CALCULATIONS OF ATOMIC DYNAMICS IN SIMPLE LIQUID METALS

S. Dalgic[*], M. Colakogullari, S. S. Dalgic

Department of Physics, Trakya University, 22030, Edirne, Turkey

We present several dynamical properties of liquid Li, Rb, and Cs near their melting points. They have been evaluated within the framework of the mode-coupling theory, using a self-consistent scheme that uses as input data only the static structure functions and the interatomic pair potantials of the simple liquid metals. In this work we have used the interatomic pair potential which is derived from second order perturbation theory with Fiolhais electron-ion pseudopotential. We carried out theoretical results to compute single-particle and collective time-dependent properties of liquid metals, and thereby to calculate their self diffusion constants. We have discussed our results in comparison with both experiment and molecular dynamics simulation.

1. Introduction

Together with rare-gas fluids, molten alkali metals have always been considered as paradigms of the behaviour shown by the so called 'simple liquids' [1,2]. In the last decades, the appearance of new accurate data for the time-dependent properties of these systems has led to a renewed interest and to the possibility of more stringent tests for our understanding of the dynamics of the liquid state. On the experimental side, neutron-scattering experiments have been performed in liquid lithium [3,4], liquid rubidium [5] and liquid caesium [6]. A neutral consequence of all this activity has been the appearance of the several simulations [7-9] and theoretical [10-12] studies near the melting points.

From a purely theoretical point of view, one can take advantage of the progress achieved in the 1980's in the development of non-phenomenological approaches for liquid-state dynamics [13]. An important result in this respect has been the recognition [14] of two different kinds of processes ruling the decay channel determined by correlations, namely a fast decay channel determined by 'binary' collisional events and an additional long-lasting mechanism. They have associated with correlated collisions and due to the couplings of the dynamical variable of interest with the slow 'modes' present in the fluid. It is so-called mode-coupling decay channels. A simplified version of these theories has recently been developed, with quite satisfactory results for the leading transport properties such as diffusion and shear viscosity coefficients as well as for several aspects of the single-particle dynamics near the melting point [15]. It was quite important to notice that the decay of several time-dependent properties could be explained by the interplay of two different dynamical processes. The first one, which leads to a rapid initial decay is due to the effects of fast uncorrelated short range interactions (collisional effects) which can be broadly identified with binary collisions. The second processes which usually leads to a long-time tail can be attributed to the non-linear couplings of the dynamic property of interest with slowly varying collective variables (modes) as for instance density fluctuations, currents etc., and it is referred to as a mode-coupling processes.

Within the mode-coupling theory both single particle and collective dynamical magnitudes are closely interwoven. Therefore, corresponding analytical expressions should be solved self-consistently. In fact, we are not aware of any self-consistent calculations performed either within the mode-coupling theory or a simplified version thereof. For example, the intermediate scattering function has been evaluated either from the viscoeleastic model [16], or from molecular dynamic

---

[*] Corresponding author: dseyfe@yahoo.co.uk

(MD) simulations [17]. Theoretical calculations, using the variational modified hypernetted chain (VMHNC) theory of liquids [18-21], as well as MD simulations have shown that a good description all the equilibrium properties of some liquid metals can be obtained by using an interatomic pair potentials.

This paper is organized as follows. In Section 2, we describe the theory used for the calculation of the dynamic properties of the systems. We propose a new self-consistent scheme for describing the self-diffusion process. Single-particle dynamical properties such as the velocity autocorrelation functions and the self-intermediate scattering functions are discussed in the same section. In Section 3, we present the results obtained when this theory is applied to simple liquid metals at thermodynamic conditions near the melting points. Finally, Section 4 summarizes the main results of the work along with a few concluding remarks.

2. Theory

The transport coefficients of interest in the dynamics of dense fluids can be obtained via Green-Kubo relations where the coefficient is given as the time integral of a corresponding time correlation function [22,23]. Their Green-Kubo integrand is velocity autocorrelation function. The self-diffusion coefficient of a one component liquid can be expressed by an Einstein expression

$$D = \lim_{r \to \infty} \frac{\delta r^2(t)}{6t} \tag{1}$$

where with defined the mean square displacement of a tagged particle in the liquid. Second expression of the self-diffusion coefficient is Green-Kubo relation

$$D = \frac{k_B t}{m} \int_0^\infty Z(t) dt \tag{2}$$

where with defined the normalized velocity autocorrelation function and k_B is the Boltzmann constant, T denotes the temperature and m the mass of the particles. These two functions are related to each other by

$$\delta r^2(t) = \frac{6k_B t}{m} \int_0^t (t - \tau) Z(\tau) d\tau. \tag{3}$$

The memory function of the normalized velocity autocorrelation function, $K(t)$, is defined by the following Volterra-type equation,

$$\dot{Z}(t) = -\int_0^t K(t - t') Z(t') dt' \tag{4}$$

where the dot means time derivative of the normalized velocity autocorrelation function.

The memory function may be split into two contributions [13,14],

$$K(t) = K_B(t) + K_{MC}(t) \tag{5}$$

which represent two distinct dynamical regimes in the atomic dynamic of a liquid. The first term comprises all the fast decay channels. It is supposed to represent the effect of a binary collision between a tagged particle and another one from its environment whereas the second term, the mode-coupling contribution, incorporates the contribution from the collective processes associated with multiple collisions.

At very short times the memory function is well described by $K_B(t)$ only; moreover both $K(t)$ and $K_B(t)$ have the same initial value (Ω_0^2) and initial time decay (τ_D)

$$K(0) = K_B(0) = \Omega_0^2 \equiv \frac{\rho}{3m} \int \nabla^2 \phi(r) g(r) dr \tag{6}$$

and

$$\tau_D = \left[\frac{|\ddot{K}(0)|}{2K(0)}\right]^{-1/2}$$ (7)

where Ω_0 is the Einstein frequency which, as shown in equation (6), can be written in terms of the interatomic pair potential, $\phi(r)$, and the pair distribution function, $g(r)$, of the liquid with number density ρ. The second time derivative of $K(t)$ at $t = 0$ is given by

$$\ddot{K}(0) = -\frac{2\rho}{m^2}\int d\vec{r}\left\{\nabla_r\left[\frac{z\phi'(r)}{r}\right]\right\}^2 g(r)$$
$$-\left(\frac{\rho}{m}\right)^2\int d\vec{r}\int d\vec{r}'\vec{\nabla}_r\left[\frac{z\phi'(r)}{r}\right]\vec{\nabla}_{r'}\left[\frac{z'\phi'(r)}{r'}\right]\times\left(g^{(3)}(\vec{r},\vec{r}')g(r)g(r')\right)$$ (8)

where ϕ' denotes the derivates of the potential with respect to its argument. The contribution to τ_D arising from the three-body distribution function can be computed rather accurately by using the superposition approximation.

As the detailed features of the binary dynamics of systems with continuous potentials are rather poorly known, we resort to a semi-phenomenological approximation by writing [16]

$$K_B(t) = \Omega_0^2 \sech^2(t/\tau_D)$$ (9)

which besides of incorporating to correct short time behaviour, also allows the computation of $K_B(t)$ from the static structural function only.

The inclusion of a slowly decaying time tail in memory function is known to be an essential ingredient for the correct description of the dynamics of a tagged particle in a fluid [24]. In principle, coupling to several modes, should be considered such as density-density coupling, density-longitudinal current coupling and density transversal current coupling but for the density/temperature range considered in this work the most important contribution arises from density-density coupling. Restricting the mode-coupling component to the density-density coupling term [25]

$$K_{MC}(t) = \frac{\rho k_B T}{24\pi^3 m}\int d\vec{k}\, k^2\, c^2(k)[F_s(k,t)F(k,t) - F_{sB}(k,t)F_B(k,t)]$$ (10)

Here $c(k)$ denotes the direct correlation function of the liquid. $F(k,t)$ and $F_s(k,t)$ are the intermediate scattering function and its self part, whereas $F_B(k,t)$ $F_{sB}(k,t)$ denote the binary part of $F(k,t)$ and $F_s(k,t)$ respectively.

The binary part of the self intermediate scattering function as its value for free particles and its self part are given by

$$F_{sB}(k,t) = F_0(k,t) \equiv \exp\left[-\frac{k_B T}{2m}k^2 t^2\right]$$ (11)

$$F_B(k,t) = \frac{F_0(k,t)}{F_s(k,t)}F(k,t)$$ (12)

where $F_{sB}(k,t) = F_0(k,t)$. It was shown that this new equation leads to very small changes in the $K(t)$ of liquid Rb as compared with the previous one [14,25]. The final expression for the mode-coupling part of the memory function of the normalized velocity autocorrelation function then becomes

$$K_{MC}(t) = \frac{\rho k_B T}{24\pi^3 m}\int d\vec{k}\, k^2\, c^2(k)\left[F_s(k,t) - \frac{F_0^2(k,t)}{F_s(k,t)}\right]F(k,t)$$ (13)

As already mentioned, Ballucani *et.al.* [15] have calculated the dynamical properties of liquid alkali metals by using, basically the same coupling term as given in equation (13). For liquid lithium near melting we have recently obtained an overall good agreement when comparing the results of the viscoelastic model with MD simulations [26]. Finally, in the case of $F_s(k,t)$ we have used the gaussian approximation

$$F_s(k,t) = \exp\left[-\frac{1}{6}k^2\delta^2(t) \right] \qquad (14)$$

which gives correct results for both small and large wavevectors and it also gives the correct time behaviour.

We propose here self-consistent calculation of the memory function itself, by using the following procedure. We start with some estimation for the mode-coupling component of the memory function, for instance, $K_{MC}(t) = 0$. using the known values of $K_B(t)$ and equation (5) a total memory function is obtained which, when taken to equation (4), gives a normalized velocity autocorrelation function and through equation (3) leads to the mean square displacement. Now, by using the gaussian approximation for $F_s(k,t)$ and the viscoelastic model for F(k,t), the evaluation of the integral given in equation (13) leads to a new estimate for the mode-coupling component of the memory function. Finally, this loop is iterated until self-consistency is achieved between the initial and final total memory function, K(t).

3. Results and discussion

We have applied the theoretical formalism to study the dynamic properties of liquid Li, Rb and Cs near their melting points. The input data required by the theory are both the interatomic pair potential and its derivatives as well as the liquid static structural properties. We have used the interatomic pair potential which is derived from second-order perturbation theory with individual version of Fiolhais electron-ion pseudopotantial [27]. When it is used in conjunction with VMHNC theory of liquids has proved to be highly accurate for the calculation of the liquid static structure and the thermodynamic properties. In Table 1, we give the input data which has been used to determine the parameters for the interatomic pair potential, densities and temperatures. The potential parameters are taken from Ref.[27].

We have applied the iterative scheme described at above. We found that a number of (5-8) iterations are enough to achieve self-consistency in the memory function. The results are shown in Fig.1a where we have plotted the theoretical total memory functions for liquid Li, Rb and Cs. In the same figure, inset shows the first minima and maxima of normalized memory functions. The initial time decay values, τ_D, are 0.0326 ps, 0.234 ps, 0.324 ps for Li, Rb and Cs respectively. The binary part dominates the behaviour of K(t) for $t \leq 2\tau_D$ for longer times the mode-coupling part completely determines the shape of K(t). The theoretical results do not correctly reproduce long-lasting tail for longer times. In order to explain this fact, we have analyzed which wavevoctors are really relevant in the integral appearing in equation (10).

Table 1. The input parameters for the potential.

Metals	ρ(atoms/Å^3)	α	R	T(K)
Li	0.04440	4.113	0.342	463
Rb	0.01040	3.197	0.760	313
Cs	0.00833	3.138	0.848	303

The normalized velocity autocorrelation functions obtained from theoretical K(t) are shown in Fig.1b where we have calculated total Z(t) for liquid Li, Rb and Cs. Also in this figure inset shows the first minima of normalized velocity autocorrelation functions. In this systems the initial decay of Z(t) is very well reproduced, since its initial value Z(0)=1. Both the second frequency moment due to Ω_0^2 and the fourth frequency moment due to Ω_0^2 and τ_D are implicitly imposed by taking expression (9) for the binary component of K(t). The position of the subsequent maxima and minima of Z(t) are also well reproduced, although for $t \geq 2\tau_D$, the amplitude of oscillations is overestimated.
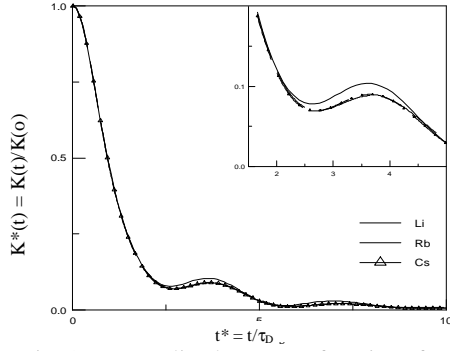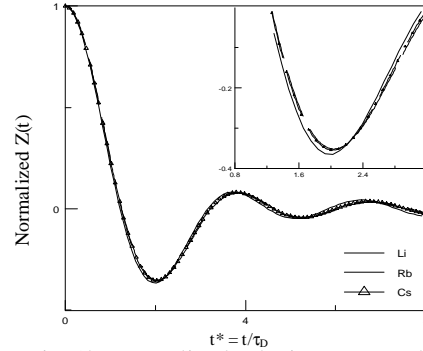
Fig. 1a. Normalized memory functions for
Li, Rb and Cs.

Fig. 1b. Normalized velocity autocorrelation
functions for Li, Rb and Cs.

The results obtained for the self-diffusion coefficients D are shown in Table 2 for the three systems in this work as compared experimental and molecular dynamic results. The theoretical results show good agreement with the experimental results for Rb, Cs but a little different for Li.

Table 2. Diffusion coefficients.

Metals	D ($\mathring{A}^2$/ps)	D_{exp} ($\mathring{A}^2$/ps)	D_{MD} ($\mathring{A}^2$/ps)
Li	0.59	0.64 ± 0.04 [a]	0.69 ± 0.02 [a]
Rb	0.25	0.27 ± 0.04 [b]	0.36 ± 0.02 [b]
Cs	0.22	0.22 [b]	0.24 ± 0.01 [b]

[a] Ref. [9], [b] Ref. [10]

The intermediate scattering functions obtained within this formalism are shown in Fig.2 along with MD data and viscoelastic results for liquid Li. It is observed that F(k,t) exhibits an oscillatory behaviour for small k, which persists until around $k \approx 2k_p/3$. The k_p is the position of the main peak of the static structure factor which is about 1.5 A^{-1} for both Rb and Cs and is about 2.5 A^{-1} for Li. The amplitude of oscillations of F(k,t) is stronger for the smaller k values and the oscillations take place around a globally decaying positive tail. The viscoelastic data do show an oscillatory behaviour for small k with the frequency of the oscillations rather well reproduced, but they are out of phase with the MD ones for the smaller k values and the oscillations occur basically zero.
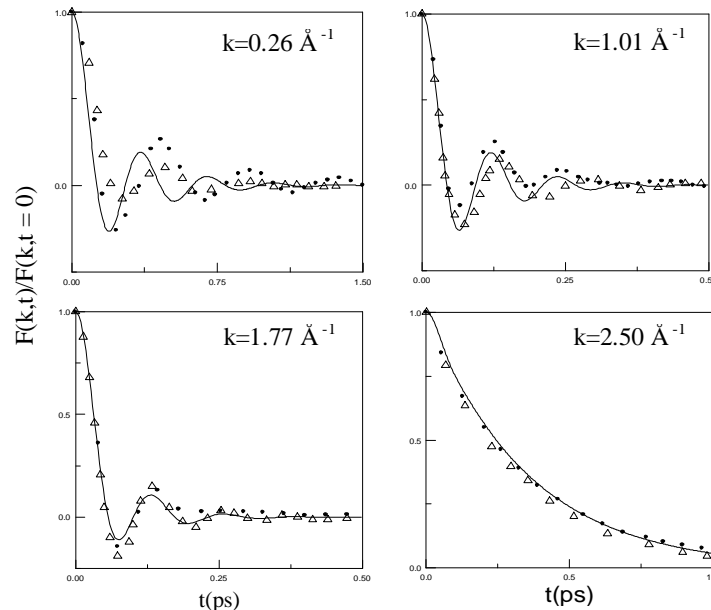

Fig. 2. Intermediate scattering functions at several k values for liquid Li. Continuous lines:
present results; triangles: viscoelastic results [8]; circle: MD results [8].

For the three larger values of k shown in Fig.3 the agreement is on a quantitative level, whereas for k=0.60 A^{-1} we find that Rb data are well reproduced, whereas the Cs data do show oscillations around decaying tail of roughly the correct amplitude and with the correct phase. But they are too weak compared with the MD ones. For even smaller values of k, the smallest allowed by the simulation boxes the oscillations of the theoretical F(k,t) in fact become also out of phase with the MD ones, both in Rb and in Cs, in contrast to the case of Li [8].

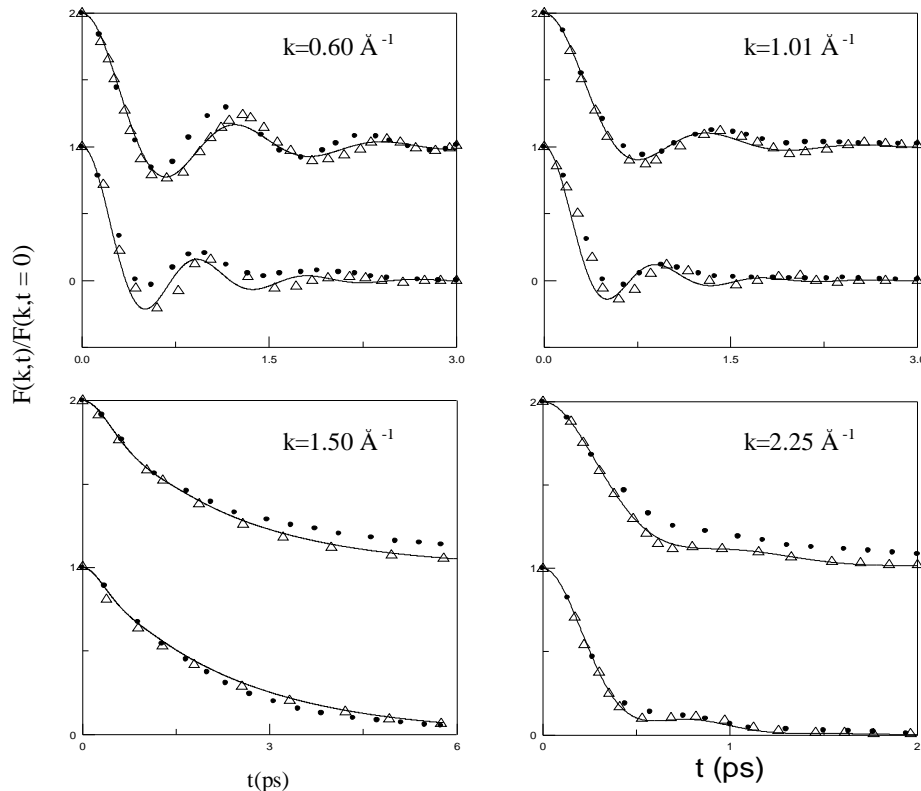Fig. 3. Intermediate scattering functions at several k values for liquid Rb and Cs (shifted upwards one unit). Continuous lines: present results; triangles: viscoelastic results [10]; circle: MD results [10].

In this work, both K(t) and F(k,t) areobtained within a self-consistent scheme, whereas self-intermediate scattering, F_s(k,t) is computed within the Gaussian approximation by using VACF deduced from self-consistent process. Now by Fourier transforming F(k,t) we get S(k,ω) is obtained. The dynamic structure factors are shown in Fig.4 together with calculation results and experimental ones which are obtained Ref.[28] for Rb and Ref.[6] for Cs. Comparing first, in smaller k values, dynamic structure factors are out of phase with experimental data whereas near the first peak of static structure factor the our viscoelastic results are in a good agreement with experimental ones for liquid Rb and Cs. In Fig.4 we show the viscoelastic dynamic structure factor obtained from for four wave vectors with experimental inelastic x-ray scattering (IXS) data. Comparing second viscoelastic results were obtained using neutral pseudo atom seen in F(k,t). But translated into the frequency domain; for example, the too small amplitude of the oscillations in the case of Cs is seen a too diffuse side peak in S(k,ω). It can be observed that the overall shape of S(k,ω) is qualitatively reproduced by the theoretical approach, in contrast experimental data, which is correctly the peak positions but fails to describe the overall ω dependence of the dynamic structure factor. The behaviour of S(k,ω) is of course a consequence of the time dependence of the intermediate scattering functions.
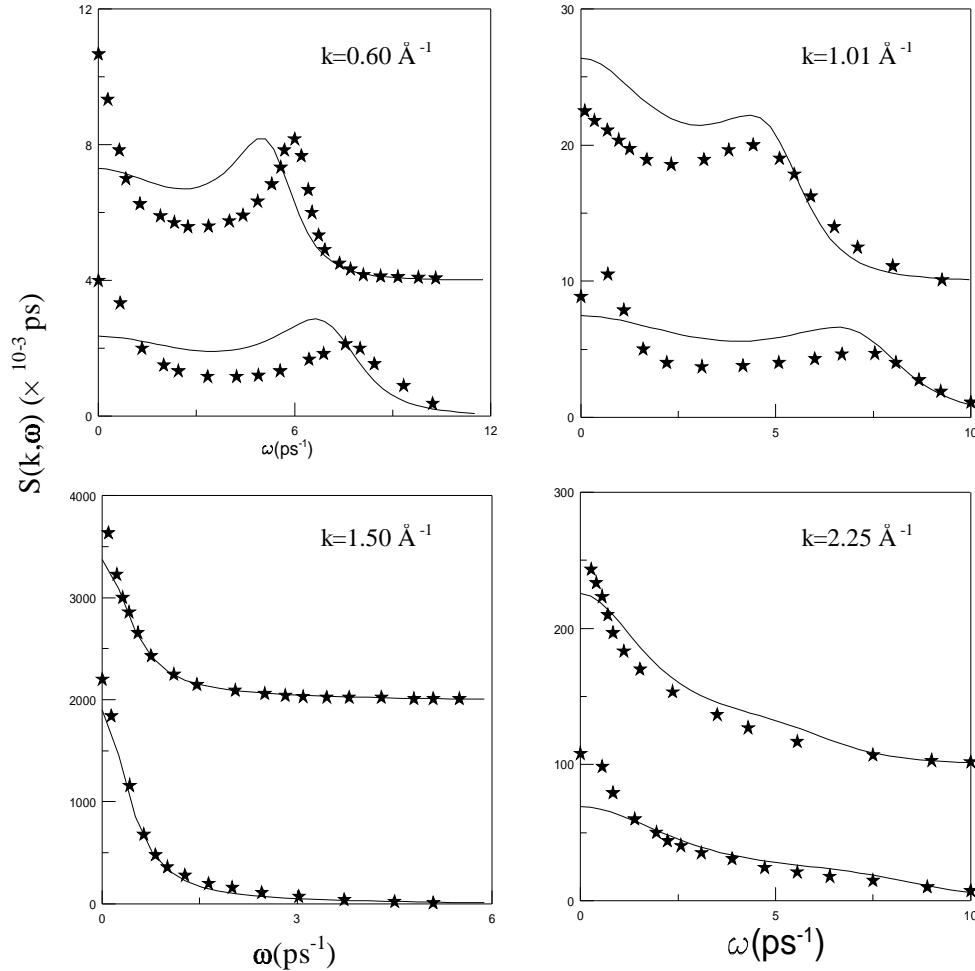
Fig. 4. Dynamic structural factors at several k values for liquid Rb and Cs (shifted upwards 0.008, 0.01, 2, 0.1ps from left to right).Continuous lines: present results; stars: experimental data.

4. Conclusion

In this paper we have evaluated several dynamic properties of liquid Li, Rb and Cs near the melting points. We have used that derived from second-order perturbation theory with individual version of Fiolhais electron-ion pseudopotantial. We have found the dynamics of the motion of single particles, as represented by the velocity autocorrelation function, its memory function, the self-diffusion coefficient and the self dynamic structure factor as well as collective properties such as intermediate structure factors and the dynamic structure factors.

The mode-coupling part, for which we have only considered the density-density coupling term, introduces the slow relaxation mechanisms in a correct semiquantitave way. In the case of the collective dynamics, there is a region, for small k, where the theory, although correct qualitatively, has some failure to reproduce quantitatively our results. This region is somewhat wider for Cs than for Rb, and both are wider than it was for Li. The main difference with liquid Li near melting is their density, which is sensibly smaller (almost 5 times less in Cs), so it is interesting to observe if the approximations involved in the theory still remain valid for these conditions.

On the theoretical side, we have shown that a simplified mode-coupling approach is able to reproduce rather well several features of single-particle motion, including both the ordinary and k-dependent diffusion coefficient. The overall quality of the agreement is good, supporting the idea that even in simple liquid metals we may adopt the type of effective potential successfully tested in the heavier alkali metals.

The theory treats in a different way the self-intermediate scattering function, on one hand, and the velocity autocorrelation function and the intermediate on the other, since the mode-coupling effects are included for the latter but not for the first.

Acknowledgments

References

[1] M. Shimoji, Liquid Metals (Academic, New York, 1973).

[2] N.H. March, Liquid Metals (Cambridge University Press, Cambridge, England 1990).

[3] C. Morkel, C. Gronemeyer, W. Glaser, J. Bosse, Phys. Rev. Lett. **18**, 1873 (1987).

[4] P. H. K. de Jong, P. Verkerk, S. Ahda, L. A. de Graaf, in Recent Developments in the Physics of Fluids, edited by W.S. Howells, A.K. Sopper (Adam Hilger, Bristol, 1992).

[5] C. Pilgirim, R.Winter, F. Hensel, C. Morkel, W. Glaser, Recent Developments in the Physics of Fluids, edited by W.S. Howells, A.K. Sopper (Adam Hilger, Bristol, 1992).

[6] C. Morkel, T. Bodensteiner, J. Phys.:Condens. Matter **2**, 251 (1990); T. Bodensteiner, C. Morkel, W. Glaser, B. Dorner,Phys. Rev. **A45**, 5709 (1992).

[7]A. Torcini, U. Balucani, P.H.K. de Jong,P. Verkerk, Phys. Rev. **E51**, 3126 (1995).

[8] J. Casas, D. J. Gonzalez, L .E. Gonzalez, M. M. G. Alemany, L. J. Gallego, Phys. Rev. **B62**, 12095 (2000); J. Casas, D.J. Gonzalez, L.E. Gonzalez, Phys. Rev. **B60**, 10094 (1999).

[9] L. E. Gonzalez, D. J. Gonzalez, M. Canales, Z. Phys. **B100**, 601 (1996).

[10] L. E. Gonzalez, D. J. Gonzalez, J. Casas, J. Non-Cryst. Solids **312-314**, 158 (2002).

[11] U. Balucani, R. Vallauri, Phys. Rev. **A40**, 2796 (1989).

[12] L. E. Gonzalez, D. J. Gonzalez, M. Silbert, J. A. Alonso, J.Phys. Condens. Matter **5**, 4283 (1993).

[13] A. Sjölander, in Amorphous and Liquid Materials, edited by E. Lüscher, G. Fritsch, G. Jacucci (Martinus Nijhoff, Dordrecht, 1987).

[14] L. Sjögren, A. Sjölander, J. Phys. **C12**, 4369 (1979).

[15] U. Balucani, R. Vallauri, T. Gaskell, S. F. Duffy, J. Phys. Condens. Matter **2**, 5015 (1990).

[16] U. Balucani, A. Torcini, R. Vallauri, Phys. Rev. **A46**, 2159 (1992); Phys. Rev. **A47**, 3011 (1993).

[17] F. Shimojo, K. Hoshino, M Watabe, J.Phys. Soc. Jpn. **63**, 1821 (1994)

[18] S. S. Dalgic, S. Dalgic, S. Sengul, M. Celtek, G. Tezgor, J. Optoelectron. Adv. Mater. **3**(4), 831 (2001).

[19] S. S. Dalgic, S. Dalgic, M. Celtek, S. Sengul, J. Optoelectron. Adv. Mater. **5**(5), 1271 (2003).

[20] H. Kes, S. S. Dalgic, S. Dalgic, G.Tezgor, J. Optoelectron. Adv. Mater. **5**(5), 1281 (2003).

[21] S. Dalgic, S.S. Dalgic, J. Optoelectron. Adv. Mater. **6**(3), 865 (2004).

[22] J. P. Hansen, I. R. McDonald, Theory of Simple Liquids, (Academic Press, London, 1986).

[23] J. P. Boon, S. Yip, Molecular Hydrodynamics, (McGraw-Hill, New York, 1980).

[24] D. Levesque, L. Verlet, Phys. Rev. **A2**, 2514 (1970).

[25] L. Sjögren, J. Phys. **C13**, 705 (1980).

[26] M. Canales, L. E. Gonzalez, J. A. Padro, Phys. Rev. **E50**, 3656 (1994).

[27] C. Fiolhais, J. P. Perdew, S. Q. Armster, J. M. MacLaren, M. Brajczewska, Phys. Rev. **B51**, 14001 (1995); *ibid*. **53**, 13193 (1996).

[28] J. R. D. Copley, M. Rowe. Phys. Rev. Lett. **32**, 49 (1974); Phys. Rev. **A9**, 1656 (1974).