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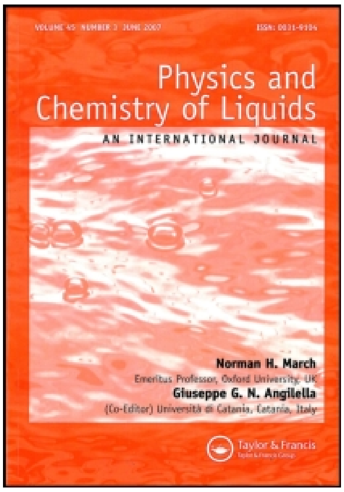

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Continued fraction description of density fluctuation spectrum in liquids

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Continued Fraction Description of Density Fluctuation Spectrum in Liquids

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So far many different approximate expressions of the density response have been proposed by using meanfield approximations and perturbative expansion methods. In this paper few of the these expressions are concisely stated by using generalized langevin equation approach.

Density response function for a simple classical liquid is a convenient factor for the study of the collective behavior in the strongly interacting disorder systems, e.g., classical liquids. In the past, few theories based on random phase approximation of effective field approximation and perturbative expansion methods have been proposed to explain the experimentally observed behavior of density response function of simple liquids. Memory function formalism has also been introduced to understand these scattering data. The most remarkable approach in these lines is the generalized Langvin equation approach, which is an approach implicitly of Mori (1965) and explicitly of Zwanzig (1961). The present work is mainly based on this approach.

Mori (1965) has shown that in Langevin equation the generalized force for a dynamical operator obeys a Langevin equation with a random force which obeys yet another Langevin equation and so on. The net result of Mori's analysis is an infinite sequence of Langevin equations in which the dynamical property in the n-th equation is the random force of the (n-1) th equation. Under Laplace transformation these sets of equations lead to continued fraction representation. In principle one can always calculate the density autocorrelation function from the

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above continued fraction representation by taking density fluctuation as the dynamical operator.

To achieve this, one has to start with the intermediate scattering function, F (K,t) which, in terms of local density, is of the form:

$$F(k, t) = \left\langle n^{-1} \sum_{i,j} \exp(i\vec{k} \cdot (\vec{r}_{i,0} - \vec{r}_{j,t})) \right\rangle \tag{1}$$

The first few equilibrium moments of this function is given as (deGennes, 1959);

$$\langle\omega^{\circ}\rangle = S(k) \ , \ \langle\omega^{2}\rangle = k^{2}/\beta m \tag{2}$$

$$\langle\omega^{4}\rangle = \frac{k^{2}}{\beta m} \left[\frac{3k^{2}}{\beta m} + \frac{n}{m} \int d\vec{r}\, g(r)\,(1 - \cos(\vec{k}.\vec{r}))\, \frac{\partial^{2}\phi}{\partial z^{2}}(r) \right. \tag{3}$$

where the symbols have their usual meanings. Let the Laplace transform (in t-space) of F(k,t) is F(k,p), i.e.

$$F(k, p) = \int_{0}^{\infty} e^{-pt}\, F(k, t)\, dt \ , \tag{4}$$

The density response function, $\chi(k,p)$, is related with F(k,p) through the following well known relation:

$$\chi(k,p) = \beta\, [\, p\, F(k,p) - F(k,o)\,] \tag{5}$$

Thus, in continued fraction representation the intermediate scattering function is written as

$$F(k,p) = S(k)/p + K_{1}/p + K_{2}/p + \ldots \tag{6}$$

where K_1, K_2 etc. can be expressed in terms of equilibrium moments of F(k,t) and has the explicit form: $K_{1} = k^{2}/\beta m S(k)$

and $$K_{2} = \frac{2k^{2}}{\beta m} + \frac{k^{2}}{\beta m}\, C(k) + \frac{n}{m} \int d\vec{r}\, g(r)\,(1 - \cos(\vec{k}.\vec{r}))\, \frac{d^{2}\phi(r)}{dz^{2}} \tag{7}$$

For the noninteracting systems these moments have the form:

$$K_{1}^{0} = k^{2}/\beta m \quad \text{and} \quad K_{2}^{6} = 2k^{2}/\beta m \tag{8}$$

where for noninteracting systems S(k) is unity.

Eq. (6) is the main equation of this paper. Here it is shown that by putting different hierarachy of approximation in Eq. (6), various semiphenomenalogical expressions of density response functions can be obtained.

Let in the first approximation, the first order random force correlation term

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has a known spectrum, which is equivalent of truncating the continued fraction at very first step, i.e.,

$$F(k,p) = \frac{S(k)}{p + K_1\ K(k,p)} \tag{9}$$

Further, if it is considered that K(k,p) behaves as the memory function associated with the ideal gas density autocorrelation function, one gets the Nelkin and Ranganathan (1967) expression of F(k,p), i.e.,

$$K(k,p) \equiv K^{o}(k,p) \quad = \frac{1}{K_1^{o}} \left(\frac{1}{F^{o}(k,p)} - p \right) \tag{10}$$

where superscript zero represents the case of noninteracting system. Thus form Eq. (9) and (10) we get:

$$F(k,p) = \frac{S(k)\, F^{o}(k,p)}{1 + (1 - K_1 / K_1^{o})(p\, F^{o}(k,p) - 1)}$$

or

$$= \frac{S(k)\, F^{o}(k,p)}{1 + C(k)(p\, F^{o}(k,p) - 1)} \tag{11}$$

which is also the Nelkin anganathan's (1967) expression, calculated from mean field approximation.

Similarly if one carries out the same type of calculation by taking the first order random force correlation term to be the memory function of the self part of density autocorrelation function, one gets the Kerr's (1968) expression for F(k,p). It is necessary to point out here that the zeroth and first equilibriun moments of $F_s(k,t)$ and $F^{o}(k,t)$ are same.

The expression of density response function given by Pathak and Singwi (1970) can also be cast in the form of continued fraction. To do this one has to start with the general relation of density response function, i.e.,

$$\chi(k,p) = \frac{\chi^{sc}(k,p)}{1 + \psi(k)\, \chi^{sc}(k,p)} \tag{12}$$

where $\chi^{sc}(k,p)$ is the screened density response function and is the effective interparticle potential. Pathak and Singwi (1970) have proposed the following form of $\chi^{sc}(k,p)$ and $\psi(k)$ for classical liquids for which $\chi(k,p)$ satisfies first few low order moment relations.

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$$\mathrm{Im}\chi^{sc}(k,p) = -\frac{2npk^2\,\beta}{2k^2 + m\beta\Gamma(k)}\left(\frac{\pi m\beta}{2k^2 + m\beta\Gamma(k)}\right)^{\frac{1}{2}} \tag{13}$$

$$\times \exp\left(-m\beta p^2/(2k^2 + m\beta\Gamma(K)\right)$$

and

$$\psi(k) = \frac{3}{2n\beta}\,c(k) + \frac{1}{2k^2}\quad d\vec{r}\,g(r)\,(1 - \cos(\vec{k},\vec{r}))\,\frac{d^2\phi(r)}{dz^2}$$

$$= \frac{K_1}{K_1^\circ} - \frac{K_2}{K_2^\circ} \tag{14}$$

where

$$\Gamma(k) = \frac{k^2}{m\beta}\,c(\vec{k}) + \frac{n}{m}\int d\vec{r}\,g(r)\,(1 - \cos(\vec{k},\vec{r}))\,\frac{d^2\phi(r)}{dz^2}$$

$$= K_2 - K_2^\circ \tag{15}$$

By using Eqs. (5), (13), (14), and (15) in Eq. (12) which can be transformed in term of F(k,p), i.e.,

$$[pF(k,p) - S(k)] = \frac{[p\,F^{sc}(k,p) - K_2^\circ/K_2]}{1 - \left(\frac{K_1}{K_1^\circ} - \frac{K_2}{K_2^\circ}\right)(p\,F^{sc}(k,p) - \frac{K_2^\circ}{K_2})}$$

or

$$F(k,p) = \frac{S(k)}{p + K_1\dfrac{\left(\frac{K_2^\circ}{K_2} - p\,F^{sc}(k,p)\right)\frac{K_2}{K_2^\circ}}{K_1^\circ\,F^{sc}(k,p)}} \tag{16}$$

Thus the memory function associated with F(k,p) comes out as:

$$K(k,p) = \frac{\left[\frac{K_2^\circ}{K_2} - p\,F^{sc}(k,p)\right]}{K_1^\circ\,F^{sc}(k,p)}\quad K_2\,/\,K_2^\circ \tag{17}$$

which can be easily recognized as the memory function of a modified ideal gas density autocorrelation function, i.e.,

$$K(k,t) = K_{i.g}\,(K_2\,/\,K_2^\circ\,t^2) \tag{18}$$

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Thus, one finds that the first order truncation in continued fraction representation for memory function of Eq. (18) type reproduces very well the expression of density autocorrelation function given by Pathak and Singwi (1970).

Finally if one truncates the continued fraction at the second order random force term and approximate it to be the second order random force correlation term of ideal gas, one gets the expression of density autocorrelation function given by Lado (1970).

The second order random force correlation function of ideal gas can be written in terms of memory function, $K^o(k,p)$ associated with the density autocorrelation function of ideal gas in the following way:

$$K_2\,(k,p) = \frac{K_1^o}{K_2^o\,K^o(k,p)} - \frac{p}{K_2^o} \tag{19}$$

Substituting Eq. (19) in the truncated continued fraction expression for density autocorrelation function yields:

$$F\,(k,p) = \cfrac{S\,(k)}{p + \cfrac{K_1}{p + K_2\left(\cfrac{K_1^o}{K_2 K^o(p)} - \cfrac{p}{K_2^o\,(o)}\right)}} \tag{20}$$

The memory function associated with the above F(k,p) can be written as:

$$K_1\,(k,p) = \frac{K_1\,K_1^o\,K^o\,(k,p)}{K_2 K_1^o + (K_2^o - K_2)\,p\,K^o\,(p)}.$$

This is exactly the same expression of memory function as derived by Lado (1970) by using perturbative expansion technique.

TABLE 1

Memory function	Order of truncation	Authors	Moments of F(k,t) satisfied
Ideal gas for density	Ist order of random force	Nelkin and Ranganathan (1967)	0, 2
Self motion for density	Ist order of random force	Kerr (1968)	0, 2
Modified ideal gas for density	Ist order of random force	Pathak and Singwi (1970)	0, 2, 4
Ideal gas for current	IInd order of random force	Lado (1970)	0, 2, 4
Self motion for current	IInd order of random force	Kurkijarivi (1970)	0, 2, 4

Thus, it can be concluded that all the above various proposed expressions of density autocorrelation function can be easily derived from the continued fraction representation formalism. In Table I this has been briefly summarised.

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