

## The structural and dynamical liquid-glass transition for metallic sodium

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1993 J. Phys.: Condens. Matter 5 4325

(<http://iopscience.iop.org/0953-8984/5/26/006>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 11/05/2010 at 01:26

Please note that [terms and conditions apply](#).

# The structural and dynamical liquid–glass transition for metallic sodium

S K Lai and H C Chen

Department of Physics, National Central University, Chung-li 32054, Taiwan, Republic of China

Received 14 December 1992, in final form 4 March 1993

**Abstract.** We perform a molecular-dynamics simulation for the liquid metal sodium with the intention to study the glass transition temperature. Using the same set of liquid→glass structure factors, this is done (a) structurally by calculating the Wendt–Abraham parameter and (b) dynamically by solving the non-linear integral equation embodied in the mode-coupling theory. It is found that the glass transition temperature obtained from the former is distinctly lower than that from the latter. In an attempt to explain such a difference in the glass transition temperature, we draw attention to some recent works on shear viscosity coefficients and analyse the latter results in light of the basic hypothesis of the mode-coupling formulation. It appears that the glass transition point obtained in the context of mode-coupling theory for metallic sodium is reasonably predicted, and that the Wendt–Abraham glass transition point, determined directly from the structure data, seems numerically closer to the calorimetric glass transition temperature. Also, we compare the metallic non-ergodicity form factor obtained from the present molecular-dynamics simulation with the corresponding asymptotic formula proposed in the mode-coupling theory, and they are found to agree reasonably well with each other. The effect of the pair potential on the non-ergodicity form factor is also discussed briefly for both the hard-sphere and the metallic systems.

## 1. Introduction

A liquid can freeze into a disordered solid phase if the slow nucleation process in the supercooled state can be overcome. The liquid–glass transition phenomenon has been observed to occur in laboratory experiments. To account for this microscopic behaviour, computer simulation experiments have been playing a crucial role. One of the early attempts from computer simulations which is of relevance to the present work is the Monte Carlo simulation on the pair correlation function  $g(r)$  carried out by Wendt and Abraham (1978) and Abraham (1980). By studying the change of  $\mathcal{R} = g_{\min}(r)/g_{\max}(r)$ ,  $g_{\min}(r)$  and  $g_{\max}(r)$  being respectively the first minimum and the first maximum for the pair correlation function, versus temperature  $T$  they were able to deduce a structural criterion signalling the onset of the glass transition. Specifically, Wendt and Abraham noticed that a liquid transforms into a glassy state when the supercooled branch of  $\mathcal{R}$  versus  $T$ , which is linear, changes in slope and bends over linearly also to a glassy branch. They further asserted the liquid–glass transition point to be the extrapolated interception of these two branches and defined the corresponding temperature as the glass transition temperature  $T_g^{\text{WA}}$ . This particular parameter  $\mathcal{R}$ , which indicates the inception of the liquid–glass transition, has subsequently received substantial attention in the literature. An interesting feature common among subsequent computer simulation experiments is that the  $\mathcal{R}_{\text{LG}}$  (at the liquid–glass transition point) for any monatomic liquid, whether it be a liquid metal or a non-metallic

simple liquid such as a Lennard-Jones system, satisfies quite well  $\mathcal{R}_{LG} = 0.1 \pm 0.02$  at the glass transition temperature. An account of all these related works has been summarized in a recent article by the present author (Lai 1988a). (The interested reader should consult the following very recent work, which relates to  $\mathcal{R}$ : Lai (1988b), Li *et al* (1988), Shen *et al* (1990) and Tanaka and Ichimaru (1987).)

In the theoretical approach to  $T_g$ , Bengtzelius, Götze and Sjölander (BGS) (Bengtzelius *et al* 1984, Bengtzelius 1986a, b), and independently Leuthusser (1984), formulated a microscopic theory to study glass transition problems. This so-called mode-coupling approach, based on many-body methods and the kinetic theory, has made considerable progress in recent years (Sjölander 1980, 1985, 1989, Jäckle 1989, Götze and Sjögren 1992). Underlying this mode-coupling theory is the memory effect. The latter describes the influence that each atom in a liquid system experiences as a disturbance (that it creates on the medium) propagates through its surrounding atoms and as this disturbance reacts back on the same tagged atom at a later time. This kind of non-linear feedback mechanism becomes more transparent as the temperature of a liquid system is lowered. Accordingly, the existence of the memory effect has resulted in the occurrence of slowly decaying correlation functions in which are buried most of the physics of glass transition. Bengtzelius *et al* (1984) first succeeded in deriving a closed non-linear coupled integral equation for the density-density correlation function. By appealing to the argument that the density fluctuation should remain 'long-lasting' at sufficiently reduced temperature and that the finite solutions of the non-linear coupled equation would then indicate the onset of a non-ergodic state, they subsequently applied their formalism to both the hard-sphere (Bengtzelius *et al* 1984) and the Lennard-Jones (Bengtzelius 1986a, b) systems. Satisfactory agreement between theory, simulation data and experiments was obtained. In the following years, Götze and Sjögren (1987a, b, 1989a) and Buchalla *et al* (1988) proposed a modification to the mode-coupling model by adding an extra (linear) memory term to the integral equation. Specifically, they considered explicitly the coupling between density and longitudinal current fluctuations in deriving the mode-coupling contribution to the memory function. This modification enables one to make a more quantitative analysis of the dynamics of the glass transition, particularly in the vicinity of the liquid-glass domain, which is found to exhibit significant changes in viscosity measurements (Taborek *et al* 1986). Although the mode-coupling model of BGS can be extended readily to include coupling between density and temperature fluctuations, leading thus to the study of the glass transition via examining various thermodynamic quantities (see Bengtzelius and Sjögren (1986) for further details), in this work we confine ourselves solely to the evaluation of  $T_g$  through the study of the density fluctuation.

Our motive to carry out the work is threefold. First, we present a quantitative application of the mode-coupling theory to a real metal using a realistic potential constructed rigorously from the electron theory of metals. The results of calculations may serve to indicate whether a metallic fluid is an exception in the kind of dynamical transition that has so far been applied only to non-metallic liquids such as the hard-sphere or the Lennard-Jones system. Furthermore, anomalies in viscosity were reported that reveal the fact that liquid metals show a deviation in the power-law behaviour contrasted to a class of 'fragile' liquids investigated (Taborek *et al* 1986). Secondly, by virtue of the non-linear integral equation of BGS we estimate the  $T_g$  and the root-mean-square displacement. We compare the BGS  $T_g$  with the one corresponding to the  $\mathcal{R}_{LG}$  parameter. Because we make use of the same  $g(r)$  or its Fourier transform, the static structure factor  $S(q)$ , both in obtaining the  $T_g$  via the Wendt-Abraham criterion and in solving for the non-trivial solutions of slowly decaying density correlation functions at long time, such a comparison, in addition to ascertaining further the role played by the structure parameter  $\mathcal{R}$ , should clarify certain ambiguities raised recently

by Yip (1989) in relation to the glass transition temperature. Thirdly, to delve further into the mode-coupling theory, we shall discuss briefly certain properties of the present realistic non-ergodicity form factor obtained here from the molecular-dynamics (MD) simulation, and compare it with the recent proposed asymptotic formula of Götze and Sjögren (1992). This comparison will give us information regarding the relaxation process of a supercooled liquid.

This paper is organized as follows. In section 2 we first describe our MD simulation and in executing the algorithm introduce a reasonable approximation for estimating the change in density of Na metal with the quenching temperature. We present the mode-coupling theory in section 3 by summarizing briefly relevant equations for the time-dependent density-density correlation function. Our results of calculations for (i) the MD simulation and (ii) the mode-coupling theory will be given in section 4 along with a discussion on any implications that may be drawn from this work. In section 5 we give our conclusion.

## 2. Molecular-dynamics simulation

We performed an MD simulation for the pure sodium system starting from a liquid state at  $T = 423$  K and quenching down to  $T = 23$  K. A total of 686 particles were confined in a cubic cell subject to the standard periodic boundary condition at the cubic walls. Following our previous work (Lai and Lin 1990), we adopted Beeman's algorithm (Beeman 1976) in numerical integration of the equation of motion. The temperature quenching process was divided into stages and at each stage we carried out 4500 time steps for the equilibrium pair correlation function, after performing a series of heat-bath contacts (Tanaka 1981, 1982) to achieve the stationary state. The time step is here taken to be  $10^{-15}$  s, which corresponds to a quenching rate higher than our previous work (Lai and Lin 1990). Since the interatomic potential  $V(r)$  and the density of Na metal are prime inputs to MD simulation, we describe in sections 2.1 and 2.2 below how we obtained these quantities.

### 2.1. Interatomic potential

Given a system of  $N$  pseudoatoms confined in a volume  $\Omega$  at a given density  $n = N/\Omega$  and temperature  $T$ , we assume that the pseudoatoms interact via a symmetric pairwise potential  $V(r)$ , which is constructed using the modified generalized non-local model pseudopotential of Li *et al* (1986) and Wang and Lai (1980). According to the latter works we write

$$V(r) = \frac{Z_{\text{eff}}^2}{r} \left( 1 - \frac{2}{\pi} \int_0^\infty dq G_N(q) \frac{\sin(qr)}{q} \right) \quad (1)$$

where  $G_N(q)$  is the normalized energy-wavenumber characteristic and  $Z_{\text{eff}}^2 = Z^2 - \rho_d^2$ ,  $Z$  and  $\rho_d$  being the nominal valence and the depletion charge, respectively. It is worth while to note that in (1) proper attention has been given to the one-electron energy and pseudo-wavefunction by carefully incorporating higher-order perturbative corrections through introduction of a parameter in the bare-ion pseudopotential.

### 2.2. Estimation of atomic volume

In view of the fact that the densities of real materials were observed (Owen 1985, Brawer 1985) to undergo continuous change in magnitude with temperature in the liquid→glass transition, it is therefore necessary to include this realistic effect throughout the glass

transition process. The present method of determining the atomic volume  $\Omega_0$  versus  $T$  follows that of our very recent work (Lai *et al* 1993) and proceeds as follows.

First, we performed an MD simulation to calculate the  $g(r)$  using  $V(r)$  evaluated at each temperature with the  $\Omega_0$  obtained from a linear interpolation between the experimental liquid and crystalline densities (Borgstedt and Mathews 1987). Secondly, from the calculated  $g(r)$ , we determined the associated Wendt–Abraham  $\mathcal{R}$  at each  $T$ . The interception of the linear supercooled liquid branch and the linear glassy solid branch (Lai *et al* 1987, Lai 1988a, Lai and Lin 1990) allows us to locate a glass transition temperature, say with a value  $T_g^{(1)}$ . Next, we returned to the  $\Omega_0$  versus  $T$  curve and modified it such that for  $T \leq T_g^{(1)}$  the  $\Omega_0$  versus  $T$  behaviour follows that of the crystalline phase. In other words, for  $T \leq T_g^{(1)}$  we assumed the same gradient for the modified  $\Omega_0$  versus  $T$  curve and for the crystalline Na metal. This assumption is based on the observation that below  $T_g$  the glassy branch is almost solid-like (Owen 1985, Zallen 1983). With this new set of  $\Omega_0$  versus  $T$  data we constructed  $V(r)$  and repeated MD simulations for pair correlation functions. The corresponding  $\mathcal{R}$  versus  $T$  curve can be plotted to obtain a new  $T_g^{(2)}$ . For liquid Na we noticed that  $T_g^{(2)}$  was higher than  $T_g^{(1)}$ . Our next step was to modify again the  $\Omega_0$  versus  $T$  relation. Since  $T_g^{(2)} > T_g^{(1)}$ , a physically reasonable modification was to shift the glassy  $\Omega_0$  versus  $T$  branch (in parallel with the crystalline one) until it intersects at  $T_g^{(2)}$ . The whole MD simulation for  $g(r)$  and a corresponding plotting of  $\mathcal{R}$  versus  $T$  to locate a new  $T_g^{(i+1)}$ ,  $i = 2, 3, \dots$ , were repeated. This procedure was carried out iteratively for  $i = 2, 3, \dots$  until  $T_g^{(i+1)} \simeq T_g^{(i)}$ . In actual simulation we terminated the iterative procedure when a difference in  $T_g$  of less than 5 K was detected. Albeit approximated, the present procedure did take into account the density effect realistically (Elliott 1984).

### 3. Mode-coupling theory

In this section we present some basic formulae that permit calculation of  $T_g$  within the so-called ideal glass transition and then move on to the equations for studying the prediction of Götze.

#### 3.1. Basic formulae

Central to the mode-coupling theory is the time-dependent density–density correlation function  $F(q, t) = \langle \delta n(q, t) \delta n(-q, 0) \rangle$  where  $\delta n(q, t)$  is the Fourier transform of  $\delta n(r, t)$ , being the microscopic density fluctuation from the homogeneous equilibrium value, and  $\langle \dots \rangle$  is the usual ensemble average. This function contains useful information on the local atomic structure as well as accounting for its time evolution. Let us write the Laplace transform of  $F(q, t)$  as

$$\hat{F}(q, z) = i \int_0^\infty dt e^{izt} F(q, t) \quad \text{Im } z > 0. \quad (2)$$

Its relation written in terms of the so-called memory function  $\hat{M}(q, z)$  can be shown (Bengtzelius 1986b) to be

$$\hat{R}(q, z) \equiv \frac{\hat{F}(q, z)}{S(q)} = - \frac{z + \hat{M}(q, z)}{z^2 - q^2/m\beta S(q) + z\hat{M}(q, z)} \quad (3)$$

where  $\beta = 1/k_B T$  is the inverse temperature and  $m$  is the atomic mass. As discussed in the work of BGS (Bengtzelius *et al* 1984a), one can identify two separate mechanisms pertaining to the decaying behaviour of  $F(q, t)$  in terms of its associated memory function  $M(q, t)$ . Specifically, it can be shown that  $F(q, t)$  consists of a short-time rapidly decaying part representing essentially uncorrelated binary collisions and of a collective long-lasting decaying part  $\Gamma(q, t)$  involving non-linear couplings of the slowly varying  $F(q, t)$ . At high densities or at low temperatures, the former contribution is insignificantly small while the latter effect is dominant. Bengtzelius *et al* (1984) and Bengtzelius (1986a) derived a non-linear self-consistent dynamical equation for which the solidification condition

$$f(q) = F(q, t \rightarrow \infty)/S(q) \neq 0 \tag{4}$$

is related to the memory function  $\Gamma(q, t)$  through

$$f(q)/[1 - f(q)] = [m\beta S(q)/q^2]\Gamma(q, t \rightarrow \infty). \tag{5}$$

By making a two-mode approximation, BGS (Bengtzelius *et al* 1984) showed that the slowly decaying part  $\Gamma(q, t)$  satisfies

$$\Gamma(q, t) = \frac{n}{8mq\beta\pi^2} \int_0^\infty dq' q' \int_{|q'-q|}^{|q'+q|} dq'' q'' \left( \frac{q'^2 - q''^2}{2q} [c(q') - c(q'')] \right) + \frac{q}{2} [c(q') + c(q'')]^2 S(q')S(q'')R(q', t)R(q'', t) \tag{6}$$

where  $R(q, t \rightarrow \infty) \rightarrow f(q)$ , and  $c(q) = [1 - 1/S(q)]/n$  is the direct correlation function. It is appropriate to note at this point that  $f(q)$  can be checked against experiments such as Mössbauer scattering (Champeny and Sedgwick 1972), neutron scattering (Mezei *et al* 1987a, b, Frick *et al* 1990, Börjesson *et al* 1990), dynamic light scattering (Van Megen and Pusey 1991), and Brillouin scattering (Elmroth *et al* 1992).

In a similar vein, we can calculate the self-part of  $f(q)$ ,  $f^s(q)$ , by replacing  $M(q, t)$  and  $R(q, t)$  in the above equation with  $M^s(q, t)$ , having the same mathematical form, and  $F^s(q, t)$  respectively (note, in particular, that for the self-part  $f^s(q)$  the liquid structure factor  $S(q) = 1$ ). The root-mean-square displacement  $\langle \Delta r^2(t) \rangle$  can thus be defined in terms of  $F^s(q, t)$  as

$$\langle \Delta r^2(t) \rangle = -3 \lim_{q \rightarrow 0} \left( \frac{\partial^2 F^s(q, t)}{\partial q^2} \right) \tag{7}$$

where  $F^s(q, t)$  satisfies an integral equation similar to (6). Equations (5) and (6) are basic formulae derived previously by BGS. Given a means to determine  $S(q)$  as a function of the control parameter (temperature or density), the above equations should be solved iteratively (and quantitatively when  $S(q)$  is given as a smooth and continuous function especially in an analytic form) for non-zero solutions  $f(q)$  and accordingly  $f^s(q)$ . The temperature at which this just happens is defined to be  $T_g^{\text{BGS}}$ .

However, in a series of important works (Götze 1985, 1986, 1987), Götze studied (5) and (6) in some detail. He proposed that the analytic properties for  $f(q)$  should be examined. Indeed, as shown in the appendix, near the glass transition point  $f(q)$  is given analytically by equation (A17):

$$f(q) = f^{\text{BGS}}(q) + \alpha h^{\text{BGS}}(q)\xi^{1/2}$$

where  $f^{\text{BGS}}(q)$  is the non-ergodicity form factor at the transition point,  $\alpha$  is a parameter defined in the appendix by (A15),  $h^{\text{BGS}}(q) \propto [1 - f^{\text{BGS}}(q)]^2$  is the critical amplitude depending on the physical system and  $\xi = (T^{\text{BGS}} - T)/T^{\text{BGS}}$  is the separation parameter.

#### 4. Numerical results and discussion

In this section we input the MD Fourier-transformed  $S(q)$  into the non-linear integral equation (5) and determine  $T_g^{\text{BGS}}$  by requiring the eigenvalue of  $C_{qk}^{\text{BGS}}$  to approach one. We compare first in section 4.1 the resulting  $T_g^{\text{BGS}}$  with that  $T_g^{\text{WA}}$  determined from the  $\mathcal{R}$  versus  $T$  curve. The variation of the eigenvalue in the vicinity of the critical point will be examined and compared in section 4.2 with the theoretical prediction of Götze.

##### 4.1. Comparison of $T_g^{\text{WA}}$ and $T_g^{\text{BGS}}$

We first assess our MD data by comparing in figure 1 the Fourier-transformed and the experimental  $S(q)$  at  $T = 423$  K and 373 K. The simulated  $g(r)$  at lower  $T$  displays similar change as our previous works (Lai *et al* 1987, Lai 1988a, b, Lai and Lin 1990). In figures 2 and 3, we present respectively the  $\Omega_0$  versus  $T$  and  $\mathcal{R}$  versus  $T$  curves calculated iteratively from pair correlation functions. We note three relevant points.

(i) Our calculated  $S(q)$  at the melting point and at higher temperatures agree very well with the x-ray results (Huijbin and van der Lugt 1979).

(ii) The  $g(r)$  versus  $T$  results display the same subtle changes in structure (such as the flattening of the second maximum near  $T_g^{\text{WA}}$ , the development of the double-peak structure, enhanced oscillations at large  $r$  and at sufficiently low  $T$ , etc) in accord with our previous findings (Lai *et al* 1987, Lai 1988a, b, Lai and Lin 1990) and with those observed in laboratory experiments.

(iii) We see from figure 3 that  $\mathcal{R}$  exhibits a change in slope and that  $\mathcal{R}_{\text{LG}}$  at  $T_g^{\text{WA}} = 189$  K is equal to 0.105 satisfying the criterion  $\mathcal{R}_{\text{LG}} = 0.1 \pm 0.02$ . We note at this point that this universal criterion has so far been confirmed only for a monatomic system. For a binary system Lewis (1991), however, has recently found an  $\mathcal{R}_{\text{LG}}$  that deviates far from this criterion.

All these three points reinforce our belief that the present non-local pseudopotential is adequate for structural studies.

Having gained confidence in our simulated  $g(r)$ , we may use them as input to the mode-coupling theory. To this end, we need, first of all, to Fourier-transform the  $g(r)$ . The resulting  $S(q)$  are sole inputs to the integral equations (5) and (6) and are to be solved iteratively as follows. Initially we arbitrarily set  $f(q) = 0.5$  and insert it into (5) and (6) along with the MD  $S(q)$  at the appropriate temperature. Next, the obtained  $f(q)$  versus  $q$  is substituted back into the equations and the procedure is repeated iteratively. At  $T \geq 223$  K we observe that we always have the trivial solution  $f(q) = 0$ . A first non-vanishing  $f(q)$  occurs at  $T = 198$  K; here we find that  $f(q)$  stabilizes to show a well developed structure and this behaviour persists for more than 220 iterations (see figure 4). Consequently, we may expect  $T_g^{\text{BGS}}$  to lie in between 198 and 223 K for the Na element. To locate  $T_g^{\text{BGS}}$ , one has two alternatives. One is to search for it manually, that is, starting at a temperature a few kelvins above 198 K, say with an interval  $\Delta T^{(j)}$ . We progressively increase the temperature and perform iterative calculations at each  $T$  until  $f(q) = 0$  is encountered. The whole procedure is repeated each time starting at the next highest  $T$  for which  $f(q) \neq 0$  and with a  $\Delta T^{(j+1)} < \Delta T^{(j)}$ . Because the MD simulation is carried out stepwisely, this method is generally quite tedious to implement numerically. In particular, we have to resort to interpolation for the intermediate  $g^{(i)}(r)$  at  $T^{(i)}$  using  $g^{(i-1)}(r)$  and  $g^{(i+1)}(r)$  respectively at  $T^{(i-1)}$  and  $T^{(i+1)}$ . Fortunately with a refined algorithm (Davis and Polonsky 1972), the interpolated  $g(r)$  is well justified by the quality of the  $g(r)$  obtained (see figure 5 and the inset showing the magnitude of the error).

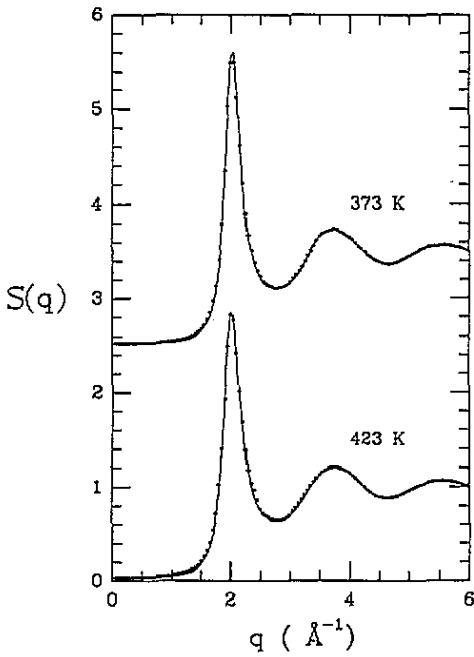


Figure 1. Structure factor  $S(q)$  for the liquid metal sodium (full curve) compared with x-ray experiments (full circles) from Huijbin and van der Lugt (1979).

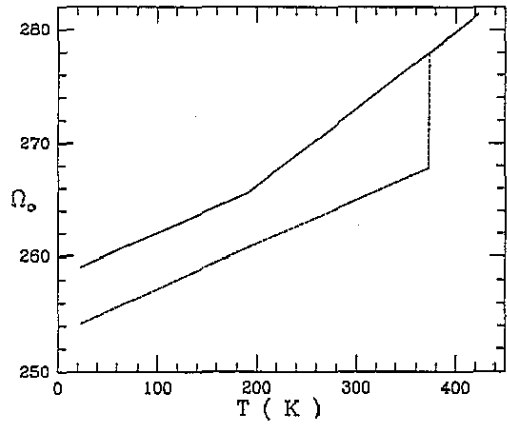


Figure 2. Atomic volume  $\Omega_0$  versus temperature  $T$  in kelvins for the sodium system. The broken line is the expected path taken by the crystalline phase (taken from Borgstedt and Mathews (1987)) whereas the full line refers to the liquid-glass path obtained iteratively as described in the text.

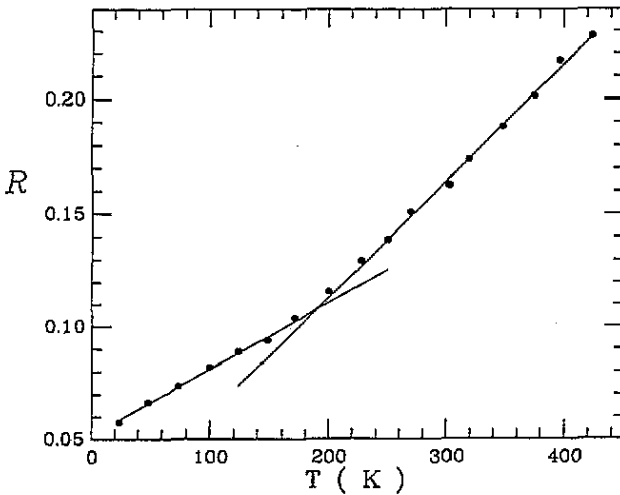


Figure 3. Wendt-Abraham parameter  $\mathcal{R}$  plotted against temperature  $T$  in kelvins for the sodium element.

Equivalently one can follow the analytic prescription of Götze (1985) and examine the stability matrix  $C_{qk}$  as defined in (A5). According to Götze  $C_{qk}$  possesses a largest eigenvalue  $E_0$  and this eigenvalue decreases as the temperature is lowered. In fact from the



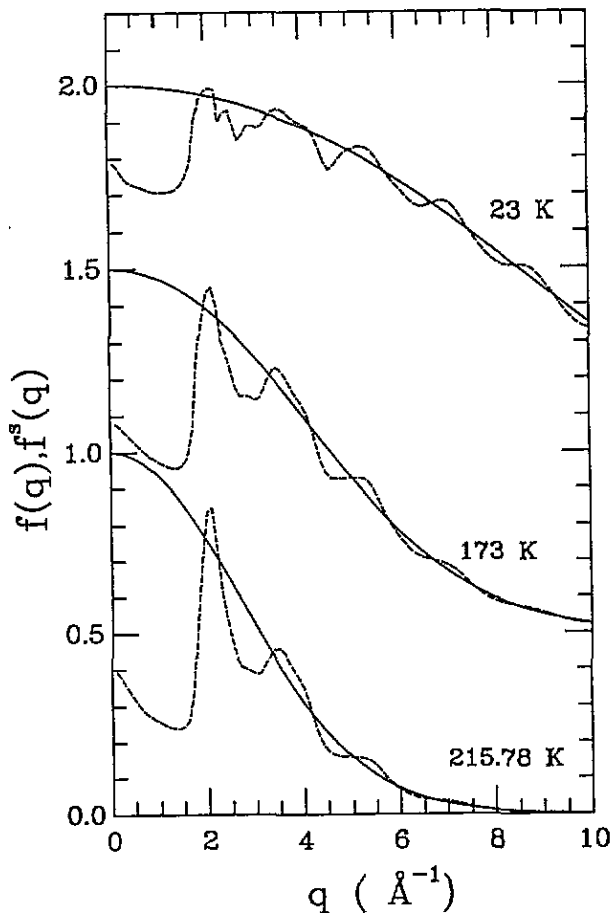


Figure 4. Non-ergodicity form factor  $f(q)$  (broken curve) for the sodium element calculated iteratively (see text) from (5) and (6). The corresponding self-part  $f^s(q)$  is given by the full curve.

definition of  $C_{qk}$  one can derive easily a relation for  $E_0$  which, near to  $T_g^{\text{BGS}}$ , is given by

$$E_0 = 1 - 2\alpha(1 - \lambda)\xi^{1/2}.$$

In other words one can determine  $T_g^{\text{BGS}}$  by plotting  $[1 - E_0(T)]^2$  versus  $T$  and looking for a  $T$  that yields  $[1 - E_0(T)]^2 = 0$ . Practically the method of Götze is straightforward and appears a lot easier to operate. We have followed and cross-checked both approaches. We found that  $T_g^{\text{BGS}} = 215.78$  K seems to agree quite well by both means. At this point it is appropriate to digress for a moment and make a comment on this  $T_g^{\text{BGS}}$ . We note that  $T_g^{\text{BGS}}$  moderately depends on the treatment of  $S(q)$  at small  $q$  due to truncation in the Fourier transform of  $g(r)$ . We have tested the Percus–Yevick hard-sphere, Verlet–Weiss hard-sphere and charged hard-sphere analytic formulae in order to extrapolate  $S(q)$  from just before the first peak ( $q < 1 \text{ \AA}^{-1}$ ) to  $q = 0$ . For reasons of regularity and smoothness in the extrapolation process, we adopted  $S_{\text{PY}}(q)$ , although  $T_g^{\text{BGS}}$  determined differs by a few kelvins from that using  $S_{\text{CHS}}(q)$ . Furthermore because we are using  $S_{\text{PY}}(q)$  to approximate the small- $q$  behaviour, our estimation for the eigenvalue of the stability matrix was found numerically to be  $0.984 \pm 0.0007$  (at  $T = 215.7961$  K our calculation after 150 iterations yields  $f(q) = 0$ ), an accuracy limited by our MD-simulated  $S(q)$ .

We are now in a position to compare the above  $T_g^{\text{BGS}}$  with that determined via the Wendt–Abraham criterion. We notice in the first place that  $T_g^{\text{BGS}}$  is higher than  $T_g^{\text{WA}}$  by

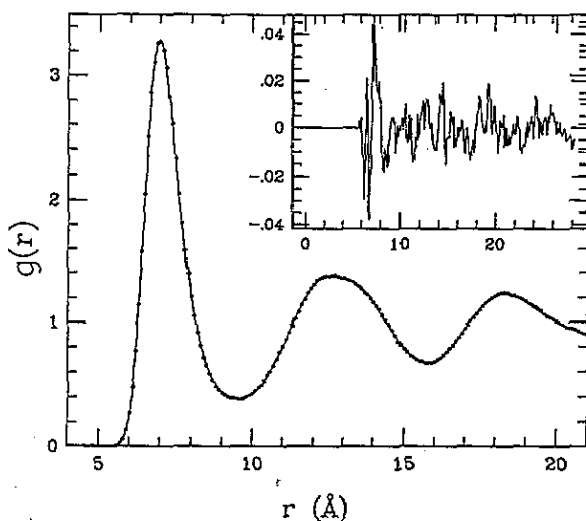


Figure 5. Pair correlation function  $g(r)$  for the sodium element calculated at  $T = 198$  K (full curve) compared with an approximated  $g(r)$  (full circles) interpolated between  $g(r)$  at  $T = 223$  K and  $T = 173$  K respectively. The inset shows the difference between the calculated and interpolated  $g(r)$ .

about 27 K. What implication does this number convey? In order to answer this question, let us recall a recent paper by Yip (1989). Yip made an assessment of the validity of mode-coupling theory by analysing its theoretical framework and by studying comparatively the viscosity measurements. He observed two points. Firstly, he noticed from his study of the experimental shear viscosity coefficient  $\eta$  (Taborek *et al* 1986) for a class of diverse 'fragile' liquids that the glass transition temperature extrapolated from the data in the low- $\eta$  region to infinity viscosity and defined by Taborek *et al* to be  $T_0$  is distinctly greater than the calorimetric glass transition point  $T_g$ . In particular he found that this  $T_0$  delineates an interesting feature in that it marks the boundary between two types of viscous behaviour: power-law for  $T > T_0$  and approximately Arrhenius (where the viscosity changes rapidly from a value about a factor of 10 times that in a normal liquid to several orders of magnitude greater) for  $T < T_0$ . Secondly, Yip (1989) made a detailed comparison between the mode-coupling theory in the context of (5) and (6), so-called ideal glass transition, and that in the more refined version (Götze and Sjögren 1987b, Das and Marzenko 1986, Das 1987) where the coupling between density and current fluctuations is explicitly included. Based on the numerical data of  $\eta$  by Das and Marzenko (1986) and Das (1987), he came to the conclusion that  $T_g^{\text{BGS}}$  is perhaps more appropriately identified to be  $T_0$ , an ideal glass transition temperature. Accordingly if one were to *assert* that  $T_g^{\text{WA}}$ , being determined directly from *structural* data, is a temperature closer to the calorimetric glass transition temperature  $T_g$ , it is thus not surprising to see the difference in the  $T_g^{\text{BGS}}$  and  $T_g^{\text{WA}}$ . There are ample evidences from computer simulations (Kimura and Yonezawa 1983, Nöse and Yonezawa 1985, Tanaka 1986a, b, Watanabe and Tsumuraya 1988) that such an assertion for  $T_g^{\text{WA}}$  is physically reasonable. It should be noted, however, that although the cooling rate has a non-negligible effect on  $T_g^{\text{WA}}$ , its influence is inconsequential here because we are using the same set of  $g(r)$  or  $\hat{S}(q)$  for both calculations. Furthermore the relation  $T_g^{\text{BGS}} > T_g^{\text{WA}}$  is not an exception for the metallic Na but occurs also in the Lennard-Jones system (Bengtzelius 1986a).

The same calculational procedure has been repeated for the self-part  $f^s(q)$ . Since the latter in the present mode-coupling theory is proportional to  $f(q)$ , the iteration of  $f^s(q)$  begins at  $T = 215.78$  K at which  $f(q)$  has a non-zero solution. The results for  $f^s(q)$  at three quenched temperatures are displayed in figure 4 together with their respective

$f(q)$ . From these  $f^s(q)$ , we determined the root-mean-square displacement using either the half-width method (Bengtzelius *et al* 1984) or directly via (7), which has a finite value for  $t \rightarrow \infty$ . These results are plotted in figure 6 and serve to illustrate the change of the single-particle mean-square displacement from a small value to infinity in going from the glass-like to the liquid state, thereby recovering the quite similar Lindemann's melting criterion. This, of course, is not surprising since in the present version of the mode-coupling theory the root-mean-square displacement is determined from  $F^s(q, t)$  or from the half-width method, and either method leads naturally to the temperature  $T_g^{\text{BGS}}$ . We note that although both methods yield  $\langle u_x^2 \rangle^{1/2}/r_1$ , being the root-mean-square displacement in one direction measured relative to the position of the first maximum of  $g(r)$ , very close to 0.1, the temperature at which this happens is the same as  $T_g^{\text{BGS}}$ . What implication can we draw from this  $T$ ? In order to dwell on this point, we recall (Götze 1986) that the mode-coupling theory as used here only describes the dynamical motion of atoms where the possibility of the activated or hopping process is excluded explicitly. In other words, the whereabouts of any atom is coupled dynamically to its neighbouring atoms such that any disturbance that the tagged atom creates and exerts on the other surrounding atoms can merely propagate via this type of collective interaction. This (memory) effect will in turn act back on the tagged atom after an elapse of a certain time (see, for example, figure 10 in Sjölander 1980). As  $T$  is lowered this kind of collective coupling between atoms is surely enhanced, and gradually a point is reached where it becomes dynamically unfavourable for the tagged atom to push its way through the many neighbouring atoms. When this happens the resulting atomic motion is then found to undergo a (dynamical) transition displaying a trapped-like behaviour with the tagged atom confined to move within a cage formed by the surrounding atoms. Such vibrational motion delineates a liquid  $\rightarrow$  viscous-like behaviour, a scenario whereby an atom wanders back and forth within a restricted region. In the absence of the thermally activated mechanism, this is perhaps the only method of phase transition. We stress that the physical origin of this kind of vibrational motion is quite different from that implied by the structural parameter  $\mathcal{R}$ . The latter, which describes the variation of 'localized' points  $g(r_{\text{max}})$  and  $g(r_{\text{min}})$  with temperature, is perhaps more appropriately associated with the structural origin. Nevertheless, it is still possible to get some feeling of this dynamical transition if one were to examine the change in  $g(r)$  with  $T$  for the half-width at half-maximum (HWHM, Lai 1988a). Physically the HWHM roughly describes the vibrational amplitude of ions and when divided by the first-nearest-neighbour  $r_1$ , i.e.  $\text{HWHM}/r_1$ , is equivalent to the well known Lindemann's criterion from the liquid side. Figure 7 shows  $\text{HWHM}/r_1$  versus  $T$  for Na metal. It is interesting to note that  $\text{HWHM}/r_1$  changes linearly in slope and intercept at  $T_g^{\text{HWHM}} = 206$  K. As in our previous work (Lai 1988a) for Y and Zr (for Y metal  $T_g^{\text{WA}}$  and  $T_g^{\text{HWHM}}$  are given by 1020 and 1040 K whereas for Zr metal the corresponding temperatures are 1350 and 1380 K), we find that this temperature is higher than the  $T_g^{\text{WA}}$  by about 17 K. This result implies that the origin of the above (mode-coupling) 0.1 criterion is likely dynamical rather than structural. Accordingly we may thus mark the above 0.1 description to be the beginning of the slowing down of structural relaxation and that the value 0.1 is just the ratio of the oscillatory amplitude (within the cage) to an average distance between the tagged atom and neighbouring atoms in the supercooled regime. Since we have identified  $T_g^{\text{BGS}}$  to be the viscosity-predicted  $T_0$  where the viscosity coefficient changes from a liquid-like magnitude to a relative value about a factor of 10–100 larger, the physical picture presented above nonetheless appears to correlate with it quite well.

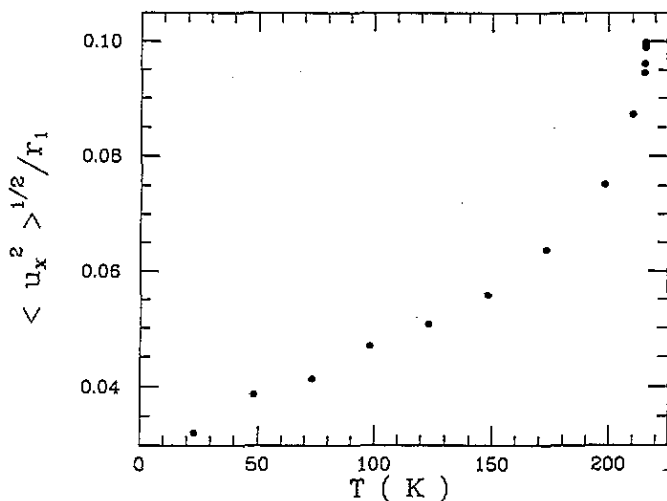


Figure 6. Ratio of the asymptotic value of the root-mean-square displacement in one direction  $\langle u_x^2 \rangle^{1/2}$  in units of the first-nearest-neighbour  $r_1$  calculated from (7) and the MD-simulated  $g(r)$  for the sodium element.

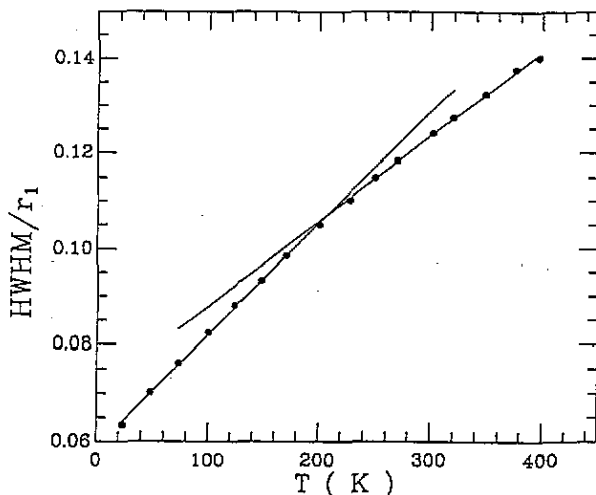


Figure 7. Ratio of the half-width at half-maximum HWHM in units of the first-nearest-neighbour  $r_1$  calculated from the MD-simulated  $g(r)$  for the sodium element.

#### 4.2. Numerical evidence of Götze's prediction

We now turn to an examination of (A17). There are several features deserving discussion here. First of all, since  $T_g^{\text{BGS}}$  was determined above to be 215.78 K, the right-hand side of (A17) can be calculated at each  $q$  provided  $\alpha$  given by (A15) is known. We have, in fact, evaluated the latter parameter at the transition temperature. When this parameter is substituted into (A17) we obtain immediately the metallic asymptotic  $f(q)$  at different  $T$  near  $T_g^{\text{BGS}}$ . On the other hand  $f(q)$  at these same temperatures have been iterated separately using (6) and the MD-simulated  $S(q)$ . Both sets of data are plotted together in figure 8. As the figure shows, these two sets of non-ergodicity parameters vindicate the asymptotic  $\xi^{1/2}$  dependence of  $f(q)$  in agreement with Götze's hypothesis (compare also figure 4 of Van Meegen and Pusey (1991)). The temperature dependence of  $f(q)$  at the first peak and at the first minimum of  $S(q)$  are also depicted separately in figure 9. This latter figure further illustrates the predictive power of the mode-coupling theory, for although a direct

comparison with experiments is not possible, it nevertheless dictates the same asymptotic  $f(q)$  behaviour similar to that of a hard-sphere system (Fuchs *et al* 1992) and bears many close resemblances to those of related measurements (Frick *et al* 1990, Elmroth *et al* 1992).

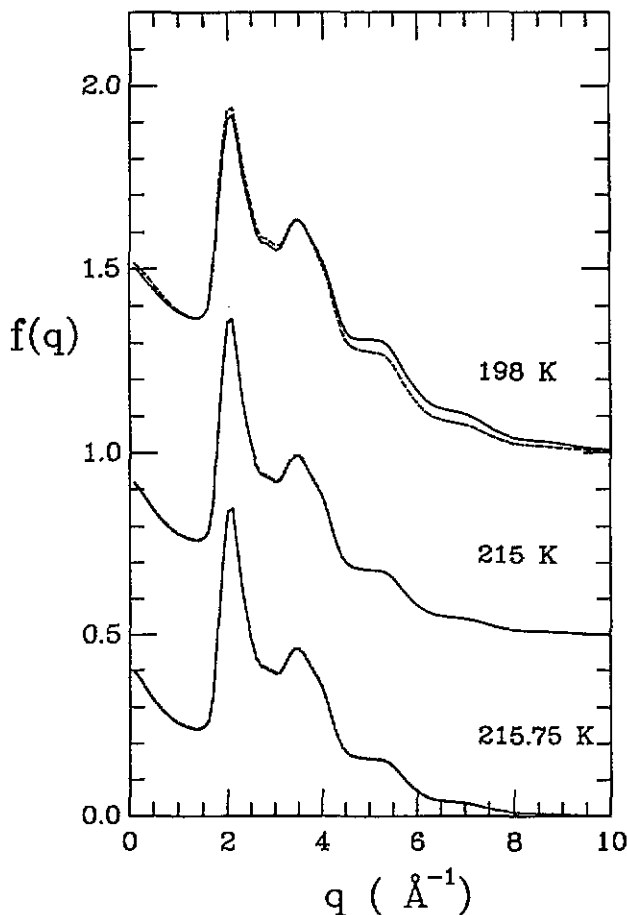


Figure 8. Non-ergodicity form factor  $f(q)$  for the sodium element obtained from (6) and the Fourier-transformed  $S(q)$  (full curve) compared with the asymptotic formula of Götze,  $f(q) = f^{\text{BGS}}(q) + 1.123h^{\text{BGS}}(q)\xi^{1/2}$  (broken curve). The separation parameter  $\xi = (T_g^{\text{BGS}} - T)/T_g^{\text{BGS}}$ , where  $T_g^{\text{BGS}} = 215.78$  K, for  $T = 198, 215$  and  $215.75$  K is given by  $8.2 \times 10^{-2}, 3.6 \times 10^{-3}$  and  $1.4 \times 10^{-4}$  respectively.

Further insight into the Debye–Waller factor  $f(q)$  can be extracted if one were to focus on the effect of the pair potential. To this end, we first compare the exponent parameter  $\lambda$  given by (A16). For metallic Na we obtain  $\lambda = 0.687$ , which appears to be a reasonable value since the hard-sphere (Barrat *et al* 1989) (having an infinitely repulsive potential) and the Lennard-Jones (Bengtzelius 1986b) (having still large repulsive potential but less than the hard-sphere one) systems yield respectively 0.758 and 0.714. Although it is not the main purpose of this work, we find it worth while to mention that from  $\lambda$  it is possible to determine two critical parameters,  $0 < a < 1/2$  and  $0 < b \leq 1$ . The parameter  $a$  may be used to study the so-called  $\beta$  dynamics through a formula that can be shown to satisfy (Götze and Sjögren 1989b, Sjögren 1989, Götze 1990, 1991)

$$R(q, t) = f^{\text{BGS}}(q) + h^{\text{BGS}}(q)(t_0/t)^a \quad t_0 \ll t \ll \omega_\xi^{-1} \quad (8)$$

where  $t_0$  is a microscopic time scale, the correlator  $R(q, t)$  is that in (6) and  $\omega_\xi \propto |\xi|^{1/(2a)}$ . On the other hand the parameter  $b$  enters the  $\alpha$  relaxation process (Götze and Sjögren 1987a,

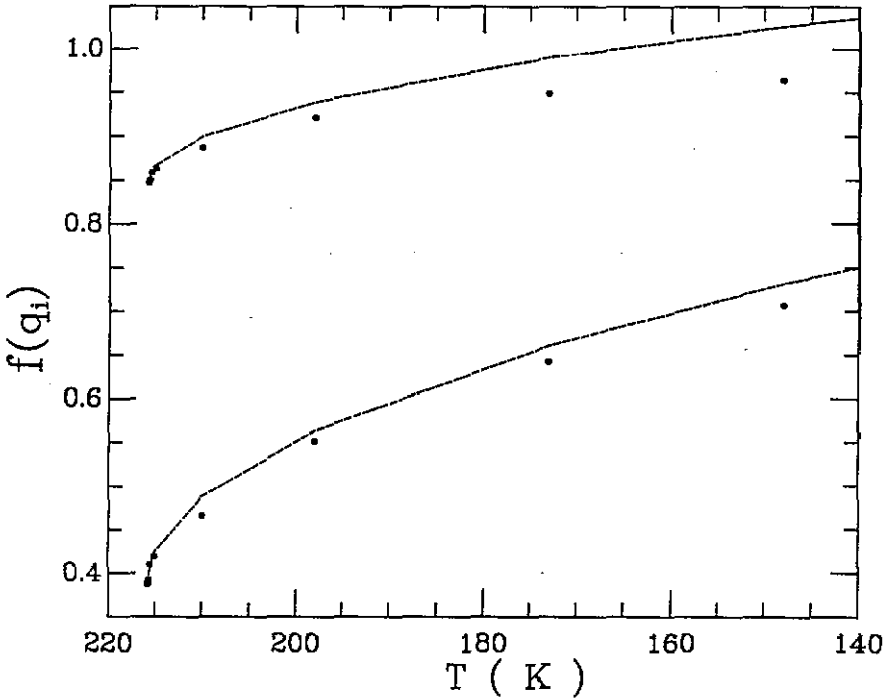


Figure 9. Non-ergodicity form factor  $f(q_i)$  (full circles) for the sodium element with  $q_i$  at the first peak (top) and at the first minimum (bottom) of  $S(q)$  compared with the asymptotic formula of Götze,  $f(q) = f^{\text{BGS}}(q) + 1.123h^{\text{BGS}}(q)\xi^{1/2}$  (broken curve).

Sjögren 1989, Sjögren and Götze 1991), which is ruled by a time scale  $\tau_\alpha$  defined by

$$\tau_\alpha \propto |\xi|^{-\gamma} \quad \gamma = 1/(2a) + 1/(2b) \quad \xi \rightarrow 0^- \quad (9)$$

For Na these critical exponents  $a$  and  $b$  are collected in table 1 along with those for the hard-sphere and the Lennard-Jones systems. It is gratifying to notice from this table that as the pair potential changes from an ideally infinite repulsive (hard-sphere system), to a still highly repulsive but weakly attractive (Lennard-Jones system), and to much softer repulsive part accompanied by long-range Friedel oscillations (liquid metal), these critical exponents vary systematically, implying the increasingly important role played by the interparticle interaction.

Table 1. Parameters  $\lambda$ ,  $a$  and  $b$  calculated from the present work for metallic Na compared with those of the hard-sphere (HS) and the Lennard-Jones (LJ) systems.

System	$\lambda$	$a$	$b$
HS	0.758	0.301	0.545
LJ	0.714	0.321	0.617
Na	0.687	0.332	0.663

Finally, it is of great theoretical interest to compare the spatial variation of the critical amplitudes for the hard-sphere and metallic systems. In  $r$ -space this system-dependent

quantity is given by

$$H(r) = \frac{1}{(2\pi)^3 n} \int dq S(q) h^{\text{BGS}}(q) e^{-iq \cdot r} \quad (10)$$

being the Fourier transform of  $S(q)h^{\text{BGS}}(q)$  (see (A17)). We depict in figure 10 the  $H(r)$  for both systems. A noticeable feature in this figure is that even for a realistic Coulomb system such as the liquid metal the  $\beta$  dynamics is also characterized only by a nearest-neighbour interaction. However, in contrast to the hard-sphere system, the behaviour of the metallic  $H(r)$  beyond the first-nearest neighbour is much less oscillatory. This is one manifestation of the realistic potential being described by a softer interparticle potential and contrasted to a typical hard-sphere potential being unrealistically 'hard'. As a consequence all fluctuations for  $r < 2.48\sigma$  move qualitatively in phase. But since  $H(r)$  vanishes rapidly for  $r > 2.48\sigma$  the physical picture that  $\beta$  relaxation is a localized excitation remains true also for a metallic system.

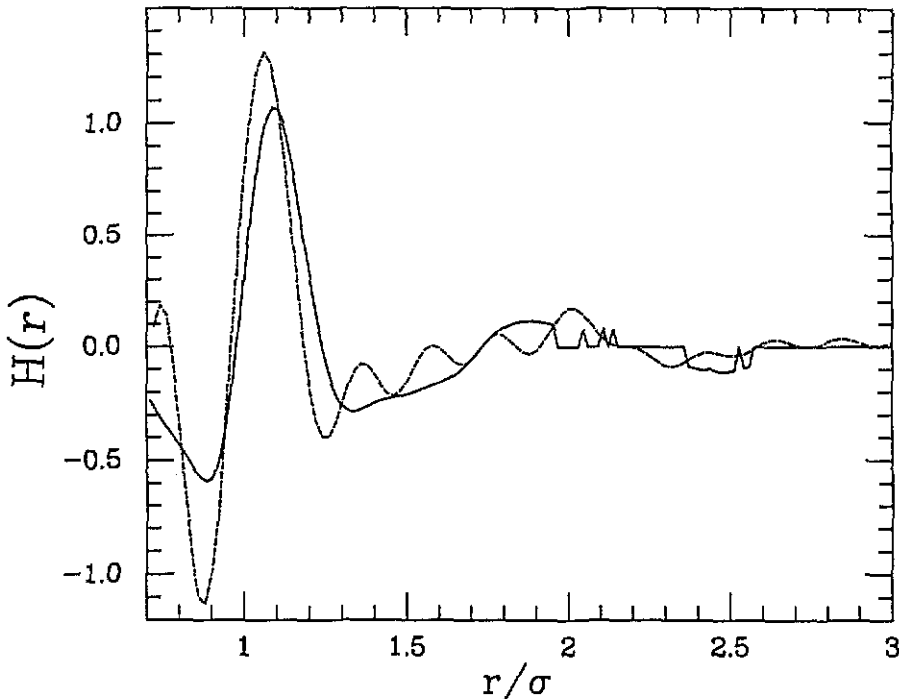


Figure 10. Spatial variation of the critical amplitude  $H(r)$  for the sodium element (full curve) compared with the same quantity for a hard-sphere system (broken curve). The hard-sphere diameter  $\sigma$  is related to the packing ratio  $\eta$  by  $\eta = \pi\sigma^3 n/6$ .

## 5. Conclusion

Starting with a full non-local model pseudopotential, we have applied the electron theory of a metal to construct a first-principles interatomic potential for Na liquid metal for use in

molecular-dynamics simulation. The pair correlation functions obtained are tested against experiments at the melting point and at an elevated temperature. Excellent agreement with x-ray measurements is found. This prompts us to extend the MD technique to study the undercooled liquid and glassy states of Na. To execute this program we need to know the temperature dependence of the density of Na. A novel method to estimate the density of the sodium system from the liquid via supercooling to the glassy phase is proposed. Basically this is an iterative scheme making use of the Wendt-Abraham structure parameter in conjunction with the experimental thermal linear expansion coefficient data of the Na crystalline state. We find that the pair correlation function simulated from quenching displays several features in accord with our previous simulation data using the Monte Carlo method and similar to those observed in laboratory glass experiments. From the calculated Wendt-Abraham structure parameter  $\mathcal{R}$  at various  $T$ , we obtain  $\mathcal{R}_{LG} = 0.105$  at  $T_g^{WA} = 189$  K, in agreement with our previously proposed hypothesis (Lai 1988a) for the universality of  $\mathcal{R}_{LG}$ . As an alternative to the determination of  $T_g$  we make use of the *same* MD structure data and insert them into the non-linear self-consistent integral equation of Bengtzelius *et al* (1984) for the time-dependent density fluctuation within the context of the mode-coupling theory. It turns out that the predicted glass transition point  $T_g^{BGS} = 215.78$  K is somewhat higher than  $T_g^{WA}$ . This difference in  $T_g$  is not unexpected if one recalls the basic hypothesis of the mode-coupling theory. Physically, the difference in the glass transition point can be further corroborated by referring to shear viscosity measurements. Based on the latter data, it appears that  $T_g^{WA}$ , determined directly from the structure data, is numerically much closer to the real glass transition temperature such as that defined in the calorimetric measurement. To proceed further we analyse the non-ergodicity form factor  $f(q)$  in light of Götze's prediction. The good agreement between our MD iterated  $f(q)$  and the asymptotic functional form of  $f(q)$  at two selected wavevectors versus  $T$  lends great credence to Götze's conjecture. The effects of the pair potential on  $f(q)$  are also discussed in the context of systematic change of the critical exponent parameters. These parameters, which contain information on the relaxation dynamics, are seen to change consistently as the repulsive part of the interparticle potential varies from an ideally infinite hard-sphere system to a softer metallic system. Finally comparison of the spatial critical amplitudes between the hard-sphere and sodium systems shows discernible differences, which can be interpreted physically to be related to the detail of structure.

### Acknowledgments

This work has been supported by the National Science Council under contract No NSC82-0208-M-008-060. We thank the Computer Center of the Department of Physics, National Central University, for support of computing facilities.

### Appendix

In this appendix we shall outline briefly the derivation of the asymptotic  $f(q)$ . Let us begin by writing the right-hand side of (5) as

$$\mathcal{F}_q(f(k)) = [m\beta S(q)/q^2]\Gamma(q, t \rightarrow \infty) \quad (A1)$$

where  $\mathcal{F}_q(f(k))$  is a functional of  $f(k)$ , which appears in the integral in (6). The iterative numerical method to solve (5) and (6) implies

$$f^{(i)}(q)/[1 - f^{(i)}(q)] = \mathcal{F}_q(f^{(i-1)}(k)) \quad i = 1, 2, \dots \quad (A2)$$



Götze examined the structure of (A2) and hypothesized the existence of a possible fixed point  $T_g^{\text{BGS}}$  such that close to  $T_g^{\text{BGS}}$  where  $f^{(i)}(q)$  approaches  $f(q)$  one can expand (A2) as

$$\mathcal{F}_q(f^{(i-1)}(k)) = \mathcal{F}_q(f(k)) + \sum_k \left( \frac{\partial \mathcal{F}_q}{\partial f^{(i-1)}(k)} \right)_{f^{(i-1)}(k)=f(k)} [f^{(i-1)}(k) - f(k)] + \dots \quad (\text{A3})$$

Introducing a  $g^{(i)}(q)$ , which satisfies

$$f^{(i)}(q) - f(q) = [1 - f(q)]^2 g^{(i)}(q) \quad (\text{A4})$$

we find that  $g^{(i)}(q)$  would be a small perturbation when the physical system is near the fixed point  $T_g^{\text{BGS}}$ . In fact it can be shown that in the vicinity of  $T_g^{\text{BGS}}$  (A2)–(A4) mutually agree provided that  $g^{(i)}(q)$  satisfies the following linearized evolution equation:

$$g^{(i)}(q) = \sum_k C_{qk} g^{(i-1)}(k) \quad (\text{A5})$$

where  $C_{qk} = [1 - f(k)]^2 \partial \mathcal{F}_q / \partial f(k)$ , which is a matrix having several properties. One important property is that all the matrix elements  $C_{qk}$  are non-negative. This latter property ensures that the matrix  $C_{qk}$  satisfies the theorems of Perron and Frobenius (Bellman 1960), which state that for a matrix  $C_{qk} \geq 0$  there exists a largest non-degenerate real eigenvalue  $E_0$  such that any other eigenvalue  $E_\gamma$ ,  $\gamma = 1, 2, \dots$ , of  $C_{qk}$  obeys the inequality

$$|E_\gamma| < E_0. \quad (\text{A6})$$

Since the largest eigenvalue is non-degenerate, the corresponding left- and right-hand eigenvectors, denoted by  $\hat{l}_k$  and  $l_k$  respectively,

$$\sum_k C_{qk} l_k = E_0 l_q \quad (\text{A7})$$

$$\sum_q \hat{l}_q C_{qk} = E_0 \hat{l}_k \quad (\text{A8})$$

are uniquely determined up to an additive constant. Götze called  $C_{qk}$  a stability matrix because the unique (maximum) eigenvalue sets a necessary and sufficient condition for searching for the solution. For the other properties, the interested reader is referred to the original works of Götze (1985, 1986, 1987).

To make further progress, we take temperature to be our control parameter. Varying the temperature and by appealing to (5), the found solution  $f^{(i)}(q)$  suffers a corresponding change which, from (A4),  $\delta f = [1 - f(q)]^2 g(q)$ , permits a straightforward derivation of the following equation:

$$\sum_k (\delta_{qk} - C_{qk}) g(k) = -[1 - f(q)] g^2(q) + \sum_{k', k''} g(k') C_{q, k', k''} g(k'') + \frac{\delta T}{T} C_q + O(g^3, (\delta T)^2, g \delta T). \quad (\text{A9})$$

Here  $C_q = T(\partial \mathcal{F}_q / \partial T)_{f(k)}$  and  $C_{q, k', k''} = [\partial^2 \mathcal{F}_q / \partial f(k') \partial f(k'')]_T$ . Equation (A9) constitutes a basic formula for solving (A2) asymptotically. To obtain an asymptotic  $f(q)$ , let us define a separation parameter

$$\xi = (T_g^{\text{BGS}} - T) / T_g^{\text{BGS}} \quad (\text{A10})$$

and expand

$$g(q) = g^{(1)}(q)\xi^{1/2} + g^{(2)}(q)\xi. \quad (\text{A11})$$

By virtue of (A10) and (A11), (A9) can be written in ascending powers of  $\xi^{1/2}$ . The coefficients of  $\xi^{1/2}$  and  $\xi$  lead respectively to two equations, viz.

$$\sum_k (\delta_{qk} - C_{qk}^{\text{BGS}}) g^{(1)}(k) = 0 \quad (\text{A12})$$

$$\sum_k (\delta_{qk} - C_{qk}^{\text{BGS}}) g^{(2)}(k) = -[1 - f^{\text{BGS}}(q)][g^{(1)}(q)]^2 + \sum_{k',k''} g^{(1)}(k') C_{q,k',k''}^{\text{BGS}} g^{(1)}(k'') + \xi C_q^{\text{BGS}}. \quad (\text{A13})$$

In the above equations, we have designated appropriate quantities at the critical point by the superscript BGS. From (A12) we see that  $g^{(1)}(k)$  is an eigenvector of the stability matrix  $C_{qk}^{\text{BGS}}$  corresponding to the largest eigenvalue  $E_0^{\text{BGS}} = 1$ . Since this eigenvalue is non-degenerate it is possible to write

$$g^{(1)}(q) = \alpha l_q^{\text{BGS}} \quad (\text{A14})$$

where  $\alpha$  is a parameter that can be shown from (A13) to read

$$\alpha^2 = \left( \sum_q \hat{l}_q^{\text{BGS}} C_q^{\text{BGS}} \right) / (1 - \lambda) \quad (\text{A15})$$

and

$$\lambda = \sum_{q,k',k''} \hat{l}_q^{\text{BGS}} C_{q,k',k''}^{\text{BGS}} \hat{l}_{k'}^{\text{BGS}} \hat{l}_{k''}^{\text{BGS}}. \quad (\text{A16})$$

Accordingly (A4), (A11) and (A14) yield

$$f(q) = f^{\text{BGS}}(q) + \alpha[1 - f^{\text{BGS}}(q)]^2 l_q^{\text{BGS}} \xi^{1/2} = f^{\text{BGS}}(q) + \alpha h^{\text{BGS}}(q) \xi^{1/2} \quad (\text{A17})$$

which is the formula sought.

## References

- Abraham F F 1980 *J. Chem. Phys.* **72** 359  
 Barrat J L, Götze W and Latz A 1989 *J. Phys.: Condens. Matter* **1** 7163  
 Beeman J 1976 *J. Comput. Phys.* **20** 130  
 Bellman R 1960 *Introduction to Matrix Analysis* (New York: McGraw-Hill) pp 276-301  
 Bengtzelius U 1986a *Phys. Rev. A* **33** 3433  
 — 1986b *Phys. Rev. A* **34** 5059  
 Bengtzelius U, Götze W and Sjölander A 1984 *J. Phys. C: Solid State Phys.* **17** 5915  
 Bengtzelius U and Sjögren L 1986 *J. Chem. Phys.* **84** 1744  
 Borgstedt H U and Mathews C K 1987 *Applied Chemistry of the Alkali Metals* (New York: Plenum) p 21  
 Börjesson L, Elmroth M and Torell L M 1990 *Chem. Phys.* **149** 209  
 Brawer S A 1985 *Relaxation in Viscous Liquids* (Columbus, OH: American Ceramic Society)  
 Buchalla G, Dersch U, Götze W and Sjögren L 1988 *J. Phys. C: Solid State Phys.* **21** 4239  
 Champeney D C and Sedgwick D F 1972 *J. Phys. C: Solid State Phys.* **5** 1903

- Das S P 1987 *Phys. Rev. A* **36** 211
- Das S P and Marzenko 1986 *Phys. Rev. A* **34** 2265
- Davis P J and Polonsky I 1972 *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables* ed M Abramowitz and I A Stegun (New York: Dover) p 875
- Elliott S R 1984 *Physics of Amorphous Materials* (London: Longman) pp 23–38
- Elmroth M, Börjesson L and Torell L M 1992 *Phys. Rev. Lett.* **68** 79
- Frick B, Farago B and Richter D 1990 *Phys. Rev. Lett.* **64** 2921
- Fuchs M, Götze W, Hildebrand S and Latz A 1992 *Z. Phys. B* **87** 43
- Götze W 1985 *Z. Phys. B* **60** 195
- 1986 *Phys. Scr.* **34** 66
- 1987 *Amorphous and Liquid Materials* ed E Lüscher, G Fritsch and G Jacucci (Dordrecht: Nijhoff) p 34
- 1990 *J. Phys.: Condens. Matter* **2** 8485
- 1991 *J. Non-Cryst. Solids* **131/133** 161
- Götze W and Sjögren L 1987a *J. Phys. C: Solid State Phys.* **20** 879
- 1987b *Z. Phys. B* **65** 415
- 1989a *Dynamics of Disordered Materials* ed D Richter, A J Dianoux, W Petry and J Teixeira (Berlin: Springer) p 18
- 1989b *J. Phys.: Condens. Matter* **1** 4183
- 1992 *Rep. Prog. Phys.* **55** 241
- Huijbin M J and van der Lugt W 1979 *Acta Crystallogr. A* **35** 431
- Jäckle J 1989 *J. Phys.: Condens. Matter* **1** 267
- Kimura M and Yonezawa F 1983 *Topological Disorder in Condensed Matter* ed F Yonezawa and T Ninomiya (Berlin: Springer) pp 80–110
- Lai S K 1988a *J. Phys. F: Met. Phys.* **18** 1663, and references therein
- 1988b *Mater. Sci. Eng.* **97** 187
- Lai S K, Chou M H and Chen H C 1993 *Phys. Rev. E* at press
- Lai S K and Lin M S 1990 *J. Non-Cryst. Solids* **117/118** 907
- Lai S K, Wang S and Wang K P 1987 *J. Chem. Phys.* **87** 599
- Leutheusser E 1984 *Phys. Rev. A* **29** 2765
- Lewis L J 1991 *Phys. Rev. B* **44** 4245
- Li D H, Li X R and Wang S 1986 *J. Phys. F: Met. Phys.* **16** 309
- Li D H, Moore R A and Wang S 1988 *J. Chem. Phys.* **88** 2700, **89** 4309
- Mezei F, Knaak W and Farago B 1987a *Phys. Rev. Lett.* **58** 571
- 1987b *Phys. Scr.* **T19** 363
- Nóse S and Yonezawa Y 1985 *Solid State Commun.* **56** 1005
- Owen A E 1985 *Amorphous Solids and the Liquid State* ed N H March, R A Street and M P Tosi (New York: Plenum)
- Shen T, Wang J T and Wang S 1990 *J. Non-Cryst. Solids* **117/118** 559
- Sjögren L 1989 *Phys. Scr.* **T29** 282
- Sjögren L and Götze W 1991 *J. Non-Cryst. Solids* **131/133** 153
- Sjölander A 1980 *Liquid and Amorphous Metals* ed E Lüscher and H Coufal (Netherlands: Sijthoff and Noordhoff) pp 63–100
- 1985 *Phys. Scr.* **32** 314
- 1989 *Physica B* **156/157** 177 and references therein
- Taborek P, Kleiman R N and Bishop D J 1986 *Phys. Rev. B* **34** 1835
- Tanaka M 1981 *Proc. 4th Int. Conf. on Rapidly Quenched Metals* (Amsterdam: North-Holland) p 297
- 1982 *J. Phys. Soc. Japan* **51** 3802
- 1986a *J. Phys. Soc. Japan* **55** 2970
- 1986b *J. Phys. Soc. Japan* **55** 3428
- Tanaka S and Ichimaru S 1987 *Phys. Rev. A* **35** 4743
- Van Meegen W and Pusey P N 1991 *Phys. Rev. B* **43** 5429
- Wang S and Lai S K 1980 *J. Phys. F: Met. Phys.* **10** 2717
- Watanabe M S and Tsumuraya K 1988 *J. Chem. Phys.* **88** 1991
- Wendt H R and Abraham F F 1978 *Phys. Rev. Lett.* **41** 1244
- Yip S 1989 *J. Stat. Phys.* **57** 665
- Zallen R 1983 *The Physics of Amorphous Solids* (New York: Wiley-Interscience)