldsymbol{u}^\star(\boldsymbol{k})\cdot\boldsymbol{u}(\boldsymbol{k})\mathrm{d}\boldsymbol{k}\\ &-\frac{1}{2}\mathrm{e}^2\int\limits_{\mathrm{BZ}}\boldsymbol{u}^\star(\boldsymbol{k})\cdot\hat{T}(\boldsymbol{k})\cdot\boldsymbol{u}(\boldsymbol{k})\mathrm{d}\boldsymbol{k}\,,\end{aligned} \tag{5}$$

where the integral is performed over the Brillouin zone and $\hat{T}(\boldsymbol{k})$ is the Fourier transform of the dipol–dipol interaction tensor:

$$\hat{T}(\boldsymbol{k})=\sum_{\boldsymbol{r}_n\neq 0}\hat{T}(\boldsymbol{r}_n)\mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{r}_n} \tag{6}$$

with the summation over the lattice points.

Since the above Hamiltonian is quadratic form in $\boldsymbol{u}(\boldsymbol{k})$, we are able to express any solution of the equation of motion in terms of the normal modes (polarization waves) of the form:

$$\boldsymbol{u}_n = \boldsymbol{A}\mathrm{e}^{i[\boldsymbol{k}\cdot\boldsymbol{r}_n - \omega(\boldsymbol{k})t]} \tag{7}$$

with three mutually orthogonal polarizations for each $\boldsymbol{k}$. The frequencies $\omega_i(\boldsymbol{k})$ of the modes are given by:

$$\omega_i(\boldsymbol{k}) = \sqrt{\omega_o^2 - \frac{\mathrm{e}^2}{m}\lambda_i(\boldsymbol{k})} = \omega_o\sqrt{1-\alpha_o\lambda_i(\boldsymbol{k})} \qquad \mathrm{i}= 1,\, 2,\, 3\,, \tag{8}$$

where $\alpha_o = \frac{\mathrm{e}^2}{m\omega_o^2}$ is a static polarizability in Drude–Lorentz model and $\lambda_i(\boldsymbol{k})$ are eigenvalues of $\hat{T}(\boldsymbol{k})$.

We see that these eigenvalues are connected with the frequencies of collective oscillations of Drude–Lorentz oscillators (eigenvectors of $\hat{T}(\boldsymbol{k})$ give the directions of vibration). In particular, one can show that in the long-wave case ($\boldsymbol{k} \to 0$) the above described three polarization waves reduce to one longitudinal and two degenerate transverse waves.

We can now define the density of states in Drude–Lorentz model $\rho_D(\omega)$ [2,3]: $\rho_D(\omega)d\omega$ is the number of the polarization waves with the frequencies between ω and $\omega + d\omega$.

The above Drude–Lorentz model of a nonpolar dielectric has a simple electrostatic counterpart. Namely let us consider a crystal lattice in each site of which there is a polarizable dipole with polarizability α. Next consider a uniform electric field E_0 acting only locally on one of the lattice sites. The electric dipole moment induced in this site will in its turn induce dipole moments in other sites and so on. As a result of these interactions, in each lattice site point dipoles are induced with values determined by:

$$\boldsymbol{\mu_j} = \alpha\left[\boldsymbol{E}_0\delta_{j1} + \sum_{j\neq k}\hat{T}_{jk}\cdot\boldsymbol{\mu_k}\right], \tag{9}$$

where we used an index "1" for the selected site where E_0 is applied.

The renormalized polarizability $\alpha^{'}$ is defined as the ratio of μ_1 to the applied field:

$$\boldsymbol{\mu_1} = \alpha^{'}\cdot\boldsymbol{E}_0 \tag{10}$$

(due to the symmetry of the problem α' is a scalar). This quantity is a very important characteristics of a dielectric. Nevertheless, the problem of finding α' has not been solved yet, even for such simple systems as the cubic lattices.

From Eqs. (9) and (10) one can show that:

$$\alpha^{'}(z) = \frac{v}{24\pi^3} \sum_{i=1}^{3} \int_{BZ} \frac{d\mathbf{k}}{z - \lambda_i(\mathbf{k})}\,, \tag{11}$$

where $z = \frac{1}{\alpha}$.

Thus $\alpha'(z)$ has the following spectral representation:

$$\alpha^{'}(z) = \int_{-\infty}^{\infty} \frac{\rho(\nu)}{z - \nu} d\nu \tag{12}$$

with positive, normalized to unity spectral density:

$$\rho(z) = \lim_{\epsilon \to 0} \frac{v}{24\pi^4} \mathrm{Im} \left(\sum_{i=1}^{3} \int_{BZ} \frac{1}{z - \lambda_i(\mathbf{k}) - i\epsilon} d\mathbf{k} \right)\,. \tag{13}$$

The relation (8) allows us to connect the spectral density $\rho(\nu)$ with the density of states in Drude-Lorentz model $\rho_D(w)$. We have namely:

$$\rho_D(\omega) = \frac{2m\omega}{\mathrm{e}^2} \rho(\nu = \frac{m}{\mathrm{e}^2}(\omega_o^2 - \omega^2))\,. \tag{14}$$

Hence the problem of finding the dynamical properties of the Drude – Lorentz model may be reduced to analysis of the simple electrostatic system.

3. The calculation of the spectral density $\rho(z)$

According to Eq. (13) to find the spectral density one should perform the Fourier transform of the dipol – dipol interaction tensor $\hat{T}(\mathbf{k})$, solve its eigenproblem and carry out the integral (13) over the Brillouin zone. The sum (6) can be calculated using the method described by Nijboer and de Wette in [7] based on the Ewald summation procedure.

There exist numerous methods of computing the integrals of the form (13) — such integrals arise often in all frequency distribution functions calculations. Different methods of dealing with such integrals are described at length in the review article by Gilat [8]. Here we are going to use two of the standard methods described in there. The first is RS ("root sampling") method in which one solves the $\hat{T}(\boldsymbol{k})$ eigenproblem for $\boldsymbol{k}$ vectors forming a fine uniform mesh in the irreducible section of the first Brillouin zone. Then those values are sorted out into number of channels thereby forming a histogram which approximates the spectrum.

The second method applied by us was LA ("linear analytic") method, in which one computes the eigenvalues $\lambda_i(\boldsymbol{k})$ as well as their gradients $\nabla\lambda_i(\boldsymbol{k})$ at evenly spaced points in reciprocal space and then finds λ in between by means of a linear extrapolation.

Finally, we used an alternative semi-analitical method of calculating $\rho(z)$ with use of the continued-fraction representation of $\alpha'(z)$ (CF method). The possibility of finding such representation is ensured [9, 10] by the fact that renormalized polarizability has a spectral representation of the form (12). We have proceeded in the way analogous to that described in [1]. In this paper, CF method was used to calculate electrostatic spectrum of renormalized polarizability in fluids. In such systems, because of the lack of periodicity, one cannot apply standard solid state methods using the reciprocal-space formulation.

However in our case one can compare the results of continued fraction method with those of the well known techniques (like RS or LA method) and thereby check the accuracy of the CF method.

Fig. 1 presents the spectra obtained by the use of RS, LA and CF methods. We see that the three methods give practically undistinguishable results (except for the neighbourhood of critical points — here the curve obtained by CF method would be a bit smoothed-out, because, as we have mentioned, CF gives the semi-analytical expression for $\rho(z)$).

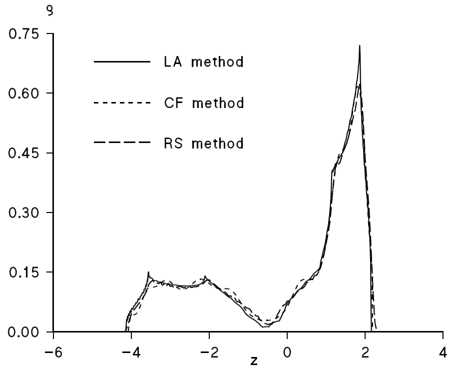

Fig. 1. The electrostatic spectrum for the fcc lattice

4. The comparison of the obtained spectrum with the analogous results for fluids and conlusions

Fig. 2 shows the $\rho(z)$ spectrum for the fcc lattice together with the analogous spectra of a fluid of hard spheres, each having in its center a polarizable dipole with polarizability α [2]. We use the variable $z' = zv$ where v is the specific volume and then rescale the spectrum to satisfy the normalization condition. The fluid spectrum was calculated for the

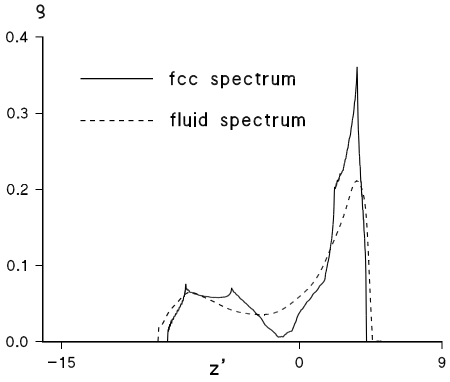

Fig. 2. The comparison of the electrostatic spectrum of a dense fluid $\rho(z')$ with the fcc spectrum.

volume fraction (*i.e.* the ratio of the volume occupied by spheres to the total volume) $\Phi = 0.5$, what corresponds to the dense fluid. We see that the $\rho(z)$ spectrum for the crystal lattice is modelling the behaviour of ρ for the dense fluid in a quite a good way. Of course, in the fluid spectrum we will not find singularities (because of the lack of periodicity). That is why there are no sharp peaks in the fluid spectrum and on the whole it is much more smooth than the solid one. The structure, however, remains the same. In particular, one can find the characteristic two peaks in the fluid spectrum, the counterparts of which for the solid are connected with the longitudinal and transverse polarizability modes.

What is even more interesting, this two-peaked structure survives also in the diluted fluid — the traces of it can be seen even for the $\Phi = 0.1$! This can be seen in Fig. 3 that shows the renormalized polarizability spectra taken

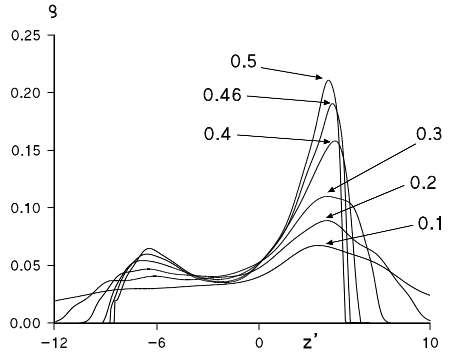

Fig. 3. The electrostatic spectra for the fluid for the volume fractions $\Phi = 0.1, 0.2, 0.3, 0.4, 0.46, 0.5$.

from [2] for 5 different volume fractions (starting from the dense ($\Phi = 0.5$) down to the very diluted ($\Phi = 0.1$) fluid). We observe here that, although the spectrum broadens and smooths down, the structure remains the same. The peaks, in particular, appear for the same values of z, independent on density. We know from the Fig. 2 that at these z values are localized also the peaks in the solid dielectric spectrum. Therefore it seems that even for the low densities the fluid "feels" the transverse and longitudinal polarization modes.

It is worth to point out that this structure was not so far described analytically. The approximate analytical expression for $\rho(z)$ derived by Cichocki and Felderhof [6] in the low density limit does not show the above mentioned two-peak structure. The problem seems to be that in fluid one cannot decompose $\rho(z)$ into the contributions coming from the respective eigenvalues of $\hat{T}(\boldsymbol{k})$. Instead one performs an average over configurations which does not favour any direction in space. Hence simple approximations lead in a "natural way" to one-peak structure. The above facts must be taken into consideration is one wants to describe the fluid spectra in a proper way.

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