ELSEVIER

Physica A 268 (1999) 513–524

PHYSICA A

www.elsevier.com/locate/physa

Frequency moments analysis of the dynamic structure factor of statistical systems

O.I. Gerasimov[a,b], P.P.J.M. Schram[b,*]

[a] *Department of General and Theoretical Physics, Odessa State Hydrometeorological Academy, Lvovskaya str. 15, Odessa 270016, Ukraine*

[b] *Faculty of Physics, Laboratory for Fluid Dynamics and Heat Transfer, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

Received 6 November 1998

Abstract

General relations of the theory of classical moments and orthogonal polynomials are applied to the construction of approximate expressions for the dynamic structure factor of statistical systems. With the help of the Nevanlinna theorem the respective expressions which interpolate the dynamic scattering function are constructed in terms of the static structure factor and a set of moments which are considered to be given because of their connection with spectral line shape parameters (integral intensitivity of scattering; shift, dispersion and asymmetry of spectral line, etc.). The efficiency of choice of respective interpolational expressions is proposed to be controlled self-consistently with the help of appropriate Tchebycheff–Markov inequalities. The correct limiting transitions to well-known results obtained within the memory function formalism are demonstrated. The possible application of the given approach to studying critical dynamic light scattering data, is demonstrated.

PACS: 05.20.-y; 61.20.-p; 61.20.lc

Keywords: Dynamic structure; Frequency moments; Orthogonal polynomials; Limiting transitions; Classical moments

1. Introduction

The detailed analysis of dynamic structure factors is one of the main interests of statistical mechanical theories of condensed systems in particular because of its close relation to the cross-section of external radiations scattering (neutrons, light). The

* Corresponding author. Fax: +31-40-2464157/2445534.
E-mail address: pschram@tnl.phys.tue.nl (P.P.J.M. Schram)

0378-4371/99/$ - see front matter
PII: S0378-4371(99)00068-0

development of a formalism for the description of the microscopic dynamic behavior of different statistical systems has a long history (see, for instance [1,2]) and comprises the different approximate methods mostly based on a phenomenological analysis (for example, on the projection operator formalism). Nevertheless, in many cases, the theories are formally even exact, because the introduced frequency and wavelength-dependent quantities are expressed in terms of phenomenological parameters (like relaxation times) the calculation of which is not self-consistently prescribed. This makes the general microscopic theory of dynamic structure factors incomplete. Therefore, an extension of detailed analysis is required which may operate by alternative adjustable parameters and which could thus provide a comparison between the different alternative approaches and respective scattering experiments. In such way we apply here the general statements of the theory of moments from functional analysis for the semiphenomenological analysis of dynamic scattering functions. The class of probe functions (which include the appropriate constants, extracted from the comparison of given function with the experimental one) interpolating the dynamic scattering function is built on the basis of the Nevanlinna theorem and rigorous relations from the theory of orthogonal polynomials in terms of frequency moments. Limiting transitions to well-known results which were obtained with the help of memory function modelling are performed.

As a practical application of the developed approach a description of the time behavior of the intermediate dynamic light scattering in real complex statistical systems – ordered colloids – in terms of the spectral line shape parameters will be proposed.

2. The frequency moments analysis

The frequency moments $M_j(\mathbf{k})$ of the dynamic structure factor $S(\mathbf{k},\omega)$ are defined as follows:

$$M_j = \int_{-\infty}^{\infty} \omega^j S(\mathbf{k},\omega)\,\mathrm{d}\omega, \quad j = 0,1,2,\ldots\,. \tag{1}$$

Knowing the normalized moments μ_j,

$$\mu_j = \frac{M_j}{M_0}\,, \tag{2}$$

gives us the possibility to narrow the class of functions that includes the dynamic structure factor. According to the theorem by Nevanlinna from functional analysis [3–7] every nonnegative function $I(\mathbf{k},\omega)$ that has the first $2n$ moments in common with the function $S(\mathbf{k},\omega)$ may be represented as

$$I^{(n)}(\mathbf{k},\omega) = \frac{M_0\Delta_n^2}{\pi} \frac{\nu^{(n)}(\omega)}{[\Theta_{n+1}(\mathbf{k},\omega) + M_{2n+1}(\mathbf{k})\Theta_n(\mathbf{k},\omega) + V^{(n)}(\omega)\Theta_n(\mathbf{k},\omega)]^2} \frac{}{+\cdots+[\nu^{(n)}(\omega)]^2\Theta_n^2(\mathbf{k},\omega)}\,, \tag{3}$$

where

$$\Delta_n = \begin{vmatrix} 1 & \mu_1 \dots \mu_n \\ \mu_1 & \mu_2 \dots \mu_{n+1} \\ & \\ \mu_n & \mu_{n+1} \dots \mu_{2n} \end{vmatrix}, \qquad \Theta_n = \begin{vmatrix} 1 & \mu_1 \dots \mu_n \\ \mu_1 & \mu_2 \dots \mu_{n+1} \\ \mu_{n-1} & \mu_n \dots \mu_{2n-1} \\ 1 & \omega \dots \omega^n \end{vmatrix}, \tag{4}$$

$\Theta_0 = 1$, and $v(\omega)$ and $V(\omega)$ are, respectively, the imaginary and real parts of the boundary value $q(\omega + \mathrm{i}0)$ of some function $q(\zeta)$

$$q(\zeta) = V(\zeta) + \mathrm{i}v(\zeta) \tag{5}$$

defined by

$$q(\zeta) = \lambda + \int_{-\infty}^{\infty} [(t-\zeta)^{-1} - t(t^2+1)^{-1}]\,\mathrm{d}s/t \tag{6}$$

$$\mathrm{Im}(\lambda) \geqslant 0, \quad \mathrm{Im}\zeta > 0$$

with nondecreasing function $s(t)$ that satisfies the condition

$$\int_{-\infty}^{\infty} \frac{s(t)}{1+t^2}\,\mathrm{d}t < \infty\,. \tag{7}$$

Standard relations from the classical problem of moments and formulas from the Christoffel–Darboux theory of orthogonal polynomials [5] allow us to establish the functions q_n

$$q_n(\zeta) = \frac{\Delta_{n+1}}{\Delta_{n-1}} \left[\mu_{2n+1} - \frac{1}{q_{n+1}(\zeta) + \zeta} \right]\,. \tag{8}$$

Now, if one has determined the $2n$ moments within the limited given interval of frequencies, it is possible to approximate the dynamic structure factor using (3). For simplicity, theory allows us even to substitute the function $q(\zeta)$ with a constant $\mathrm{i}h (h > 0)$ assuming $q(\zeta)$ to depend weakly on frequency in the considered interval. In practice, this constant and the moments, which are included in the consideration can be determined from coincidence of the experimental data for $S(\mathbf{k}, \omega)$ with the constructed approximation in every particular case. Let us give now several particular examples of extrapolational formula (3) for given numbers of moments. Assuming $S(\mathbf{k}, \omega)$ to be an even function of ω (as well as of $\mathbf{k}$), which is rigorously speaking only correct in the case of classical systems like under our consideration), putting all odd moments μ_{2n+1} equal to zero, and using the zero- and the second-moments sum rules for $S(\mathbf{k}, \omega)$[1, 2]

$$\int_{-\infty}^{\infty} S(\mathbf{k}, \omega)\,\mathrm{d}\omega = S(\mathbf{k})\,, \tag{9}$$

$$\int_{-\infty}^{\infty} \omega^2 S(\mathbf{k}, \omega)\,\mathrm{d}\omega = k^2 \cdot \left(\frac{k_B T}{m} \right) \equiv \omega_0^2\,, \tag{10}$$

where T and m are the temperature and particle mass, respectively (note, that second moment sum is an extension of particle conservation) and $S(\mathbf{k})$ is a static structure factor, from (3) for $n = 0, 1, 2, 3$ we obtain, respectively,

$$I^{(0)}(\mathbf{k},\omega) = \frac{S(\mathbf{k})}{\pi} \cdot \frac{v^{(0)}}{\omega^2 + [v^{(0)}]^2}\,, \tag{11}$$

$$I^{(1)}(\mathbf{k},\omega) = \frac{S(\mathbf{k})}{\pi} \cdot \frac{\tilde{\omega}_0^2 \tau_1(\mathbf{k})}{\tau_1^2(\mathbf{k})(\omega^2 - \tilde{\omega}_0^2)^2 + \omega^2}\,, \tag{12}$$

$$\tau_1(\mathbf{k}) = \frac{\tilde{\omega}_0^2}{v^{(1)}}, \quad \tilde{\omega}_0^2 = k^2 \left(\frac{k_B T}{m}\right) \frac{1}{S(\mathbf{k})}$$

$$I^{(2)}(\mathbf{k},\omega) = \frac{S(\mathbf{k})}{\pi} \frac{\tau_2(\mathbf{k})}{[\tau_2(\mathbf{k})\omega(\omega^2 - \omega_{1l}^2)]^2 + (\omega^2 - \tilde{\omega}_0^2)^2}\,, \tag{13}$$

$$\tau_2(\mathbf{k}) = \frac{\tilde{\omega}_0^2}{v^{(2)}}(\omega_{1l}^2 - \tilde{\omega}_0^2)\,,$$

$$\omega_{1l}^2 = \frac{\mu_4}{\mu_2} = \frac{M_4}{\omega_0^2}\,,$$

$$I^{(3)}(\boldsymbol{k},\omega) = \frac{S(\boldsymbol{k})}{\pi} \frac{(\omega_{1l}^2 - \tilde{\omega}_0^2)^2(\mu_6 - \omega_{1l}^2\mu_4)\tau_3(\mathbf{k})}{\tau_3^2(\mathbf{k}) \cdot [\omega^2(\omega_{1l}^2\omega^2 - \mu_6/\tilde{\omega}_0^2) - \omega_0^2\omega^2(\omega^2 - \omega_{1l}^2)} \\ \frac{}{+ \cdots + (\mu_6 - \omega_{1l}^2\mu_4)]^2 + \omega^2(\omega^2 - \omega_{1l}^2)^2(\omega_{1l}^2 - \tilde{\omega}_0^2)^2}\,, \tag{14}$$

$$\tau_3(\mathbf{k}) = \frac{\mu_6 - \omega_{1l}^2 \cdot \mu_4}{v^{(3)}},$$

where $\{v^{(i)}\}$ are constants (with respect to ω) which have individual dimensions, for example

$$[v^{(0)}] = [\omega], \quad [v^{(1)}] = [\omega^3], \quad [v^{(2)}] = [\omega^5], \quad [v^{(3)}] = [\omega^7].$$

Replacing for example in (11) the constant $v^{(0)}$ (which is a constant with respect to frequency dependence) by the expression $v = Dk^2$ one can see an exact correspondence to the well-known expression for the so-called single-particle dynamic structure factor $S_c(\mathbf{k},\omega)$ which is a Lorentzian curve centered on $\omega = 0$ with a half-width equal to $2Dk^2$

$$S_c(\mathbf{k},\omega) = \frac{1}{\pi} \cdot \frac{Dk^2}{\omega^2 + (Dk^2)^2} \tag{15}$$

and $S(\mathbf{k}) = 1$ (ideal gas limit). General expression (3) in the form of (11) with $v^{(0)}$ replaced by Dk^2 describes the Rayleigh line in dynamic light scattering spectra (see, for instance [1,2]) and is also in exact accordance with the analytical expression for $S_c(\mathbf{k},\omega)$ obtained within the alternative (hydrodynamic) approach. The appropriate

choice of the form for $\tau_1(\mathbf{k})$ and $\tau_2(\mathbf{k})$ in expressions (12) and (13) gives rise to well-known model relations for spectra of, respectively, transverse current fluctuations and the self-dynamic structure factor (last one is related to the cross section for incoherent scattering) obtained within the alternative memory function approach under the particular assumption, given on a quite phenomenological level, of exponentional relaxation properties. Expression (14) therefore gives us a more detailed interpolational expression for $S(\mathbf{k},\omega)$ in terms of higher moments, namely M_0, M_2, M_4 and M_6. Note here that our approach permits without any difficulties to include in the analysis also the effects of shift and asymmetry of spectral lines which are connected with the odd moments M_1, M_3, etc., respectively. The constructed expression for $S(\mathbf{k},\omega)$ after the calibration (with respect to a set of parameters $\{v^{(j)}(\mathbf{k})\}$) can be inverted to give the system of algebraic equations providing the possibility of the determination of the moments themselves included in the consideration in every particular case. Sometimes, we need to make estimates for the moments of spectra which give information about the parameters of spectral line style (such as: line shift or asymmetry, dispersion, etc.), but at the same time the scattering function can be determined only in a few points of the frequency spectrum. For such a case the inverse problem within the given scheme of interpolation becomes useful and practical for a self-consistent analysis of the shape and parameters of spectra. At last note, that because all the expressions (11)–(14) include the moments $\{\mu_j\} = \{M_j/M_0\}$ and $M_0 = S(\mathbf{k})$, not only the amplitude, but also other parameters of the dynamic scattering function (like dispersion) demonstrate a strong k-dependence which is closely related to the shape of the static structure factor $S(\mathbf{k})$.

Collecting the different interpolations for $S(\mathbf{k},\omega)$ such as

$$I(\mathbf{k},\omega) = AI^{(0)}(\mathbf{k},\omega) + BI^{(1)}(\mathbf{k},\omega) + \cdots , \tag{16}$$

where A, B, etc. are constants which can be found phenomenologically, one has the possibility of a combinational approach in describing the structure of the dynamic scattering function, for example; central peaks (Rayleigh lines) are described by $I^{(0)}(\mathbf{k},\omega)$, sound peaks (Brillouin lines) or plasma peaks (in the case of charged systems) are described by $I^{(1)}(\mathbf{k},\omega)$, etc.

3. Estimate of the efficiency of the proposed interpolation formulas on basis of the Tchebycheff–Markow inequalities

Using the general theory of orthogonal polynomials one can propose a scheme of estimating the frequency region in which the given interpolation formulas (or other approximations for the dynamic structure factor) become most adequate. Note, that in the case of our analysis such a scheme of estimates becomes self-consistent. Namely, the most tight lower and upper bounds of the integral $\int_0^{\omega} S(\mathbf{k},\omega')\,\mathrm{d}\omega'$ with the interpolational expression $S(\mathbf{k},\omega)$ are determined by non-model Tchebycheff–Markow

inequalities [3–7] for the given n moments of $I(\mathbf{k},\omega)$

$$\sum_{\omega_z<\omega} g(\omega_s) \leqslant \int_{-\infty}^{\omega-0^+} I^{(n)}(\mathbf{k},\omega')\,\mathrm{d}\omega' \leqslant \int_{-\infty}^{\omega+0^+} I^{(n)}(\mathbf{k},\omega')\,\mathrm{d}\omega' \leqslant \sum_{\omega_s<\omega} g(\omega_s) + g(\omega)\,, \tag{17}$$

where $g(\omega_s)$ are the point masses of the canonical representation fixed in the points $\{\omega_s\}$ which are distributed on the left-hand side of the given frequency ω' on a frequency axis, being the roots of the equation

$$\Theta_{n+1}(\omega')\Theta_n(\omega) - \Theta_{n+1}(\omega)\Theta_n(\omega') = 0\,, \tag{18}$$

where $\{\Theta_n(\omega)\}$ are the polynomials defined by (4) and the masses $g(\omega_s)$ are to be found by the solution of the following equation:

$$M_l = \omega^l g(\omega) + \sum_{s=1}^{n} \omega_s^l g(\omega_s), \quad l = 0,\ldots,2n\,. \tag{19}$$

Here n is the number of given moments. The Tchebycheff–Markow inequalities (17) become precise in the case of a "correct" (or genuine) function $S(\mathbf{k},\omega)$ and can be violated at some points ω if the number of moments which are used to calculate the masses $g(\omega_s)$ by (19), exceeds the number of existing moments included in the construction of the interpolational expression for $I^{(n)}(\mathbf{k},\omega)$ utilized as an integrand in $\int_{-\infty}^{\omega} I^{(n)}(\mathbf{k},\omega')\,\mathrm{d}\omega'$.

For instance, if we limit ourselves in the construction of TM-inequalities to only zeroth and second moments $S(\mathbf{k})$ and ω_0^2 of the dynamic structure factor, the respective calculations based on (19), (18) and (4) lead to

$$1 - \frac{\omega_0^2}{\omega^2+\omega_0^2} \leqslant \frac{2}{S(\mathbf{k})}\int_0^{\omega} I(\mathbf{k},\omega')\,\mathrm{d}\omega' \leqslant 1\,. \tag{20}$$

If we choose now self-consistently the interpolational expression (11) for $I^{(0)}(\mathbf{k},\omega)$, it follows from (20) that

$$\frac{1}{1+\omega_0^2/\omega^2} \leqslant \frac{2}{\pi}\cdot \operatorname{arctg}\frac{\omega}{\nu^{(0)}} \leqslant 1\,. \tag{21}$$

Thus the limiting frequency ω_c for $I^{(0)}$ is to be found as a solution of the equation

$$\frac{1}{1+\omega_0^2/\omega_c^2} = \frac{2}{\pi}\cdot \operatorname{arctg}\frac{\omega_c}{\nu^{(0)}}\,. \tag{22}$$

For $\omega_c/\nu^{(0)} > 1$, one can determine this frequency by considering the asymptotic expansion for the right-hand side of Eq. (22)

$$\omega_c = \frac{2}{\pi}\frac{\omega_0^2}{\nu}\,. \tag{23}$$

Then $I^{(0)}(\mathbf{k},\omega)$ adequately describes the "low-frequency" behavior $(0<\omega<\omega_c)$ of $S(\mathbf{k},\omega)$. Otherwise Eq. (22) can be solved numerically.

The same analysis can be done in the case of all other approximate forms $I^{(n)}(\mathbf{k},\omega)$, giving of course also modifications of frequency intervals for the validity of the higher-order interpolation formulas for $I^n(\mathbf{k},\omega)$.

4. Intermediate scattering function and critical modes analysis

Consider now as an example the description of coherent dynamic light scattering from colloidal systems which consist of dispersions of charged or neutral macroions suspended in, say, water, in the presence or absence, respectively, of counterionic components which stabilize the system charge. It is known that such system for appropriate values of the internal parameters (such as charges – in the case of charged suspensions and volume fraction – in the case of neutral systems) can create Wigner crystallic states for the colloidal component with a lattice parameter within a few diameters of the hard core of the particles. For a detailed review of this subject see, e.g. [8,9]. From typical light scattering experiments (see [10–12]) the coherent intermediate partial scattering function $g(\mathbf{k},t)$ (which is a Fourier transform of $S(\mathbf{k},\omega)$), as a function of scattering vector $\mathbf{k}$ and delay time t can be determined.

To make a preliminary comparison of our theoretical results with the experimental data, one should first find the intermediate scattering function. For instance Fourier transforming (16), with the help of (11), (12), we obtain

$$g(\mathbf{k},t) = \frac{S(\mathbf{k})}{\pi} \cdot \{A\mathrm{e}^{-\nu^{(0)}t} + B \cdot \tilde{I}^{(1)}(\mathbf{k},t)\}\,, \tag{24}$$

where

$$\tilde{I}^{(1)}(\mathbf{k},t) = \begin{cases} \dfrac{\tilde{\omega}_0^2 \tilde{\nu}^{(1)}}{2\sqrt{2}(1-(\tilde{\nu}^{(1)2}/2\tilde{\omega}_0^6))\sqrt{1+(\tilde{\nu}^{(1)2}/2\tilde{\omega}_0^6)}} \cdot \mathrm{e}^{-t\sqrt{2}\tilde{\omega}_0\sqrt{1-(\nu^{(1)2}/2\tilde{\omega}_0^6)}}, & 1 > \dfrac{\nu^{(1)2}}{2\tilde{\omega}_0^6}\,, \\ \dfrac{1}{2\sqrt{\frac{\nu^2}{2\tilde{\omega}_0^6}-1}} \cdot \left[\dfrac{\mathrm{e}^{-t\tilde{\omega}_0\sqrt{(\nu(1)2/2\tilde{\omega}_0^6)-1-(\nu/\tilde{\omega}_0^3)\sqrt{(\nu^2/4\tilde{\omega}_0^6)-1}}}}{\tilde{\omega}_0\sqrt{(\nu^2/2\tilde{\omega}_0^6)-1-(\nu/\tilde{\omega}_0^3)\sqrt{(\nu^2/4\tilde{\omega}_0^6)-1}}} \right. \\ \left. - \dfrac{\mathrm{e}^{-t\tilde{\omega}_0}\sqrt{(\nu^{(1)2}/2\tilde{\omega}_0^6)-1+(\nu/\tilde{\omega}_0^3)\sqrt{(\nu^2/4\tilde{\omega}_0^6)-1}}}{\tilde{\omega}_0\sqrt{\tilde{\omega}_0^2((\nu^{(1)2}/2\tilde{\omega}_0^6)-1)+(\nu/\tilde{\omega}_0)\sqrt{(\nu^2/4\tilde{\omega}_0^6)-1}}} \right], & 1 < \dfrac{\nu^{(1)2}}{2\tilde{\omega}_0^6}\,. \end{cases} \tag{25}$$

From (25) it is straightforward to show that

$$\ln g(\boldsymbol{k},t) = \ln\frac{AS(\mathbf{k})}{\pi} - \nu^0 t + \ln\left(1+\frac{B}{A}\tilde{I}^{(1)}(\boldsymbol{k},t)\,\mathrm{e}^{\nu^{(0)}t}\right)\,. \tag{26}$$

Thus it is evident that for all values of k the long-time k^2t -dependence of $\ln g(\mathbf{k},t)$ is roughly linear and the function $g(\mathbf{k},t)$ is quite well described by a single exponential for large enough t. Consider the short- and the long-time behavior of intermediate scattering function given in the second-moment approximation (26). Namely, when

$t \to \infty$ it follows simply from (26) (if we put also for definiteness $1 > v^{(1)2}/2\tilde{\omega}_0^6$) that

$$\ln\left\{\frac{g(\mathbf{k},t)}{S(\mathbf{k})}\right\} = \ln\left(\frac{A}{\pi}\right) - v^{(0)}t + 0\left[\frac{\tilde{B}}{A}\,\mathrm{e}^{-(\Gamma - v^{(0)})t}\right], \tag{27}$$

where

$$\tilde{B} = \frac{\pi\cdot\tilde{\omega}_0^2\cdot B}{2\sqrt{2}(1-(\tilde{v}^{(1)2}/2\tilde{\omega}_0^6))\sqrt{1+(\tilde{v}^{(1)2}/2\tilde{\omega}_0^6)}},$$

$$\Gamma = \sqrt{2}\tilde{\omega}_0\sqrt{1-\frac{v^{(1)2}}{2\tilde{\omega}_0^6}}\,. \tag{28}$$

Thus the long-time k^2t dependence of $\ln(g(\mathbf{k},t)/S(\mathbf{k}))$ as mentioned before, is roughly linear. This also clearly coincides with the experiment [12], see Figs. 1 and 2. Due to the condition of satisfying expression (27) and experimental data plotted in Fig. 1 we have $\ln A = -0.062$ and $v^{(0)}/k^2 = 8.56\times10^{-8}\,\mathrm{cm}^2/\mathrm{s}$. The last numerical value gives rise to the conclusion that $v^{(0)} = \overline{D_0}$, where $\overline{D_0}$ - s.c. mean free-particle diffusion coefficient for the dilute suspension. If we compare (27) with the data extracted from experiments with more dense suspensions, see Fig. 2, one has $v^{(0)}/k^2 \simeq 3.5\times10^{-7}\,\mathrm{cm}^2/\mathrm{s}$, which again allows us to put $v^{(0)} = \overline{D_{eff}}\cdot k^2$, where $\overline{D_{eff}} \simeq 3.5\times10^{-7}\,\mathrm{cm}^2/\mathrm{s}$ practically coincides with the value of the effective diffusion coefficient under the appropriate parameters of the system (remember here that we calibrate the value of $v^{(0)}$ in every particular case independently). If we look now for the short-time limit $t \to 0$, assuming $\tilde{B}/A\,\mathrm{e}^{-(\Gamma - v^{(0)})t} > 1$, from (26) and (27) we can obtain

$$\ln\left\{\frac{g(\mathbf{k},t)}{S(\mathbf{k})}\right\} = \ln\tilde{B} - \Gamma t\,. \tag{29}$$

Thus, in the short-time limit we have again single-exponential behavior of the scattering function but with a relaxation-time Γ which of course differs from $v^{(0)}$ (see Figs. 1 and 2). The best agreement of (29) with the experimental data could be achieved with the help of a particular choice of parameter $v^{(1)}$ (note that definitely, for the considered colloidal systems we have $v^{(0)} = \overline{D}_{0,\,eff} < 2\tilde{\omega}_0 = k_0/S\pi\sqrt{2k_b\Gamma/m}$, where k_0 is the fixed value of a wave vector, which is normally put equal or close to the coordinate of the first peak in the static structure factor. In Figs. 1 and 2 we can see (after the calibration of constant A and $v^{(0)}$), a good agreement between theory and experimental data from [12] in the limit of large times. For the intermediate time as one can see from (25)–(28) we definitely have a two-exponential fit in describing $g(\mathbf{k},t)$. These theoretically predicted facts, as follows from data presented in Figs. 1 and 2, are in good agreement with the experiment. Consider now the critical mode formalism to describe the line shape close to the critical region of ordering in the considered systems. As expounded in [13], when $k \to k_0$ (where k_0 is a critical value of the wave vector for mode generation) $S(k_0) \to \infty$, i.e. mimics singular behavior. From (25)–(28) it follows that in this case the contribution $S(\mathbf{k})\cdot\tilde{I}^{(1)}(\mathbf{k},t)/\pi$ also becomes singular, repeating the singular behavior of $S(\mathbf{k})$ due to other than amplitude effects. This tendency in the dynamic

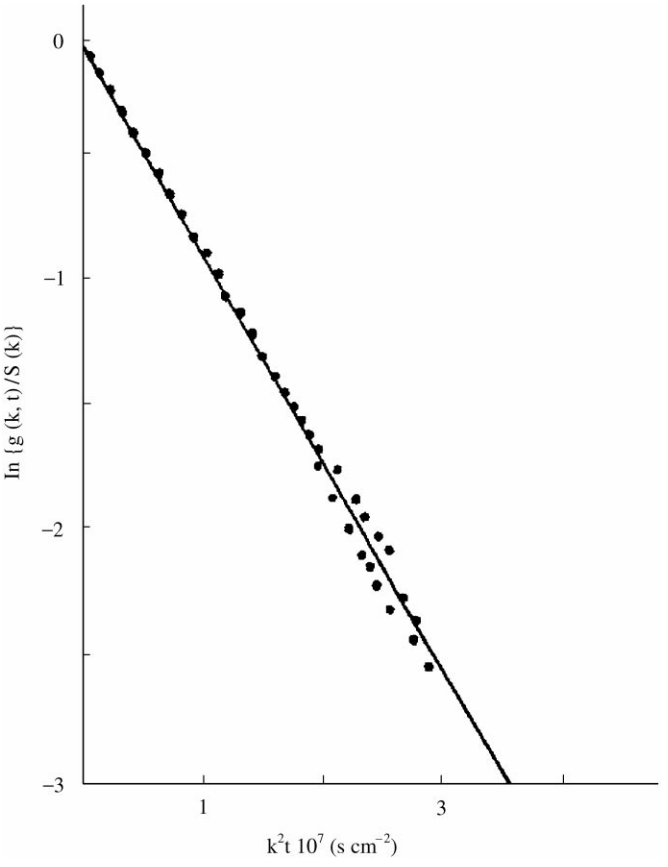

Fig. 1. Normalized intermediate scattering function $g(\mathbf{k},t)/S(\mathbf{k})$ against k^2t in semilogarithmic scale: closed circles represent the experimental data for a dilute sample (with a density of the colloidal particles $\simeq 2\times10^{-4}\,\mathrm{g\,cm^{-3}}$) of the 250 Å radius polystyrene spheres in a NaCl solution, at room temperature $T=293$ K for the fixed scattering angle (or wave-vector $\mathbf{k}$) from [14]. The full line is the theoretical curve given from the single exponential fit (see expression (24) in the text) at the following numerical values of the initial parameters (which were self-consistently extracted from the comparison between theoretical and experimental curves): $\ln A=-0.062$, $\frac{\nu^{(10)}}{k^2}=8.56\times10^{-8}\ \mathrm{cm\,s^{-1}}$.

scattering function for the systems mentioned above was clearly observed in a recent experiment [14].

Using the interpolations $I^{(0)}(\mathbf{k},\omega)$, $I^{(1)}(\mathbf{k},\omega)$ and $I^{(2)}(\mathbf{k},\omega)$ in (16) let us consider also the appproximation for dynamic scattering function $I(\mathbf{k},\omega)$ in the following form:

$$I(\mathbf{k},\omega)=\frac{S(\mathbf{k})}{\pi}\cdot\left\{A\frac{\nu^{(0)}}{\omega^2+[\nu^{(0)}]^2}+B\frac{\tilde{\omega}_0^2\tilde{\nu}^{(1)}}{(\omega^2-\tilde{\omega}_0^2)^2+[\nu^{(1)}]^2\omega^2}\right.$$
$$\left.+\,C\frac{\tilde{\omega}_0^2(\omega_{1l}^2-\tilde{\omega}_0^2)\tilde{\nu}^{(2)}}{\omega^2(\omega^2-\omega_{1l}^2)+[\tilde{\nu}^{(2)}]^2(\omega^2-\tilde{\omega}_0^2)}\right\},\qquad(30)$$

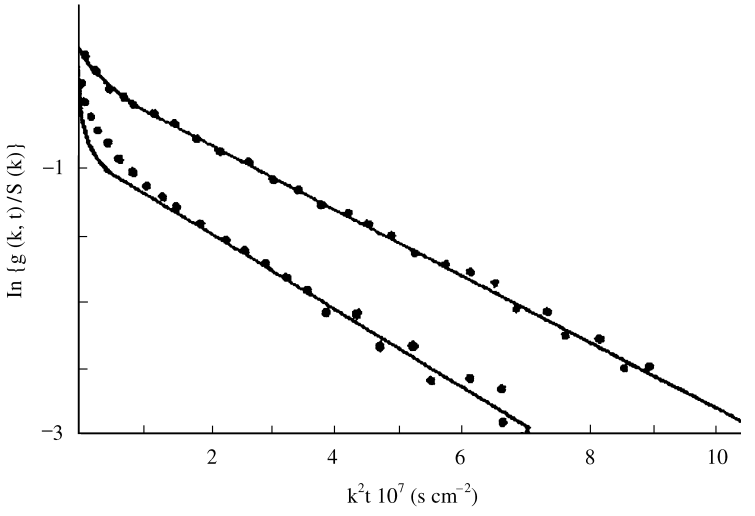

Fig. 2. Function $\ln\{g(\mathbf{k},t)/S(\mathbf{k})\}$ for a sample mentioned in the capture on Fig. 1 (upper curve) and for a sample as in Fig. 1 but with a different concentration of $1.25\times10^{-3}\,\mathrm{g\,cm^{-3}}$. Experimental data (closed circles) from [14]. Full line is the theoretical curve (24) given from the two-exponential fit (see, also the text).

applying the critical mode method. Here we use the definitions

$$\tilde{v}^{(1)}=\frac{v^{(1)}}{\tilde{\omega}_0^2},\quad \tilde{v}^{(2)}=\frac{v^{(2)}}{\tilde{\omega}_0^2(\omega_{1l}^2-\tilde{\omega}_0^2)}\,. \tag{31}$$

Considering again the critical mode generation condition:

$$S(\mathbf{k})|_{k\to k_0\neq 0}\to\infty\,.$$

(we are speaking here again about the s.c. 'hard' critical modes which satisfy to crystallic state generation criteria, say within a colloidal suspension), one can see that close to the critical region ($k\to k_0$), $\tilde{\omega}_0^2\to 0$ and thus $\tilde{v}^{(1)}$, $\tilde{v}^{(2)}\to\infty$. From $S(\mathbf{k})|_{k\to k_0}\to\infty$ it follows in this case that

$$I^{(0)}(\mathbf{k},\omega)|_{k\to k_0}\to\infty\,, \tag{32a}$$

$$I^{(1)}(\mathbf{k},\omega)\sim\left.\frac{\omega_0^4}{v^{(1)}S(\mathbf{k})\omega^2}\right|_{k\to k_0}\to 0\,, \tag{32b}$$

$$I^{(2)}(\mathbf{k},\omega)\sim\left.\frac{\omega_0^4\omega_{1l}^4}{v^{(2)}S^2(\mathbf{k})\omega^4}\right|_{k\to k_0}\to 0\,. \tag{33}$$

Thus the amplitude of the central peak in (26) is increased at the same time that the amplitudes of the shifted peaks are decreased. Note this dynamic behavior of the spectra of fluctuations, i.e., the redistribution of the intensivity (with a conservation of the integral intensivity), close to critical region well known in the theory (and less clear in the experiment) of the Rayleigh–Brillouin spectra of dynamic light scattering close to the region of hydrodynamic instabilities [18].

5. Conclusions

Clearly, we have a wide area for applications and practical use of the above results. Among them we select only several ones which are closely related to extremely interesting static and dynamic properties of ordered (within mesoscopic scale) colloidal systems like liquid suspensions and dusty plasmas (including one-component plasmas). Here dynamic light scattering plays the role of diagnostic test for the investigation of kinetic properties promising to clarify these in many respects not well-understood phenomena. We refer the readers to several recent reviews on such fields [8–11].

As follows from experiments with colloidal suspensions [12–16] the behavior of the dynamic scattering function $g(\mathbf{k},t)$ (which is a Fourier transform of $S(\mathbf{k},\omega)$) in a semilogarithmic plot as a function of time, demonstrates at least two-exponential fits in the different short-time and long-time limits. To explain this phenomenon within the memory function approach with an exponential relaxation, a specific structure of the relaxation time could be artificially assumed. In our approach, however, see expressions (11)–(14), (16) and Fig. 1, several typical relaxation times appear, providing the possibility to give quantitative and qualitative comparison between theory and experiment. Also, it is possible to show that expressions $I^{(1)}(\mathbf{k},\omega)$ and $I^{(2)}(\mathbf{k},\omega)$ have a definitive extrema (maxima) as functions of ω for the appropriate values of the parameters, and that the amplitudes of peaks increase with increasing $S(\mathbf{k})$. This suggests to use the approach developed for the dynamic analysis of critical modes in the static case, which are related to a formation of ordered states [17]. The obtained results give, of course, the possibility to use in (11)–(14), (16) any model approximate expressions for a set of frequency moments at $S(\mathbf{k},\omega)$ to construct other practical interpolational expressions for $S(\mathbf{k},\omega)$ with a controlled accuracy. A detailed analysis of this and some other related questions will be discussed in a subsequent paper.

Acknowledgements

One of the authors (O.I.G.) is very grateful to the Dutch Organization for Scientific Research (NWO) for financial support of his stay in Eindhoven. He also deeply appreciates the hospitality and fruitful atmosphere of the Eindhoven University of Technology. The work was supported in part by INTAS project 96-0617. Professor J.-P. Hansen is acknowledged for useful and fruitful discussions.

References

[1] J.-P. Hansen, J.R. MacDonald, Theory of Simple Liquids, Academic Press, London 1981.
[2] D. Forster, Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions, W.A. Benjamin, Inc. MA, 1975.
[3] N.J. Akhiezer, The Classical Moment Problem, Oliver and Boyd, Edinburgh 1965.
[4] M.G. Krein, A.A. Nudelman, The Markow moment problem and extremal problem, Translation of Mathematical Monographs vol. 50, American Mathematical Society, Providence, RI, 1977.

[5] S. Karlin, W. Studder, Tchebycheff Systems: With Applications in Analysis and Statistics Interscience publishers, A Division Wiley, New York, London 1966.
[6] O.I. Gerasimov, in: J. Prigogine, S. Rice (Eds.), Advances in Chemical Physics vol. 75, J. Wiley, USA, 1989.
[7] O.I. Gerasimov, V.M. Adamian, Phys. Rev. A 39 (1989) 6573.
[8] K.S. Schmidtz, Macroions in Solution and Colloidal Suspension, VCH Publishers, USA, 1993.
[9] A.K. Arora (Ed.), Ordering and Phase Transitions in Charged Colloids, B.V.R. Tata VCH Publishers, USA, 1996.
[10] R. Pecora (Ed.), Dynamic Light Scattering, Plenum, New York, 1985.
[11] Neutron, X-ray, Light Scattering: Introduction to an Investigate Tool for Colloidal and Polyneric Systems, P. Linder, Th. Zemb (Eds.), Elsevier, Netherlands 1991.
[12] J.C. Brown, P.N. Pusey, J.W. Coodwin, R.M. Ottewa, J. Phys. 8 (1975) 664.
[13] O.I. Gerasimov, P.P.J.M. Schram, A.G. Sitenko, A.G. Zagorodny, Physica B 228 (1996) 40.
[14] J. Harland, W. van Megen, Phys. Rev. E 55 (1997) 3054.
[15] J. Derksen, W. van de Water, Phys. Rev. A 45 (1992) 5660.
[16] M.C. Abramo, M. Parinello, M. Tosi, J. Phys. C.: Solid State Phys. 7 (1974) 4201.
[17] J.-P. Hansen, I.R. McDonald, E. Pollock, Phys. Rev. A 11 (1975) 1025.