

## THE CALCULATIONS OF THE PAIR DISTRIBUTION FUNCTIONS FOR FLUID ARGON USING STRUCTURAL DIFFUSION MODEL

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We have used the Structural Diffusion Models (SDM) to calculate the pair distribution function, for fluid argon. A general recipe is developed for analysing structural data by such models. First, we analyse fluid argon in terms of the local Structural Diffusion Model (SDM1). The SDM parameters obtained by constrained optimization describe the dependence of the pair distribution on density and temperature. Second, we use an extended version of the model (SDM2) and it enables us to obtain a refined fitting through a built in contraction function  $f(r)$ . A simple choice for  $f(r)$  in the model expression of  $g(r)$ , applied the two dense lattices, gives an improved fit for high densities. The best results are obtained with the hcp lattice.

(Received May 24, 2002; accepted June 7, 2002)

*Keywords:* Fluid argon, Structural diffusion model, Pair distribution function

### 1. Introduction

The Structural Diffusion Model (SDM) has been used in recent years to describe the structure of disordered systems such as amorphous solids and liquids [1-7]. The main aspect of the theory of SDM involves characterizing the local spatial arrangements of atoms in terms of an ordered structure in the simplest case represented by a lattice [8], and viewing the disorder as due to a spatial decay of coherence between local structure.

The study of the structure of systems in terms of the SDM can be useful in several respects [9].

- a) The models provides a fit of  $g(r)$  data for real systems by concise analytical expressions related in a simple manner to the local atomic configurations. In this respect it is of interest to compare the SDM with the recently developed Reverse Monte Carlo (RMC) approach [10]. Although the RMC produces a more detailed picture of typical atomic configurations in space, the SDM is computationally far more economical. In this sence the two approaches can be viewed as complementary.
- b) The SDM parametrization allows a very concise description of the variation of  $g(r)$  over a whole range thermodynamic states, thus providing new valuable information on atomic and structural correlations.
- c) The SDM can be used to describe accurately the structure of amorphous solids, a regime where the statistical theory of liquids is not applicable.
- d) The SDM is capable of generalization providing detailed information on the triplet and higher order distribution functions [11].

Presently, we concentrate on aspects (a) and (b) in our study of SD models. We use for this purpose the extensive  $g(r)$  molecular-dynamic (MD) data of fluid argon [12]. The data are analysed using two versions of the SDM. The first [8], denoted SDM1, includes two structure parameters, the coefficient of *structural diffusion*,  $D$ , and the average distance of closest approach,  $r_o$ . The second version [13], denoted SDM2, includes an additional *contraction function*,  $f(r)$ , and an associated

parameters, related to a nonzero first-moment term in the spatial Fokker-Planck type equation. This work provides the first extensive set of calculations using SDM2.

Following previous works on amorphous systems [1-4,6,7], our aim is to find the simplest lattice which leads to a physically comprehensive description of the fluid structure. We examine a set of different lattices in order to find an optimal lattice for each phase of the fluid.

Our analysis consists of an optimization procedure using a quasi-Newtonian method [14] including steepest descents. The optimization functions involve differences between model calculated and experimental  $g(r)$ . They are constructed so as to give special weights to regions where a fit of  $g(r)$  values is most difficult to achieve.

In this work, we present a summary of the SD models used in section 2. We discuss in detail the procedure used the result obtained using both the SDM1 and SDM2 for a number of lattices are presented in section 3. Finally we discuss briefly the results obtained in section 4.

## 2. Theory

The SDM assumes that the local configuration, i.e., the relative position of a small group of neighbouring atoms, can always be well approximated by a suitable domain in an ordered structure specified by a lattice,  $L$ . Further, the spatial disorder is introduced as a random relative displacement of the locally observed lattice structures at different process in *structure space*.

The resulting expression for the pair distribution function,  $g(r)$ , has the form of a theta-type infinite series,

$$\rho g(r) \equiv G(r) = \sum_v G_v(r) = \sum_v \rho C_v \exp(-Wb_v^2) \frac{\sin(b_v r)}{b_v r} \quad (1)$$

Here the sum extends over all points (shells) of the reciprocal lattice  $L^* = \{b_v\}$ ,  $\rho$  is the density and  $C_v$  is a unit cell structure factor given by  $C_v = C(b_v)$ , where

$$C(k) = \left| \frac{1}{n_v} \sum_{\mu} \exp(i\vec{k} \cdot \vec{a}_{\mu}) \right| \quad (2)$$

with the sum in eq. (2) extending over the  $n_v$  points in the unit cell.

A Poisson transformation of (1) leads to an equivalent expression in terms of a real space lattice sum:

$$\rho g(r) = \frac{1}{\sqrt{4\pi W}} \sum_{\mu} (4\pi r a_{\mu})^{-1} \left\{ \exp\left[\frac{-(r-a_{\mu})^2}{4W}\right] - \exp\left[\frac{-(r+a_{\mu})^2}{4W}\right] \right\} \quad (3)$$

where  $\rho$  is the number density and  $a_{\mu}$  is a distance to a point in the  $\mu$ th shell. representations of  $g(r)$  are used in our computations. Equation (1) converges rapidly for large  $r$ , whereas (3) does so for small  $r$ . Equations (1) and (3) definite SDM1.

$W = W(r) > 0$  serves as a *width function* which is a measure of the decay of coherence between local structures at two localities separated by a distance  $r$ .  $W(r) \approx Dr$  when  $r \rightarrow \infty$  and  $W(r) \rightarrow 0$  when  $r \rightarrow 0$ . The simplest choice of  $W(r)$ , which will be used below, which is consistent with  $W(r) \approx Dr$  and satisfies the asymptotic behaviour of  $g(r)$ , is given by

$$W(r) = \begin{cases} D(r-r_o) & r > r_o \\ 0 & r \leq r_o \end{cases} \quad (4)$$

where  $r_o$  is the average exclusion parameter.

In a refined model [13], equations (1) and (3) contain an extra structure function  $f(r)$ , which takes care of the finer details of  $g(r)$ .  $f(r)$  is expected to be a positive function of  $r$ , with

asymptotic behaviour  $f(r) \rightarrow 0$  when  $r \rightarrow \infty$  and  $g(r) \rightarrow 1$  when  $r \rightarrow \infty$ . The contraction function enables an inhomogeneous change in the initial position of the SDM1 peaks of  $g(r)$  resulting from the assumed local lattice. In this refined model  $g(r)$  has the following two equivalent representations

$$g(r) = \sum_{\nu} C_{\nu} \exp(-Wb_{\nu}^2) \frac{\sin b_{\nu}(r + f(r))}{b_{\nu}(r + f(r))} \quad (5)$$

and

$$g(r) = \frac{1}{\sqrt{4\pi W}} \sum_{\mu} (4\mu a_{\mu})^{-1} \left\{ \exp\left[\frac{-(r - a_{\mu} - f(r))^2}{4W}\right] - \exp\left[\frac{-(r + a_{\mu} + f(r))^2}{4W}\right] \right\} \quad (6)$$

Equations (5) and (6) define SDM2. The analysis of  $g(r)$  fitted with SDM2, suggests the following simple functional form for  $f(r)$

$$f(r) = \frac{a}{r} \quad (7)$$

where  $a$  is the contraction parameter.

The fitting of experimental data within the SDM is obtained through optimization by a quasi-Newtonian method [14] including steepest descent. We have used the following general optimization function

$$S_{opt}(\vec{p}, n, m) = \sum_{i=1}^N |\Delta g_{i opt}|^n r_i^m \quad (8)$$

where  $\Delta g_{i opt} = g_{SDM}(r_i, \vec{p}) - g_{exp}(r_i)$  is the vertical distance between  $g_{exp}(r_i)$  and  $g_{SDM}(r_i, \vec{p})$ , the experimental and SDM pair distribution function, with a vector of parameters  $\vec{p}$ , respectively. The sum in (8) extends over the values  $g_{exp}(r_i)$  at  $N$  different points  $r_i$ . The function  $S_{opt}$  gives different importance in the minimization procedure to the vertical distance  $\Delta g_{i opt}$  and to the different  $r_i$  regions depending on the choice of  $n$  and  $m$ . Large  $n$  enhances the importance of large  $\Delta g_{i opt}$  differences irrespective of  $r$ . Large  $m$  gives greater importance to  $\Delta g_{i opt}$  differences in the large  $r$  range. Thus, by choosing different values of  $n$  and  $m$  we can force the model to fit  $g(r)$  in the more problematical regions.

### 3. Results

In all our calculations we have used reduced units; thus reduced temperature and density,

$$\rho^* \cong \rho \sigma^3, \quad T^* \cong \frac{k_B T}{\varepsilon} \quad (9)$$

Other reduced parameters,

$$r^* \cong \frac{r}{\sigma}, \quad r_o^* \cong \frac{r_o}{\sigma}, \quad D^* \cong \frac{D}{\sigma}, \quad W_o^* \cong \frac{W_o}{\sigma^2} \quad (10)$$

where  $\sigma$  and  $\varepsilon$  denote, respectively, the zero position and well depth of the potential for which we have the respective argon values, namely  $\sigma = 3.405 \text{ \AA}$  and  $\varepsilon = 119.8 k_B \text{ erg}$ .

In this work we analyse data obtained through the MD simulation by Verlet [11] for a Lennard Jones potential with parameters appropriate for argon. The simulation results were found in good agreement [14, 15], with experimental data obtained from neutron and X-ray scattering experiments and other simulations. Thus we treat them as experimental results. In general, the results using SDM1 do not give a fit as good as the results obtained using SDM2. So only those aspects which have some bearing on the analysis of SDM2 results are presented in detail.

Table 1 shows that unit cell description of the lattices used in the optimization process. Also Table 2 shows that statistical parameters for different lattice types.

Table 1. Unit cell description of the lattices use in the optimization process.

Lattice type	Cartesian coordinates Of the unit cells	Number of inner points ( $nv$ )	Cartesian coordinates The inner points of the unit cell ( $sv$ )	Lattice density ( $\rho_{LAT}$ )
Hexagonal close packed ( <i>HCP</i> )	$av1 = (1.000, 0.500, 0)$ $av2 = (0, 0.866, 0)$ $av3 = (0, 0, 1.633)$	2	$sv 1 = (0, 0, 0)$ $sv 2 = (0.333, 0.333, 0.500)$	1.414
Distorted face centered close packed ( <i>FCC</i> )	$av1 = (2.438, 0, 0)$ $av2 = (0, 2.438, 0)$ $av3 = (0, 0, 2.475)$	1	$sv 1 = (0, 0, 0)$	1.346

Table 2. The results of the structural parameter of the optimization procedure for SDM1 and SDM2 (All these parameters are reduced units).

Lattice type	State no	$\rho$	$T$	<i>SDM 1</i>		<i>SDM 2</i>		
				$D$	$r_0$	$D$	$r_0$	$a$
Hexagonal close packed ( <i>HCP</i> )	1	0.880	0.591	0.0104	0.477	0.0124	0.667	0.0478
	2	0.450	2.934	0.0696	-0.899	0.0700	0.552	0.1800
Distorted face centered close packed ( <i>FCC</i> )	1	0.880	0.591	0.00578	0.237	0.0088	0.659	0.0467
	2	0.450	2.934	0.0672	-0.803	0.0700	0.597	0.1860

In Figs. 1 and 2, the  $g(r)$  obtained using the HCP and distorted FCC lattices at the same thermodynamic state,  $\rho = 0.88$  and  $T = 0.591$ . Also in the same figures show the SDM1 and SDM2 pair distribution functions for fluid Argon which are compare to the simulation data. In both cases there are problems with the fit of the first peak, which is lower and slightly shifted towards higher  $r$  values vis-a-vis the experimental data. It can be seen that the HCP fitting is marginally better in that the oscillations of  $g(r)$  follow closely the experimental, whereas the distorted FCC results exhibit a small degree of phase difference.

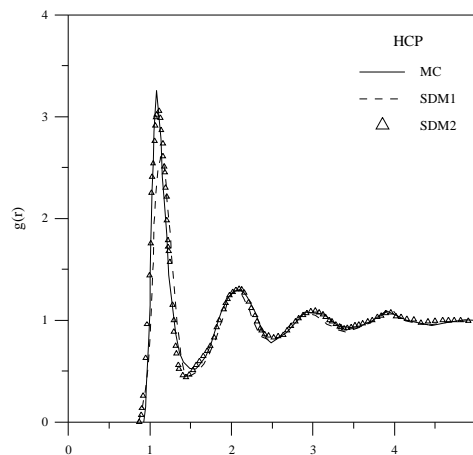


Fig. 1. Pair distribution function for fluid argon,  $\rho^* = 0.88$  and  $T = 0.591$ , using a local HCP lattice.

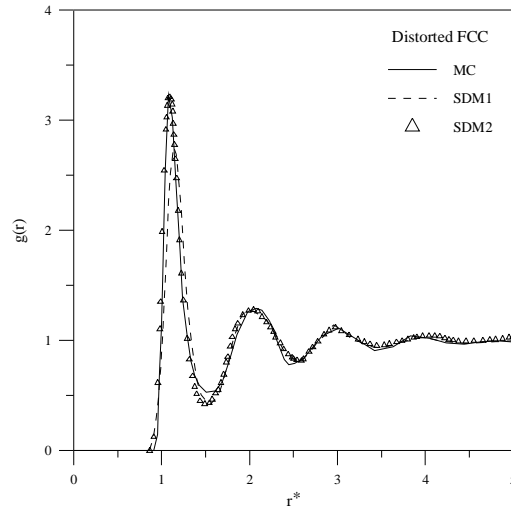


Fig. 2. Pair distribution function for fluid argon,  $\rho = 0.88$  and  $T = 0.591$ , using a local distorted FCC lattice.

In the light of the results obtained within SDM1, calculations were performed only with the more dense packed lattices, namely FCC, distorted FCC and HCP. In order to keep the optimization process within reasonable bounds the search for the optimum structural parameters was restricted to the following range of values;  $0 < D < 0.07$ ,  $-1.0 < r_o < 1.0$  and  $-1.0 < a < 2.0$ . The quality of fit for different local lattices follows the same trend as SDM1. However, as we shall see below, optimum results lead only approximately to a good fit of  $g(r)$ . As a general trend we note that higher densities and lower temperatures improve the fit of  $g(r)$ .

We now turn to The SDM2 pair distribution functions, shown in Figs. 1, and 2. Results are presented for  $g(r)$  at two different thermodynamic states obtained by using local HCP and distorted FCC lattices. The results at the high density-low temperature thermodynamic state, the sum figures exhibit a very good fit of the simulation results. Overall, the fit obtained using the HCP local lattice is quantitatively marginally better than that obtained using this distorted FCC local lattice. Noting the small unphysical shoulder appearing in the high  $r$  side of the first minimum of  $g(r)$  obtained with the HCP, one can argue that the distorted FCC is qualitatively more reliable.

The results obtained for the low density-high temperature thermodynamic state presented in Fig. 3 might suggest that the simple form  $f(r) = a/r$  the contraction function has to be modified.

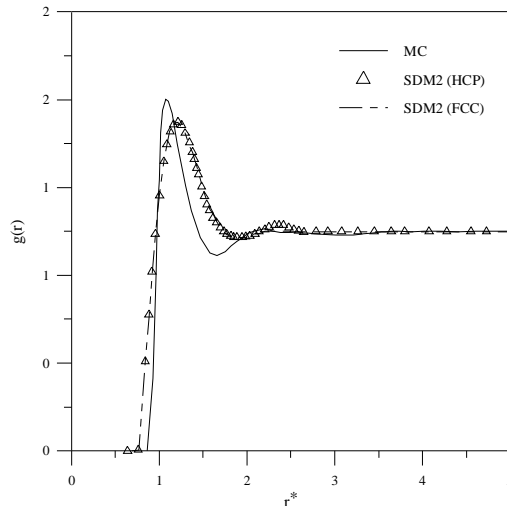


Fig. 3. Pair distribution function for fluid argon,  $\rho = 0.45$  and  $T = 2.934$ .

#### 4. Discussion

In the preceding sections we have presented the results of fitting experimental data of fluid argon using a simple approach to the physical modelling of liquid structure. This model is based on physically meaningful concepts which provide a unified scheme for specifying the liquid structures of the system of interest. In the present work we have carried out a systematic study of the choice for suitable local lattices to describe structures within the SDM for a given thermodynamic state.

The results of the work may point to deficiencies in both SDM1 and SDM2 in the description of the expanded liquid, low densities and high temperatures. Extended calculations carried out with an improved version of SDM suggest that the fit of overall data could be carried out with the same degree of reliability as the SDM2 fit of the high density states.

This generalized SDM is still computationally inexpensive when compared to Monte Carlo techniques, and likewise the latter is capable of providing a three dimensional snapshot description of the arrangements of the molecules in the liquid state.

#### Acknowledgement

We thank Shalom Baer and Moises Silbert for useful discussions.

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