Collective Coordinates Kinetics and Dynamic Structural Factor in Classical Liquids

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1. INTRODUCTION

By the kinetic equation method it is possible to investigate not only the transport phenomena in liquids, but also various "generalized susceptibilities", connected with the equilibrium fluctuation kinetics. In order to construct the kinetic equation for a classical single-atom liquid, the coordinates of the atom (ion) mass centers $\vec{R}_j$, where j is the number of particles and the conjugated momentum $\vec{P}_j = M\dot{\vec{R}}_j$, where M is the mass of the atom (ion), are used as a dynamic variables basic set. It is formally possible to receive the closed system of equations, which would describe the kinetics of liquids /1/, but actual simplification of the collision integral is possible only for small parameters (or weak interaction, or low density). In a liquid, both approximations are invalid, and the kinetic theory expressed in the variables (R_j, P_j) remains a formal one.

In solid-state theory, a similar difficulty is overcome by the introduction of the collective coordinates – phonons. The zero approximation (noninteracting oscillators ideal gas) gives a good description of the lattice thermodynamics, and the lowest order of interaction between phonons (account of the anharmonic term) permits description of the thermal expansion of solids and the lattice thermal conductivity. The phonon picture, however, is an approximation of small deviations from the fixed equilibrium states.

In a liquid, this model is invalid, nevertheless it is possible to introduce the collective coordinates "as phonons" without any model assumptions. We introduce the local particle density

$$n(\vec{r}) = \sum_{j=1}^{N} \delta(\vec{r} - \vec{R}_j) \tag{1.1}$$

and we determine its Fourier component with the wave vector $\vec{q}$:

$$\rho(\vec{q}) = \frac{1}{N} \int d\vec{r}\, n(\vec{r}) e^{-i\vec{q}\vec{r}} \tag{1.2}$$

Substituting (1.1) in (1.2), we obtain:

$$\rho(\vec{q}) = \frac{1}{N} \sum_{j=1}^{N} e^{-i\vec{q}\vec{R}_j}, \rho(0) = 1, <\rho(\vec{q})> = \delta\vec{q},0 \tag{1.3}$$

where <. . .> designates the equilibrium configurational average with particle distribution function $W(\vec{R}_1 \ldots \vec{R}_N)$ in $\vec{R}$-space. The set of $\{\rho(\vec{q})\}$ may now be considered as new (collective) variables. They were introduced by Bohm in plasma physics /2/, investigated in Zubarev's works /3/, used in statistical physics in Yuhnovski's work /4/, and in liquid metal physics in March's works /5/. The latter considered the liquid metal as two-component (electron-ion) plasma. However, in the kinetic theory of liquids these variables have not been applied.

It is convenient to use the coordinates

$$X_{\vec{q}} = \rho(\vec{q}) - <\rho(\vec{q})> = \rho(\vec{q}) - \delta_{q,0} \tag{1.4}$$

As seen from (1.3), $\rho(\bar q)=\rho(\bar q,t)$ (depends on the time by means of $\bar R_i$). The importance of the coordinates (1.4) results from their simple connection with the dynamic structural factor of the liquid /6/:

$$< X^{*}_{\bar q} X_{\bar q}(\tau) > = \frac{1}{N} S(\bar q,\tau) \qquad (1.5)$$

In order to calculate this correlator, the master equation will be obtained in §2, and in §3 the kinetic equation in the Brownian motion model. The collective coordinates kinetics in a liquid and the respective kinetic equation are discussed in §4. In §5 the main kinetic equation parameter, the friction coefficient, is found, and in §6 the dynamic structural factor of the liquid is calculated. The possibilities of comparison between theory and experiment are also discussed there.

2. MASTER EQUATION

As a first step, using the projection operators method, we obtain the general master equation, describing some S-system, which is in contact with an equilibrium thermostat. As far as our realization of projection operators differs from the standard one /7/, we give a short derivation of the master equation, using the quantum-mechanical designations (they are more compact than the classical ones). The simple transition to the classical theory will be realized at the end of the derivation. The complete Hamiltonian of the system is:

$$\hat H = \hat H_o + \hat H'(t) + \hat H_{int}, \hat H_o = \hat H_F + \hat H_S \qquad (2.1)$$

where $\hat H_F$ is the Hamiltonian of the equilibrium thermostat with the related density matrix:

$$\hat\rho_{OF} = e^{-\beta \hat H_F} / Sp_F\, e^{-\beta \hat H_F}, \beta \equiv (kT)^{-1} \qquad (2.2)$$

(and Sp_F (...) designates averaging only on thermostat variables), $\hat H_S$ – the Hamiltonian of the subsystem, $\hat H'(t)$ – the operator of interaction between the S-system and external alternating fields (if present) and $\hat H_{int}$ – the operator of interaction between the S-system and the thermostat,satisfying by its construction the condition:

$$\left\langle \hat H_{int} \right\rangle_F = SP_F\left(\hat\rho_{OF}\, \hat H_{int}\right) = 0 \qquad (2.3)$$

(If $\left\langle \hat H_{int} \right\rangle_F \neq 0$, it is always possible to redefine $\hat H_S \rightarrow \hat H_S' = \hat H_S + \left\langle \hat H_{int} \right\rangle_F, \hat H_{int} \rightarrow \hat H_{int}' = \hat H_{int} - \left\langle \hat H_{int} \right\rangle_F$, and now $\left\langle \hat H_{int}' \right\rangle_F = 0$.) Let us assume that $\hat\rho$ is the total system density matrix, and $\hat\sigma(t)$ – the S-system density matrix. Then:

$$\hat\sigma(t) = SP_F\, \hat\rho \qquad (2.4)$$

We determine the operator $\hat\eta(t)$, which describes the correlatitons between the S-system and the thermostat:

$$\hat\rho = \hat\rho_{OF} \cdot \hat\sigma(t) + \hat\eta(t) \qquad (2.5)$$

and we introduce the projection operators, $\hat{\hat V}, \hat{\hat C}, \hat{\hat I}$:

$$\hat{\hat V}\hat Q = \hat\rho_{OF}\, Sp_F\, \hat Q = \hat\rho_{OF}\, \hat Q_{(S)}, \hat{\hat I}\, \hat Q = \hat Q, \hat{\hat C} = \hat{\hat I} - \hat{\hat V} \qquad (2.6)$$

Here Q is a certain dynamic variable of the system, and the projector $\hat{\hat V}$ "cuts out" from it the S-part $\hat Q_{(S)}$, acting only on S-system variables. These operators satisfy the identities:

$$\hat{\hat V}^2 = \hat{\hat V}, \hat{\hat C}^2 = \hat{\hat C}, \hat{\hat V}\hat{\hat C} = \hat{\hat C}\hat{\hat V} = 0 \qquad (2.7)$$

(i.e. $\hat{\hat C}$ is the orthogonal addition of the projector $\hat{\hat V}$). From (2.6 - 2.7) it follows:

$$\hat\rho = (\hat{\hat V} + \hat{\hat C})\hat\rho = \hat\rho_{OF}\, \hat\sigma(t) + \hat{\hat C}\hat\rho \qquad (2.8)$$

i.e.

$$\hat{\hat V}\hat\rho = \hat\rho_{OF} \cdot \hat\sigma(t), \hat{\hat C}\hat\rho = \hat\eta(t) \qquad (2.9)$$

And, using the Balesku terminology /7/, it is possible to name $\hat{\hat{V}}$ as projector on "the subdynamics of vacuum", and $\hat{\hat{C}}$ – on "the subdynamics of correlations".

The evolution of the total system is described by Liouville's equation:

$$\frac{\partial\hat{\rho}}{\partial t}=-\frac{i}{\hbar}\left[\hat{H},\hat{\rho}\right]=-i\hat{\hat{L}}\hat{\rho} \tag{2.10}$$

(Liouville's operator $\hat{\hat{L}}=\frac{i}{\hbar}\left[\hat{H},\ldots\right]$ and the projectors belong to the same algebra.) According to (2.1), we have:

$$\hat{\hat{L}}=\hat{\hat{L}}_o+\hat{\hat{L}}'(t)+\hat{\hat{L}}_{int},\ \hat{\hat{L}}_o=\hat{\hat{L}}_F+\hat{\hat{L}}_S \tag{2.11}$$

From determinations of projectors and Liouville's operators, the following identities are obtained:

$$\begin{gathered}\hat{\hat{V}}\hat{\hat{L}}_S=\hat{\hat{L}}_S\hat{\hat{V}},\ \hat{\hat{V}}\hat{\hat{L}}'(t)=\hat{\hat{L}}'(t)\hat{\hat{V}},\ \hat{\hat{V}}\hat{\hat{L}}_F=0\\ \hat{\hat{V}}\hat{\hat{L}}_o=\hat{\hat{L}}_S\hat{\hat{V}},\ \hat{\hat{V}}\hat{\hat{L}}_{int}\hat{\hat{V}}=0\end{gathered} \tag{2.12}$$

which, in turn, yields the following identities:

$$\begin{gathered}\hat{\hat{V}}\hat{\hat{L}}\hat{\hat{V}}=(\hat{\hat{L}}_S+\hat{\hat{L}}'(t))\hat{\hat{V}},\ \hat{\hat{V}}\hat{\hat{L}}\hat{\hat{C}}=\hat{\hat{V}}\hat{\hat{L}}_{int}\hat{\hat{C}}\\ \hat{\hat{C}}\hat{\hat{L}}\hat{\hat{V}}=\hat{\hat{L}}_{int}\hat{\hat{V}},\ \hat{\hat{C}}\hat{\hat{L}}\hat{\hat{C}}=(\hat{\hat{L}}_O+\hat{\hat{L}}'(t)+\hat{\hat{C}}\hat{\hat{L}}_{int})\hat{\hat{C}}\end{gathered} \tag{2.13}$$

Acting in sequence on both parts of equation (2.10), the projector $\hat{\hat{V}}$ (or $\hat{\hat{C}}$) gives with the aid of (2.13):

$$i\hat{\rho}_{OF}\frac{\partial\hat{\sigma}(t)}{\partial t}=\hat{\rho}_{OF}\left(\hat{\hat{L}}_S+\hat{\hat{L}}'(t)\right)\hat{\sigma}(t)+\hat{\hat{V}}\hat{\hat{L}}_{int}\hat{\eta}(t) \tag{2.14}$$

$$\begin{gathered}i\frac{\partial\hat{\eta}(t)}{\partial t}=\hat{\hat{L}}_{int}\hat{\rho}_{OF}\hat{\sigma}(t)+\\ \left(\hat{\hat{L}}_O+\hat{\hat{L}}'(t)+\hat{\hat{C}}\hat{\hat{L}}_{int}\right)\hat{\eta}(t)\end{gathered} \tag{2.15}$$

Let us write the result of equation (2.15) as:

$$\hat{\eta}(t)=\hat{\eta}(0)-i\int_0^t dt'\hat{\hat{U}}(t,t')\hat{\hat{L}}_{int}\hat{\rho}_{OF}\hat{\sigma}(t') \tag{2.16}$$

where the propagator $\hat{\hat{U}}(t,t')$ satisfies the equation:

$$i\frac{\partial}{\partial t}\hat{\hat{U}}(t,t')=\left(\hat{\hat{L}}_O+\hat{\hat{L}}'(t)+\hat{\hat{C}}\hat{\hat{L}}_{int}\right)\hat{\hat{U}}(t,t') \tag{2.17}$$

and the boundary condition:

$$\hat{\hat{U}}\left(t+0^+,t\right)=\hat{\hat{I}} \tag{2.18}$$

The choice of the initial condition $\hat{\eta}(0)=0$ is now basic; it is equivalent to the initial Bogolubov's correlations weakening condition /7/. Actually, it means the existence of the temporary scales hierarchy with the minimum scale τ_o, a characteristic "smoothing" interval (by Kirkwood /8/), on which the destruction of the correlations by thermal motion in the thermostat occurs. Then it is possible to pass in a roughened temporary scale $t \gg \tau_o$, in which the interval τ_o "is concentrated in a point". Substituting (2.16) with the condition $\hat{\eta}(0)=0$ in (2.14) and using the determination of the $\hat{\hat{V}}$ projector, we obtain the basic master equation, the closed irreversible equation for the S-system density matrix in its most common form:

$$\begin{gathered}\frac{\partial\hat{\sigma}(t)}{\partial t}=-i\left(\hat{\hat{L}}_S+\hat{\hat{L}}'(t)\right)\hat{\sigma}(t)-\\ -\int_o^t dt'Sp_F\left(\hat{\hat{L}}_{int}\hat{U}(t,t')\hat{\hat{L}}_{int}\rho_{OF}\right)\hat{\sigma}(t')\end{gathered} \tag{2.19}$$

For practical application of equation (2.19), simplifications are necessary. The problem position, deriving from the opportunity of the division of the total system on the S-system and the thermostat (remaining in equilibrium state), assumes weakness of the interaction between the S-system and the thermostat, which allows to be limited in the relaxation member in (2.19) by the lowest (second) order on $\hat{H}_{int}$. Hence, it is enough to find $\hat{U}(t,t')$ in zero on $\hat{H}_{int}$ approximation, i.e., it is possible to write, instead of (2.19):

$$i\frac{\partial}{\partial t}\hat{\hat{U}}(t,t')\cong\left(\hat{\hat{L}}_o+\hat{\hat{L}}'(t)\right)\hat{\hat{U}}(t,t'),\hat{\hat{U}}(t+O^+,t)=\hat{\hat{I}} \tag{2.20}$$

Hereafter we are interested in the case where the alternating external fields are absent, i.e., $\hat{\hat{L}}'(t) = 0$. Then the equation (2.20) has the form:

$$\hat{U}(t,t') = e^{-i(t-t')\hat{L}_o} \qquad (2.21)$$

and (2.15) may be written as:

$$\frac{\partial\hat{\sigma}(t)}{\partial t} = -i\hat{\hat{L}}_S\hat{\sigma}(t) - \int_0^t dt'\hat{\hat{K}}(t-t')\hat{\sigma}(t') \qquad (2.22)$$

with the relaxation kernel:

$$\hat{\hat{K}}(\tau) = Sp_F\left(\hat{\hat{L}}_{int}e^{-i\tau\hat{\hat{L}}_o}\hat{\hat{L}}_{int}\hat{\rho}_{OF}\right) \qquad (2.23)$$

Passing to clinical physics, the quantum Liouville's operators have to be replaced by the classical ones: $-i\hat{\hat{L}} \Rightarrow \hat{L} = \{H,\ldots\}$, where $\{u,v\}$ is the Poisson's brackets; quantum density matrices – by the classical distribution functions $\hat{\sigma} \rightarrow \sigma$, and $Sp_F(\ldots)$ – by $\int d\Gamma_F$, where $d\Gamma_F$ is the thermostat phase volume measure. Then the equations (2.22 - 2.23) may be written as:

$$\frac{\partial\sigma(t)}{\partial t} = \hat{L}_S\sigma(t) + \int_0^t d\tau\hat{K}(\tau)\sigma(t-\tau) \qquad (2.24)$$

$$\hat{K}(\tau) = \int d\Gamma_F\hat{L}_{int}e^{\tau\hat{L}_o}\hat{L}_{int}\rho_{OF} \qquad (2.25)$$

3. KINETIC EQUATION IN BROWNIAN MOTION MODEL

In the beginning, we consider as an important methodical example the derivation of the usual Fokker-Planck equation for a heavy Brownian particle of mass M in a thermostat - liquid of unstructured particles of mass m. In this case, in the usual $(\vec{r},\vec{p})$ variables for the Brownian particle and the $(\vec{r}_i,\vec{p}_i)$ variables for particles of the liquid, we have:

$$H_F = \sum_{i=1}^{N}\frac{1}{2m}p_i^2 + \frac{1}{2}\sum_i{\neq}\sum_j U(|r_i - r_j|)$$

$$H_S = \frac{1}{2M}\vec{p}^2, H_{int} = \sum_{i=1}^{N}\Phi(\vec{r} - \vec{r}_i) \qquad (3.1)$$

where Φ is the potential of interaction between the Brownian particle and particles of the liquid. From (3.1) it follows that

$$\hat{L}_F = -\sum_i\vec{F}_i\frac{\partial}{\partial\vec{p}_i} - \sum_i\frac{\vec{p}_i}{m}\frac{\partial}{\partial\vec{r}_i}, \hat{L}_S = -\frac{\vec{p}}{M}\frac{\partial}{\partial\vec{r}} \qquad (3.2)$$

$$\hat{L}_{int} = -\sum_i\vec{F}_{i(F)}\frac{\partial}{\partial\vec{P}_i} - \vec{F}\frac{\partial}{\partial\vec{P}}$$

where:

$$\vec{F}_i = -\frac{\partial}{\partial\vec{r}_i}\sum_{j=1}^{N\ (\neq i)}U(\vec{r}_i - \vec{r}_j) \qquad (3.3)$$

$$\vec{F}_{i(F)} = -\frac{\partial}{\partial\vec{r}_i}\Phi(\vec{r} - \vec{r}_i) \qquad (3.4)$$

$$\vec{F} = \sum_i\left[-\frac{\partial}{\partial\vec{r}}\Phi(\vec{r} - \vec{r}_i)\right] = -\sum_i\vec{F}_{i(F)} \qquad (3.5)$$

The relaxation kernel (2.25) is written as:

$$\hat{K}(\tau) = \frac{\partial}{\partial\vec{p}}\int d\Gamma_F\,\vec{F}e^{\tau\hat{L}_o}\left(-\frac{1}{mkT}\sum_i\vec{F}_{i(F)}\vec{P}_i + \vec{F}\frac{\partial}{\partial\vec{P}}\right)\rho_{OF} \qquad (3.6)$$

as far as the $\frac{\partial}{\partial\vec{p}}$ contribution from the left-hand factor of $\hat{L}_{int}$ disappears in the integration on the thermostat phase space, and the $\frac{\partial}{\partial\vec{p}_i}$ derivative in the right-hand factor of $\hat{L}_{int}$ acts only on the equilibrium function ρ_{OF}. Now we take into account that operators $\hat{L}_F$ and $\hat{L}_S$ commutate, and

$$e^{\tau\hat{L}_S}\varphi(\vec{r}) = \varphi(\vec{r} - \tau\frac{\vec{p}}{M}) \equiv \varphi(\tau) \qquad (3.7)$$

(shift operator). We designate:

$$e^{\tau\hat{L}_F}\varphi\left(\left\{\vec{r}_i,\vec{p}_i\right\}\right)\equiv\varphi(\tau) \tag{3.8}$$

Using the equality:

$$-\frac{\dot{i}}{M}\sum_i\vec{F}_{i(F)}\vec{p}_i=\dot{H}_{int}+\frac{1}{M}\vec{F}\cdot\vec{p},\quad\left(\dot{H}_{int}\equiv\frac{d}{dt}H_{int}\right) \tag{3.9}$$

we transform (3.6) as:

$$\hat{K}(\tau)=\frac{\partial}{\partial\vec{p}}\int d\Gamma_F\vec{F}\left(\frac{1}{\kappa T}\dot{H}_{int}^{(\tau)}(\tau)+\vec{F}^{(\tau)}(\tau)\right)\left(\frac{\vec{p}}{M\kappa T}+\frac{\partial}{\partial\vec{p}}\right)\rho_{OF}\,e^{\tau\hat{L}_S} \tag{3.10}$$

(as far as $\hat{L}_F\rho_{OF}=0$). We introduce the correlation functions:

$$\int d\Gamma_F\vec{F}\otimes\vec{F}^{(\tau)}(\tau)\rho_{OF}\equiv\left\langle\vec{F}\otimes\vec{F}^{(\tau)}(\tau)\right\rangle=\frac{1}{3}\vec{\vec{I}}\left\langle\vec{F}\vec{F}^{(\tau)}(\tau)\right\rangle \tag{3.11}$$

where ⊗ is the tensor multiplication symbol, $\vec{\vec{I}}$ the unit tensor. Further, we take into consideration that:

$$\int d\Gamma_F\vec{F}\dot{H}^{(\tau)}(\tau)\rho_{OF}=\left\langle\vec{F}\dot{H}^{(\tau)}(\tau)\right\rangle=0 \tag{3.12}$$

(in consequence of isotropicity of the thermostat). We designate

$$\gamma^{(\tau)}(\tau)=\frac{1}{3kT}\left\langle\vec{F}\cdot\vec{F}^{(\tau)}(\tau)\right\rangle \tag{3.13}$$

and we write (3.11) as:

$$\hat{K}(\tau)=\frac{\partial}{\partial\vec{p}}\gamma^{(\tau)}(\tau)\left(\frac{1}{M}\vec{p}+kT\frac{\partial}{\partial\vec{p}}\right)e^{\tau\hat{L}_S} \tag{3.14}$$

Substituting (3.15) in (2.22) we obtain the function $e^{\tau\hat{L}_S}\sigma(t-\tau)=\sigma(t)$ (accurate to members of second order on interactions). Further, in the roughened temporary scale τ_o<< t and, therefore, $\gamma^{(\tau)}(\tau)\approx 0$ at $\tau>\tau_o$. Hence:

$$\int_0^t d\tau\gamma^{(\tau)}(\tau)\cong\int_0^\infty d\tau\gamma^{(\tau)}(\tau)\equiv\gamma(\vec{p}) \tag{3.15}$$

Now the equation (2.22) may be written as:

$$\frac{\partial\sigma}{\partial t}+\frac{1}{M}\vec{p}\frac{\partial\sigma}{\partial\vec{r}}=\frac{\partial}{\partial\vec{p}}\left\{\gamma(\vec{p})\left(\frac{1}{M}\vec{p}\sigma+kT\frac{\partial\sigma}{\partial\vec{p}}\right)\right\} \tag{3.16}$$

– the Fokker-Planck equation in the phase space of the Brownian particle.

Our formal conclusion relied on the approximation of weak interaction and the disparity τ_o<< T_o, where T_o is the characteristic time of relaxation of the distribution σ(t) (it provides the consequence of disparities τ_o << t ≤ T_o, i.e. the opportunity of introduction of the roughened temporary scale). Actually these conditions are not independent, since T_o is determined by the intensity of the interaction. For reasons of dimension and determinations (3.13 - 3.15), it follows:

$$T_o\sim\left(M/\gamma\right)\sim\left(MkT/\tau_o\left\langle|\vec{F}|\right\rangle\right) \tag{3.17}$$

where $\left\langle|\vec{F}|\right\rangle\equiv\sqrt{\left\langle\vec{F}^2\right\rangle}$. This value may be evaluated as $\left\langle|\Delta\vec{p}|\right\rangle=\tau_{int}\left\langle|\vec{F}|\right\rangle$, where $\left\langle|\Delta\vec{p}|\right\rangle$ is the change of Brownian particle momentum for the interaction time τ_{int}. Because of conservation law validity for pair interactions, $\left\langle|\Delta\vec{p}|\right\rangle$ has the same order of pulse as that of the thermostat particles, $\left\langle|\Delta\vec{p}|\right\rangle\sim\sqrt{mkT}$. Then from (3.17) we obtain that the condition τ_o<< T_o is equivalent to the condition $\tau_o\ll\sqrt{\frac{M}{m}}\tau_{int}$. As for the liquid, $\tau_o\sim\tau_{int}$, we reach the usual condition M >> m.

This is the physical justification of the weak interaction approximation, and, besides that, it permits the making of just one more simplification. The dependence $\gamma(\vec{p})$ arises owing to the dependence $\gamma(\tau)$ because of the temporary shift $\vec{r} \Rightarrow \vec{r} - \left(\vec{p}/M\right)\tau$, as seen from (3.7). But $\vec{F}$ depends on $\vec{r}$ only by means of $\vec{r} - \vec{r}_i$, and in consequence of thermostat dynamics the total shift is

$$\vec{r} - \vec{r}_i \Rightarrow \vec{r} - \vec{r}_i - \tau\left(\frac{\vec{p}}{M} - \frac{\vec{p}_i}{m}\right) - \Delta\vec{r}_i(\tau)$$

where the contribution $\Delta\vec{r}_i(\tau)$ is stipulated by the potential U. The order of pulses $\vec{p}$ and $\vec{p}_1$ is on the average identical, therefore, at $M >> m$ it is possible to neglect shift $\tau\vec{p}/M$, i.e. to assign $\varphi^{(\tau)}(\tau) \simeq \varphi(\tau)$, and then it does not depend on $\vec{p}$, i.e., we obtain the Kirkwood formula /8/ for the friction coefficient:

$$\gamma = \frac{1}{3kT}\int_0^\infty d\tau\left\langle \vec{F} \cdot \vec{F}(\tau)\right\rangle \tag{3.18}$$

and after transition to velocities $\vec{V} = \vec{P}/M$, equation (3.16) assumes the standard form:

$$\frac{\partial\sigma}{\partial t} + \vec{V}\frac{\partial\sigma}{\partial\vec{r}} = \frac{\gamma}{M}\frac{\partial}{\partial\vec{V}}\left(\vec{V}\sigma + \frac{kT}{M}\frac{\partial\sigma}{\partial\vec{V}}\right) \tag{3.19}$$

as it was recorded for the first time by Chandrashekhar /9/.

The Brownian model, as the universal model of relaxation at a weak interaction of a system with a thermostat, is further used in collective variables kinetics, and in this case we are oriented on the Fokker-Planck equation for a Brownian oscillator:

$$H_S = \frac{1}{2M}\vec{P}^2 + \frac{M\omega^2}{2}\vec{r}^2, \hat{L}_S = M\omega^2\vec{r}\frac{\partial}{\partial\vec{P}} - \frac{1}{M}\vec{P}\frac{\partial}{\partial\vec{r}} \tag{3.20}$$

Revising the conclusion, we receive, instead of (3.19), the equation:

$$\frac{\partial\sigma}{\partial t} + \vec{V}\frac{\partial\sigma}{\partial\vec{r}} - \omega^2\vec{r}\frac{\partial\sigma}{\partial v} = \frac{\gamma}{M}\frac{\partial}{\partial\vec{V}}\left(\vec{V}\sigma + \frac{kT}{M}\frac{\partial\sigma}{\partial\vec{V}}\right) \tag{3.21}$$

which is known as Kramer's equation /10/ (since when we built the right-hand part of (3.15) the operator $\hat{L}_S$ was not used in its explicit form; this fact expresses the universality of the Brownian model). The only change arises in evaluation of the shift:

$$\vec{r} \Rightarrow \vec{r} - (\vec{p}/M\omega)\sin w\tau$$

But on averaging, only the interval $\tau<\tau_o$, and if $\omega << \tau_o^{-1}$ (which usually is valid), then $\sin\tau \sim w\tau$, and again $\vec{r} \Rightarrow \vec{r} - (p/M)\tau$.

4. COLLECTIVE COORDINATES DYNAMICS AND KINETIC EQUATION

We write the Hamiltonian of a classical liquid in the form:

$$H = \frac{1}{2}\sum_{j=1}^{N} M\vec{V}_j^2 + \frac{1}{2}\sum\nolimits_{j\neq\ell}^{N}\sum U\left(\vec{R}_j - \vec{R}_\ell\right)\left(\vec{V}_j = \dot{\vec{R}}_j\right) \tag{4.1}$$

The j-ion equation of motion has the form:

$$M\dot{\vec{V}}_j = -\nabla_{\vec{R}j}\sum_{\ell=1}^{N}{}^{(\neq j)}U(\vec{R}_j - \vec{R}_\ell) \tag{4.2}$$

Introducing a Fourier image of a pair interionic potential:

$$U(\vec{R}) = \frac{1}{N}\sum_{k}\tilde{U}(\vec{k})e^{ikR}$$

$$U(\vec{k}) = \frac{1}{\Omega}\int d^3\vec{R}\, U(\vec{R})e^{-i\vec{k}\vec{R}}, (\Omega_o = \Omega/N) \tag{4.3}$$

where Ω - the volume of the system, we obtain:

$$M\dot{\vec{V}}_j = -\sum_{k} M\dot{\vec{V}}_j = -i\sum_{\vec{k}}\vec{k}\tilde{U}(\vec{k})e^{i\vec{k}\vec{R}}\rho(\vec{k}) \tag{4.4}$$

if (1.3) is taken into account. From it and from (4.4) we find:

$$\ddot{\rho}(\vec{k}) = -\frac{1}{N}\sum_{j}(\vec{k}\vec{V}_j)^2e^{-i\vec{k}\vec{R}_j} -$$

$$-\frac{1}{M}\sum_{\vec{k}'}(\vec{k}\vec{k}')\tilde{U}(\vec{k}')\rho(\vec{k}-\vec{k}')\rho(\vec{k}') \tag{4.5}$$

Applying the identity

$$(\vec{k}\vec{V}_j)^2 = \left[(\vec{k}\vec{V}_j)^2 - \left\langle (kV_j)^2 \right\rangle\right] + \left\langle (\vec{k}\vec{V}_j) \right\rangle \equiv$$
$$\equiv k^2\vec{V}^2 + \left[(\vec{k}\vec{V}_j)^2 - \left\langle (\vec{k}\vec{V}_j)^2 \right\rangle\right]$$

where $\langle ... \rangle$ - equilibrium averagte and $\vec{V}^2 = {}^{kT}\!/\!_{M}$; we write (4.5) as:

$$\ddot{\rho}(k) + k^2\vec{V}^2\rho(k) = \frac{1}{M}\sum_{\vec{k}'}(\vec{k},\vec{k}')\tilde{U}(\vec{k}')\rho(\vec{k}-\vec{k}')\rho(\vec{k}') -$$
$$-\frac{1}{N}\sum_{j}\left[(\vec{k}\vec{V}_j)^2 - \left\langle (\vec{k}\vec{V}_j)^2 \right\rangle\right]e^{-i\vec{k}\vec{R}_j} \tag{4.6}$$

Extracting the term of $\vec{k} - \vec{k}'$ from the sum $\sum_{\vec{k}'}$ (taking into account ρ (0) = 1) and using the coordinates (1.4), we finally obtain:

$$\ddot{X}_{\vec{k}} + \omega_o^2(k)X_{\vec{k}} = F_{\vec{k}} + f_{\vec{k}} \tag{4.7}$$

$$\omega_o^2(k) = k^2(\vec{V}^2 + \tilde{U}(\vec{k})/M) \tag{4.8}$$

$$F_{\vec{k}} = -\frac{1}{M}\sum_{\vec{k}'}{}^{(\neq\vec{k})}(\vec{k}\vec{k}')\tilde{U}(\vec{k}')X_{\vec{k}-\vec{k}'}X_{\vec{k}'} \tag{4.9}$$

$$f_{\vec{k}} = \frac{1}{N}\sum_{j}\left[(\vec{k}\vec{V}_j)^2 - \left\langle (\vec{k}\vec{V}_j)^2 \right\rangle\right]e^{-i\vec{k}\vec{R}_j} \tag{4.10}$$

Thus, the collective coordinate $X_{\vec{k}}$ is the oscillator with a natural frequency $\omega_o(k)$, which interacts with other ones (by means of force $F_{\vec{k}}$) and with single-particle excitations (by means of force $f_{\vec{k}}$). In other words, the collective variables system is not closed, but we shall see that it is closed "on the average" in the sense that on calculation of the correlator (1.5) it is possible to neglect the contribution of single-particle excitations.

We study the equilibrium liquid, in which the $\vec{k}$-mode is excited (by the fluctuation way) and behaves as a Brownian mode in a thermostat of all other collective coordinates and single-particle variables. Respectively, in the Hamiltonian, we assume:

$$H_F \equiv H_F(X) + H_F(\Pi),\ H_{int} \equiv H_{int}(X) + H_{int}(\Pi) \tag{4.11}$$

where the index X relates to the collective coordinates, and the index Π to single-particle excitations. Then:

$$\hat{L}_{F(X)} = \sum_{\vec{k}'}{}^{(\neq\vec{k})}\left(\omega_{k'}^2 X_{\vec{k}'}\frac{\partial}{\partial P_{\vec{k}'}} - P_{\vec{k}'}\frac{\partial}{\partial X_{\vec{k}'}}\right) \tag{4.12}$$

$$\hat{L}_s = \omega_k^2 X_{\vec{k}}\frac{\partial}{\partial \vec{P}_{\vec{k}}} - P_{\vec{k}}\frac{\partial}{\partial X_{\vec{k}}} \tag{4.13}$$

$$\hat{L}_{int} = -\sum_{\vec{k}'}{}^{(\neq\vec{k})}F_{\vec{k}}(X)\frac{\partial}{\partial \vec{P}_{\vec{k}'}} - F_{\vec{k}}\frac{\partial}{\partial P_{\vec{k}}} - f_{\vec{k}}\frac{\partial}{\partial P_{\vec{k}}} \tag{4.14}$$

where:

$$F_{\vec{k}'}(X) \equiv -\frac{1}{M}(\vec{k}\vec{k}')\tilde{U}(\vec{k}')X_{\vec{k}}X_{\vec{k}-\vec{k}'} \tag{4.15}$$

and $f_{\vec{k}} \equiv f_{\vec{k}}(\Pi)$. Further, $P_{\vec{k}} = \dot{X}_{\vec{k}}$. The explicit form of the operator $\hat{L}_{F(\Pi)}$ is not important. By complete analogy with (2.24), accounting for (4.13), we now obtain the kinetic equation for the Brownian $\vec{k}$-mode:

$$\frac{\partial\sigma}{\partial t} + P_{\vec{k}}\frac{\partial\sigma}{\partial X_{\vec{k}}} - \omega_o k^2 X_{\vec{k}}\frac{\partial\sigma}{\partial P_{\vec{k}}} = \int_o^t d\tau\hat{k}(\tau)\sigma(t-\tau) \tag{4.16}$$

where

$$\hat{K}(\tau) = \frac{\partial}{\partial P_{\vec{k}}}\int d\Gamma(x)\int d\Gamma(\pi)(F_{\vec{k}}^* + f_{\vec{k}}^*)e^{\tau(\hat{L}F(x)+\hat{L}F(\pi)+\hat{L}_s)}x$$
$$x\left(-\frac{A_{\vec{k}}}{kT}\sum_{\vec{k}'}{}^{(\neq\vec{k})}F_{\vec{k}'}(X)P_{\vec{k}'} + (F_{\vec{k}} + f_{\vec{k}})\right)\rho_{OF} \tag{4.17}$$

and the measured constant $A_{\vec{k}}$ is defined below (it occurs because the physical measure of $X_{\vec{k}}$ does not coincide with the spatial measure). As far as

$$H_{int}(X)=\sum_{\bar k'}^{(\neq k)}\frac{1}{M}(\bar k\bar k')\tilde{U}(\bar k')X_{\bar k}X_{\bar k-\bar k'}X_{\bar k'} \qquad (4.18)$$

then

$$\sum_{\bar k'}^{(\neq \bar k)}F_{\bar k'}(X)P_{\bar k'}=\dot{H}_{int}-F_{\bar k}P_{\bar k}-X_{\bar k}\varphi_{\bar k} \qquad (4.19)$$

where

$$\varphi_{\bar k}=-\sum_{\bar k'}^{(\neq \bar k)}\frac{1}{M}(\bar k\bar k')X_{\bar k'}P_{\bar k-\bar k'}\bar{U}(\bar k') \qquad (4.20)$$

Taking into account the fact that the operators $\hat{L}_{F(x)}$, $\hat{L}_{F(\pi)}$, $\hat{L}_s$ are mutually commutable, ρ_{OF} is $\hat{L}_F$-invariant, $F_{\bar k}$, $f_{\bar k}$, $\varphi_{\bar k}$ are independent of Brownian mode variables, we define the correlators:

$$\int d\Gamma F_{\bar k}^{*}F_{\bar k}(\tau)\rho_{OF}\equiv\left\langle F_{\bar k}^{*}F_{\bar k}(\tau)\right\rangle \qquad (4.21)$$

$$\int d\Gamma F_{\bar k}^{*}\varphi_{\bar k}(\tau)\rho_{OF}\equiv\left\langle F_{\bar k}^{*}\varphi_{\bar k}(\tau)\right\rangle \qquad (4.22)$$

$$\int d\Gamma f_{\bar k}^{*}f_{\bar k}(\tau)\rho_{OF}\equiv\left\langle f_{\bar k}^{*}f_{\bar k}(\tau)\right\rangle \qquad (4.23)$$

$$\int d\Gamma F_{\bar k}^{*}\dot{H}_{int}^{(\tau)}(\tau)\rho_{OF}\equiv\left\langle F_{\bar k}^{*}\dot{H}_{int}^{(\tau)}(\tau)\right\rangle=0 \qquad (4.24)$$

(the latter equals zero because of the isotropy in the $\bar k$-space of the macro-isotropic liquid) and taking into account that at equilibrium cross averages equal zero, we transform (4.17) as:

$$\dot{K}(\tau)=\frac{\partial}{\partial P_{\bar k}}\left(X_{\bar k}^{(\tau)}\frac{A\bar k}{kT}\left\langle F_{\bar k}^{*}\varphi_{\bar k}(\tau)\right\rangle\right)\ell^{\tau\hat{L}_s}+\frac{A\bar k}{kT}\left(\left\langle F_{\bar k}^{*}F_{\bar k}(\tau)\right\rangle\right)+$$

$$+\left\langle f_{\bar k}f_{\bar k}(\tau)\right\rangle\frac{\partial}{\partial P_{\bar k}}\left(P_{\bar k}+\frac{kT}{A\bar k}\frac{\partial}{\partial P_{\bar k}}\right)\ell^{\tau\hat{L}_s} \qquad (4.25)$$

We introduce the frequency renormalization:

$$\delta\omega_{\bar k}^{2}=\frac{A\bar k}{kT}\int_{o}^{\infty}\left\langle F_{\bar k}^{*}\varphi_{\bar k}(\tau)\right\rangle d\tau \qquad (4.26)$$

and friction coefficients:

$$\gamma_{\bar k}(X)=\frac{A_{\bar k}}{kT}\int_{o}^{\infty}d\tau\left\langle F_{\bar k}^{*}F_{\bar k}(\tau)\right\rangle \qquad (4.27)$$

$$\gamma_{\bar k}(\pi)=\frac{A_{\bar k}}{kT}\int_{o}^{\infty}d\tau\left\langle f_{\bar k}^{*}f_{\bar k}(\tau)\right\rangle \qquad (4.28)$$

$$\gamma_{\bar k}=\gamma_{\bar k}(X)+\gamma_{\bar k}(\pi) \qquad (4.29)$$

Then, in the same approximation as in §3, from (4.25) and (4.16), we finally obtain:

$$\frac{\partial\sigma}{\partial t}+\rho_{\bar k}\frac{\partial\sigma}{\partial X_{\bar k}}-\omega_{\bar k}^{2}X_{\bar k}\frac{\partial\sigma}{\partial\rho_{\bar k}}=\gamma_{\bar k}\frac{\partial\sigma}{\partial\rho_{\bar k}}\left(\rho_{\bar k}\sigma+\frac{kT}{A_{\bar k}}\frac{\partial\sigma}{\partial\rho_{\bar k}}\right) \qquad (4.30)$$

where

$$\omega_k^2=\omega_{ok}^2+\delta\omega^2 \qquad (4.31)$$

5. Coefficient of Friction $\gamma_{\bar k}(\pi)$

Let us consider the correlator

$$K_{(\pi)}(\tau)=\left\langle f_{\bar k}^{*}f_{\bar k}(\tau)\right\rangle \qquad (5.1)$$

From definition (4.10) and the statistical independence of the single-particle coordinates and velocities at equilibrium, we obtain:

$$K_{\pi}(\tau)=\frac{1}{N^2}\sum^{N}\sum_{j\neq\ell=1}\left\langle\left[(\bar k\bar V_j)^2-<(\bar k\bar V_j)^2>\right]\right\rangle x$$

$$\left[(\bar k\bar V_e)^2-\left\langle(\bar k\bar V_{\bar e})^2\right\rangle\right]x\left\langle e^{i\bar k(\bar R_j-\bar R_e(\tau))}\right\rangle \qquad (5.2)$$

According to Brownian model ideology, we shall treat single-particle velocities $\bar V_j(\tau)$ as a stationary Gaussian process. Then, as known /11/, the correlation moments of higher orders are reduced to the second order moments linear combination. In particular,

$$\left\langle V_{j\alpha}V_{j\beta}V_{\ell\gamma}(\tau)V_{\ell\delta}(\tau)\right\rangle=\left\langle V_{j\alpha}V_{\ell\gamma}(\tau)\right\rangle\left\langle V_{j\beta}V_{\ell\gamma}(\tau)\right\rangle+ \tag{5.3}$$

$$+\left\langle V_{j\alpha}V_{\ell\delta}(\tau)\right\rangle\left\langle V_{j\beta}V_{\ell\gamma}(\tau)\right\rangle+\left\langle V_{j\alpha}V_{j\beta}\right\rangle\left\langle V_{\ell\gamma}V_{\ell\delta}\right\rangle,$$

$(\alpha, \beta, \gamma, \gamma = x, y, z)$

We introduce the correlator:

$$K_{j\ell}^{(\alpha\beta)}(\tau)=\left\langle V_{i\alpha}V_{\ell\beta}(\tau)\right\rangle \tag{5.4}$$

and we take into consideration that in consequence of isotropy of the liquid

$$K_{i\ell}^{(\alpha\beta)}(\tau)=\delta_{\alpha\beta}K_{j\ell}^{\alpha\alpha}(\tau)=\frac{1}{3}\delta_{\alpha\beta}\left\langle\bar{V}_j\bar{V}_\ell(\tau)\right\rangle\equiv \tag{5.5}$$

$$\equiv\frac{1}{3}\delta_{\alpha\beta}K_{j\ell}(\tau)$$

Then, using (5.3), we transform (5.2) into the form:

$$K_{(\pi)}(\tau)=\frac{1}{N^2}\sum_{j=1}^{N}\frac{2}{9}k^4K_{jj}^2(\tau)\left\langle \ell^{i\vec{k}(\vec{R}_j-\vec{R}_j(\tau))}\right\rangle+ \tag{5.6}$$

$$+\frac{1}{N^2}\sum\sum_{j\neq\ell=1}^{N}\frac{2}{9}k^4K_{j\ell}^2(\tau)\left\langle \ell^{i\vec{k}(\vec{R}_j-\vec{R}_\ell(\tau))}\right\rangle$$

In a macro-homogeneous system, the velocity autocorrelation function $K_{ii}(\tau)$ does not depend on the number of particles, i.e. it is possible to assume $K_{jj}(\tau) = K_{11}(\tau)$, and the first term in (5.6) gives:

$$K_{(\pi)}^{(1)}(\tau)=\frac{1}{N}\frac{2}{9}k^4K_{11}{}^2(\tau)\left\langle \ell^{i\bar{k}(\bar{R}_j-\bar{R}_j(\tau))}\right\rangle\to 0 \tag{5.7}$$

(at the thermodynamic limit N → ∞). similarly, the second term in (5.6) transforms as:

$$K_{(\pi)}^{(2)}(\tau)=\frac{2}{9}k^4K_{12}^2(\tau)\left[\left\langle\frac{1}{N^2}\sum_{j=1}^{N}\sum_{\ell=1}^{N}e^{i\vec{k}(\vec{R}_j-\vec{R}_\ell(\tau)}\right\rangle-\right. \tag{5.8}$$

$$\left.-\frac{1}{N^2}\sum_{j=1}^{N}\left\langle e^{i\bar{k}(\bar{R}_j-\bar{R}_j(\tau))}\right\rangle\right]$$

and again the last term in (5.8) disappears at the thermodynamic limit, and the first one includes the factor $\left\langle\rho^*(\bar{k})\rho(k,\tau)\right.$, as results from (1.3). Because of taking into account (1.4) and (1.5):

$$\left\langle\rho^*(k)\rho(\bar{k},\tau),\right\rangle=\frac{1}{N}\left(S(\bar{k},\tau)+3\delta_{\bar{k}\,o}\right) \tag{5.9}$$

From (5.6 - 5.8), we find:

$$K_{(\pi)}(\tau)=\frac{2}{9}k^4K_{12}^2(\tau)\frac{1}{N}S(\bar{k},\tau) \tag{5.10}$$

As far as $K_{12}(O)=\left\langle V_1,V_2\right\rangle=0$, the correlator $K_{12}(\tau)\approx 0$ at all τ, and, in good approximation, $K\pi(\tau) \approx 0$, i.e. and $\gamma k(\pi) = 0$ (as seen from (4.27)). Hence:

$$\gamma_{\bar{k}}\cong\gamma_{\bar{k}}(x)=\frac{A_{\bar{k}}}{kT}\int_0^\infty d\tau\left\langle F_{\bar{k}}^*F_{\bar{k}}(\tau)\right\rangle \tag{5.11}$$

and in kinetics, described by equation (4.30), the collective variables system becomes closed.

Let us now examine the correlator

$$K_{(x)}(\tau)=\left\langle F_{\bar{k}}{}^*F_{\bar{k}(\tau)}\right\rangle \tag{5.12}$$

From definition (4.9) we receive:

$$K_{(x)}(\tau)=\frac{1}{M^2}\sum_{\vec{k}'}{}^{(\neq k)}\sum_{\vec{k}''}{}^{(\neq k)}(\vec{k}\vec{k}')(\vec{k}\vec{k}'')\tilde{U}(\vec{k}')\tilde{U}(\vec{k}'')x \tag{5.13}$$

$$x\left\langle X_{\bar{k}-\bar{k}'}^*,X_{\bar{k}}^*,X_{\bar{k}-\bar{k}'}(\tau)X_{k''}(\tau)\right\rangle$$

Using again the Ansatz like (5.3) for the stationary Gaussian process, and taking into account that, for instance:

$$\left\langle X_{\bar{k}-k'}^*X_{k-k''}(\tau)\right\rangle=\delta_{\bar{k}'\bar{k}''}S(\bar{k}-\bar{k}',\tau)\frac{1}{N}$$

from (5.13), we receive:

$$K_{(x)}(\tau)=\frac{1}{N^2M^2}\sum_{\bar{k}'}\Big[(\bar{k}\bar{k}')^2\tilde{U}^2(\bar{k})+(\bar{k}\bar{k}')(\bar{k},\bar{k}-\bar{k}')x$$

$$x\tilde{U}(\bar{k}')\tilde{U}(\bar{k}-\bar{k}')\Big]S(\bar{k}',\tau)S(\bar{k}-\bar{k}',\tau) \tag{5.14}$$

The measured constant $A_{\bar{k}}$ in (5.11) and (4.30) is determined for the following reasons. The potential energy of the liquid can be expressed by means of collective coordinates as well as $\bar{R}_j$-variables, and both expressions may be compared at the frozen lattice (glass) limit:

$$\frac{1}{2}\sum_{\bar{k}}A_{\bar{k}}\omega_k^2|X_k|^2=\frac{1}{2}\sum\sum_{j\neq\ell=1}^{N}U(|\bar{R}_j-\bar{R}_\ell|) \tag{5.15}$$

The Fourier transformation of the right-hand part gives $\frac{N}{2}\sum_k\tilde{U}(k)|X_{\bar{k}}^2|$. At the frozen lattice limit $\bar{V}^2\to 0,\omega_k^2\to k^2\frac{1}{N}\tilde{U}(\bar{k})$, and from (5.15) we receive $A_{\bar{k}}=MN(\,{}^{1}\!/_{k^2})$. Therefore, (4.30) and (5.11), considering (5.14), finally yield the form:

$$\frac{\partial\sigma}{\partial t}+P_{\bar{k}}\frac{\partial\sigma}{\partial X_{\bar{k}}}-\omega_k^2X_{\bar{k}}\frac{\partial\sigma}{\partial P_{\bar{k}}}=\gamma_k\Big(P_{\bar{k}}+\frac{kT}{MN}K^2\frac{\partial\sigma}{\partial P_{\bar{k}}}\ \Big) \tag{5.16}$$

$$\gamma_{\bar{k}}=\frac{1}{MkT}\frac{1}{k^2}\frac{1}{N}\sum_{\bar{k}'}\Big[(\bar{k}\bar{k}')^2\tilde{U}^2(\bar{k}')+(\bar{k}\bar{k}')(\bar{k},\bar{k}-\bar{k}')\times$$

$$\times\tilde{U}(\bar{k}')\tilde{U}(\bar{k}-\bar{k}')\Big]\int_0^\infty d\tau S(\bar{k}',\tau)S(\bar{k}-\bar{k}',\tau) \tag{5.17}$$

6. Dynamic Structural Factor

The expressions of the correlators of the independent variables in Kramer's equation are well known /12/, and by analogy we write:

$$\Big\langle X_{\bar{k}}^{*}X_{\bar{k}}(\tau)\Big\rangle=\frac{1}{N}S(k,\tau)=\frac{1}{N}S(k)e^{-\gamma_k\tau/2}\times$$

$$\times\left(\cos(\Omega_{\bar{k}},\tau)+\frac{\gamma_k}{2\Omega_{\bar{k}}}\sin(\Omega_{\bar{k}},\tau)\right) \tag{6.1}$$

$$\Big\langle X_{\bar{k}}^{*}P_{\bar{k}}(\tau)\Big\rangle=\frac{1}{N}\Omega_kS(k)e^{-\gamma_k{}^{\tau}\!/_{2}}\left(\begin{array}{l}\sin(\Omega_k,\tau)-\\ -\dfrac{\gamma_k}{2\Omega_{\bar{k}}}\cos(\Omega_k,\tau)\end{array}\right) \tag{6.2}$$

where

$$\Omega_k=\sqrt{\omega_k^2-\gamma_k{}^{4}\!/_{4}} \tag{6.3}$$

It should be borne in mind that $\omega_k{}^2=\omega_{ok}^2+\delta\omega_k^2$, and for the frequency renormalization $\delta\omega_k{}^2$ (4.26) it is possible to obtain:

$$\delta\omega_k{}^2=\frac{1}{MkT}\frac{1}{k^2}\sum_{\bar{k}'}\Big[(\bar{k}\bar{k}')^2\tilde{U}^2(\bar{k}')\int_0^\infty d\tau S(\bar{k}',\tau)$$

$$\Big\langle X_{k-k'}^{*}P_{k-k'}(\tau)\Big\rangle+(\bar{k}\bar{k}')(\bar{k},\bar{k}-\bar{k}')\tilde{U}(\bar{k}')\tilde{U}(|\bar{k}-\bar{k}'|) \tag{6.4}$$

$$\int_0^\infty d\tau S(\bar{k}-\bar{k}',\tau)\Big\langle X_{\bar{k}'}^{*},P_{\bar{k}'}(\tau)\Big\rangle$$

Now (5.17) and (6.1) give the closed self-consistent system of equations to determine the dynamic structural factor. Boltzmann-Maxwell's distribution is the equilibrium solution (5.16) (at the limit t → ∞)

$$\sigma_o(P_{\bar{k}},X_{\bar{k}})=C\cdot\exp\left[-\frac{MN}{2k^2}\frac{|P_{\bar{k}}|^2}{kT}\right]\exp\left[-\frac{MN\omega_{\bar{k}}{}^2}{2K^2}\cdot\frac{|X_{\bar{k}}|^2}{kT}\right] \tag{6.5}$$

From (6.5), it follows:

$$S(k)=N\Big\langle|X_{\bar{k}}|^2\Big\rangle=\frac{kT}{M}\frac{k^2}{\omega_k^2}=\frac{kT}{M}\frac{k^2}{\omega_{ok}^2+\delta\omega_k^2} \tag{6.6}$$

– a useful expression for the static structural factor, as far as even in zero approximation (when $|\delta\omega_k|$ is neglected) the nontrivial connection between S(k) and the pair interaction potential can be received, as seen from (4.8):

$$S_o(k)=\frac{kT}{M}\frac{1}{\bar{V}^2+\frac{1}{M}\tilde{U}(k)} \tag{6.7}$$

To calculate γ_k in the second order, it is enough to replace S'(k,τ) in (5.17) by the undamped expression (i.e. formally assumed $\gamma_k = 0$ in (6.1). Then from (5.17) we receive:

$$\gamma_k = \frac{\pi}{2MkT}\frac{1}{k^2}\frac{1}{N}\sum_{k'}[(\vec{k}\vec{k}')^2\bar{U}^2(\vec{k}') + (\vec{k}\vec{k}')(\vec{k},\vec{k}-\vec{k}')\times \tag{6.8}$$

$$\times\tilde{U}(k')\tilde{U}(|k-k'|]S(k')S(|k-k'|)\delta(\omega_o(k')-\omega_o(|k-k'|))$$

As seen from (4.8), the condition $\omega_o(k') = \omega_o(|k-k'|)$ is equal to $\bar{k}'=|\bar{k}-\bar{k}'|$, and, introducing the angle $\theta = \widehat{\bar{k},\bar{k}'}$, we may write:

$$\delta(\omega_o(k')-\omega_o(|k-k'|)) = \frac{\delta(k'-\dfrac{k}{2\cos\theta})}{2k|\cos\theta|[\bar{V}^2 + \dfrac{1}{M}\tilde{U}(\dfrac{k}{2\cos\theta})} \tag{6.9}$$

Then, proceeding to the integral in (6.8):

$$\sum_{k'} \Rightarrow \frac{\Omega}{(2\pi)^3}\int d\bar{k}' = \frac{\Omega}{(2\pi)^2}\int \bar{k}'^2 d\bar{k}'\int \sin\theta d\theta$$

(where $\Omega = \Omega_o N$), we receive

$$\gamma_k = \frac{\Omega_o}{32\pi}\frac{k}{MKT}\int_{k/2}^{\infty} dq\cdot q\tilde{U}^2(q)S'^2(q)\frac{1}{\bar{V}^2 + \dfrac{1}{M}\tilde{U}(q)} \tag{6.10}$$

This expression can be further simplified by using the substitution S(q)→S$_o$(q), according to (6.7) (at the accuracy of the kinetic equation. Then, finally:

$$\gamma_k = \frac{\Omega_o}{32\pi}\frac{kT}{M^3}k\int_{k/2}^{\infty} dq\frac{q\tilde{U}^2(q)}{(\bar{V}^2 + \dfrac{1}{M}\tilde{U}(q))^3} \tag{6.11}$$

Estimation of the expression (6.4), which includes cross correlators $\left\langle X_q^{*}P_q(\tau)\right\rangle$, shows that the frequency shift $\delta\omega_k^2$ is small and can be neglected. Then from (6.1) we receive:

$$S(k,\tau) = S(k)e^{-\frac{1}{2}\gamma_k\tau}\Big[\cos(\Omega_{ok}\tau) + \frac{\gamma_k}{2\Omega_{ok}}\sin(\Omega_{ok}\tau) \tag{6.12}$$

where

$$\Omega_{ok} = \sqrt{\omega_o^2(k) - \frac{1}{4}\gamma_k^2} \tag{6.13}$$

Thus, a closed expression is received for the dynamic structural factor of the liquid; to calculate it from the formulas (6.11-6.13) we need to know only the Fourier image of the pair interaction potential $\tilde{U}(q)$.

Usually the experiments measure not the factor itself, but its Fourier time-image:

$$S(k,\omega) = \int_0^{\infty} d\tau S(k,\tau)\cos(\omega\tau) \tag{6.14}$$

From (6.12) we find

$$S(k,\omega) = \frac{1}{4}\frac{S(k)\gamma_k}{\Omega_{ok}^2}\left[\frac{2+\dfrac{\omega}{\Omega_{ok}}}{(1+\dfrac{\omega}{\Omega_{ok}})^2+\Gamma_k^2} + \frac{2-\dfrac{\omega}{\Omega_{ok}}}{(1-\dfrac{\omega}{\Omega_{ok}})^2+\Gamma_k^2}\right. \tag{6.15}$$

where

$$\Gamma_k = \gamma_k/2\Omega_{ok}$$

As the function of frequency, S(k,ω) has the maximum at

$$\omega_{max}(k) = \sqrt{\Omega_{ok}^2 - \frac{\gamma_k^2}{4}} = \sqrt{\omega_o^2(k) - \frac{\gamma_k^2}{2}} \tag{6.17}$$

and the scheme of S(k,ω) is shown in Fig. 1 as a function of $u=\omega/\Omega_{ok}$ for different values of Γ.

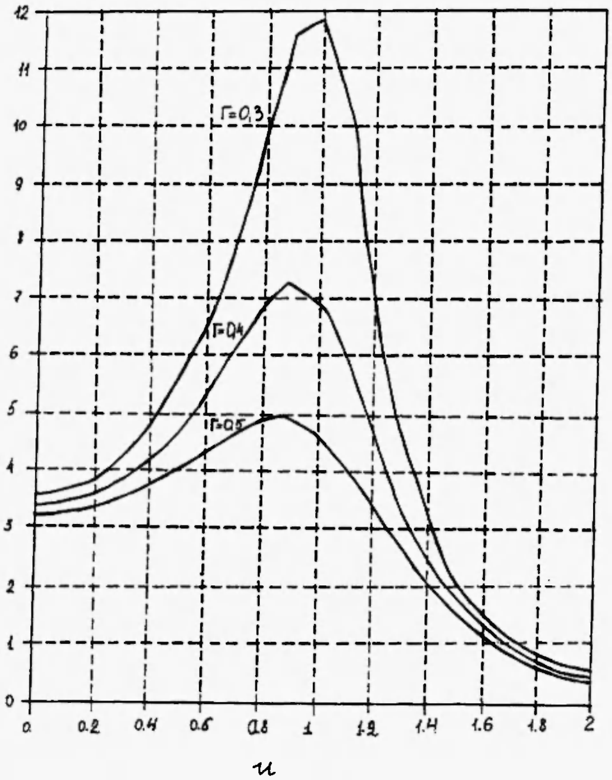

Fig. 1: Dynamic structural factor S versus $U = \omega / \Omega_{ck}$ for different values of Γ.

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