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# Atomic transport properties in barium oxide using a Tersoff potential

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We present a theoretical study of transport properties in barium oxide, by a three body potential of Tersoff. The structural properties are also predicted by Variational Hypernetted Chain (VMHNC) liquid state theory. The dynamic and atomic transport properties of BaO have been studied with the viscoelastic model approximation to compute both single-particle and collective time-dependent properties. The mean-square displacement, the velocity autocorrelation function and the intermediate scattering functions have calculated and then used to compute the diffusion constant at different temperatures. There are no experimental values of the diffusion coefficients for BaO, but the values calculated our results by several independent routes are mutually consistent. For comparison, the calculations are also performed using the rigid ion model potentials.

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## 1. Introduction

Atomic transport plays an important role in molten alkaline earth and metal oxides. The study of diffusion in these systems is a great interest because of various scientific and technological reasons. The knowledge of diffusion coefficients plays important role in design of metallurgical and solidification processes such as in casting industry. The transport properties of liquids or molten salts, together with structural and thermodynamic information, can provide experimental basis for theories of the liquid state. The self-diffusion in the liquid state is different than that in the solid state in a sense that it does not require the presence of defects like vacancies and interstitials. One of the interesting systems which are studied on is the alkaline earth oxides.

The alkali-earth oxides are compounds which have technological applications ranging from catalysis to microelectronics. They are important constituents of the Earth's lower mantle and their properties under very high pressures have been studied intensively. Furthermore, they have studied for testing the semi-empirical theories or *ab initio* calculations. Thus, a variety of theoretical and experimental studies of their properties is actually available in the literature. Metal oxides are frequently used in several important technological applications. For systematic progress in these areas, researchers are interested in oxide characteristics during the past decade [1-4]. It is well known that most of them crystallize in either the cubic zinc-blende or the hexagonal wurtzite structure (or both) where each anion is surrounded by four cations at the corners of a tetrahedron and vice versa. This is tetrahedral coordination and materials also have a substantial degree of ionic character, as indicated by the Phillips ionicities [5]. The more ionic semiconductors have the wurtzite structure instead of the zinc-blende. The really ionic materials are for example, MgO and SrO [6,7]. Among them, barium oxide is a very interesting and useful material with a variety of applications, most notably perhaps, in high current density cathodes [8]. Most potentials for oxides and halides have been based on the assumption of the fully ionic model [9] for a discussion of this assumption, with ionic polarisability treated by the shell model of Dick and Overhauser [10], and with central-force, pair wise short-range potentials most commonly the Born-Mayer potential. Further evidence polarizable ion model also has been studied for alkaline earth oxides or metal oxides [11,12]. Up to know the ionic potentials have been used to describe the microscopic mechanisms of ionic conduction of BaO using molecular dynamics simulation and integral equation theories. It has been found that the theoretical approach is difficult to extend to describe the structure and the physical properties of more complex liquids, such as non-ideal ionic melts. Molten BaO are included in this category. Another point of view has been developed on semi-empirical model potentials for alkaline earth oxides by Benkabou and co-workers [7]. They have been interested in testing the transferability of a three-body empirical potential model, (Tersoff potential (TP) [13]) for SrO. They have concluded that an empirical three body potential with MD method reproduces well the structural properties of alkaline earth oxides in their different high pressure phases except BaO.

In our previous work, we have successfully applied the Tersoff potential for structural properties of CuI [14], CuBr, CuCl [15] using the integral equation theories. It is motivated us to apply the Tersoff potential for BaO.

In this paper we present the structural, dynamical and thermal properties of BaO in the liquid structure, using the empirical interatomic potentials of Tersoff, which include the three-body interatomic interactions [13]. According to our knowledge, no structural calculations have been performed on BaO using Tersoff Potentials coupled with integral equations. The main point of the present work is the test of the transferability of semi-empirical potential models to predict structural properties of molten BaO coupled with integral equations. For this purpose, first we have calculated the inter-ionic interactions for BaO using three-body Tersoff Potential model which is used as input data in its structural calculations with the variational modified hypernetted chain (VMHNC) integral equation theory. Then, this potential accuracy has been tested in the structural calculations for BaO at different temperatures. The computed pair distribution functions of BaO have been compared with those obtained by Buckingham inter-ionic potential. We have shown that the Tersoff Potential can be applied to BaO successfully.

## 2. Theory

### 2.1 Semi empirical potential: Tersoff Potential

Among the many empirical model potentials that have been developed for tetrahedral semiconductors, that of Tersoff has been applied to many of the semiconductors successfully. The interatomic potential is taken to have the form as [13]

$$E = \sum_i E_i = \frac{1}{2} \sum_{i \neq j} V_{ij} \quad , \tag{1}$$

$$V_{ij} = f_C(r_{ij})[a_{ij}\ f_R\ (r_{ij}) + b_{ij}\ f_A\ (r_{ij})], \tag{2}$$

where E is the total energy of the system, which is decomposed for convenience into a site energy $E_i$ and band energy $V_{ij}$. The indices i and j ion over the atoms of the system and $r_{ij}$ is the distance from atom i to atom j. The function $f_R$ represents a repulsive potential and $f_A$ represents an attractive pair potential associated with bonding given as

$$f_R(r) = A\exp(-\lambda_1 r)\,, \tag{3}$$

$$f_A(r) = -B\exp(-\lambda_2 r)\,. \tag{4}$$

The term $f_c$ is merely a smooth cut of function to limit the range of potential taken as,

$$f_C(r) = \begin{cases} 1 & r < R - D \\ \frac{1}{2} - \frac{1}{2}\sin\left[\frac{\pi}{2}\frac{(r-R)}{D}\right] & R - D < r > R + D \\ 0 & r > R + D \end{cases} \tag{5}$$

where $b_{ij}$ is the many-body order parameter describing how the bond-formation energy is affected by local atomic arrangement due to the presence of other neighboring atoms (the k atoms). It is a many-body function of the positions of atoms i, j and k given as

$$b_{ij} = \left(1 + \beta^n \zeta_{ij}^n\right)^{-1/2n}, \tag{6}$$

$$\zeta_{ij} = \sum_{k(\neq i,j)} f_C(r_{ik})\, g(\theta_{ijk}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3]\,, \tag{7}$$

$$g(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos\theta)^2}\,, \tag{8}$$

$$a_{ij} = (1 + \alpha^n \eta_{ij}^n)^{-1/2n}\,, \tag{9}$$

$$\eta_{ij} = \sum_{k(\neq i,j)} f_C(r_{ik}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3]\,, \tag{10}$$

where $\zeta$ is defined as the effective coordination number and $g(\theta)$ is a function of the angle between $r_{ij}$ and $r_{ik}$. Following others [14], we assume that $\lambda_3$ and $\alpha$ are maintained to be zero, thus $a_{ij}$=1. Other adjustable fitting parameters, A, B, n, c, d, h, $\lambda_1$ and $\lambda_2$ are determined by fitting to the cohesive properties of the material.

### 2.2 Liquid State Theory

With the effective pair potential known, integral equations are able to provide us the liquid structure for metals and alloy. In our structural calculations, one of the integral equation theories which have shown very reliable theory of liquids VMHNC has been carried out [16-18]. Like most liquid state theories the VMHNC is solved the Ornstein – Zernike (OZ) equation by the MHNC exact closure relation. Thus, the partial direct correlation functions, $c_{ij}(r)$, in terms of the total correlation functions $h_{ij}(r)=g_{ij}(r)-1$ , where $g_{ij}(r)$ denote the partial pair distribution, can be obtained. The pair distribution function can be given in terms of Ashcroft-Langreth partial structure factor as,

$$g_{ij}(r) = 1 + \frac{1}{8\pi^3 (\rho_i \rho_j)^{1/2}} \int (S_{ij}(q) - \delta_{ij}) \exp(iqr) dq \tag{11}$$

### 2.3 Dynamic Properties

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 [19,20]. Thus the self-diffusion coefficient is Green-Kubo relation as

$$D = \frac{k_B T}{m} \int_0^\infty Z(t) dt \tag{12}$$

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

$$\dot{Z}(t) = -\int_0^t K(t - t') Z(t') dt' \tag{13}$$

where the dot means time derivative of the normalized velocity autocorrelation function. The memory function may be split into two contributions [21],

$$K(t) = K_B(t) + K_{MC}(t) \tag{14}$$

which represent two distinct dynamical regimes in the atomic dynamic of a liquid. The first term comprises all the fast decay channels. $K_B(t)$ is supposed to represent the effect of a binary collision between a targed particle and another one from its environment whereas the second term, $K_{MC}(t)$ is the mode coupling contribution, incorporates the contribution from the collective processes associated with multiple collisions. 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 which

besides of incorporating to correct short time behavior also allows the computation of from the static structural function only. The mean square displacement of atoms in our calculations can be easily computed from its definition:

$$MSD = \{r(t) - r(0)\}^2 . \quad (15)$$

The well known parameter in atomic dynamics is the intermediate scattering function F(q,t) which is fourier transform of dynamic structure factor given in [20-22 ].

## 3. Results and discussion

Firstly, we have presented structural properties of liquid BaO obtained by Tersoff Potential (TP) and Buckingham ionic potentials (BP). In the present work, the all parameters of TP functions used in structural calculations are determined by fitting to cohesive energy and taking into account for the cut-off procedure together with the VMHNC liquid state theory. The adjusted potential parameters for Tersoff Potential are presented in Table 1. The BP potential parameters are taken from Harris and co-workers [23].

*Table 1. The adjusted TP parameters for BaO.*

| | | | |
|---|---|---|---|
| A(eV) | 811.938 | β | $1.5724*10^{-7}$ |
| B(eV) | 18.906 | c | 121390 |
| $\lambda_1(A^{-1})$ | 2.1292 | d | 14.217 |
| $\lambda_2(A^{-1})$ | 0.7314 | R(A) | 8.525 |
| n | 0.7245 | D(A) | 0.85 |
| h | -5.7058 | | |

In Fig. 1, we present our VMHNC results of g(r) used TP and BP potentials for BaO at 1600 K. We notice that the position of the main peak of g(r) obtained by semi-empirical potentials are almost the same. The amplitude of the oscillation in both curve are the same phase but results of TP is died out more rapidly than that of BP. The height of the first peak of BP is greater than TP one.

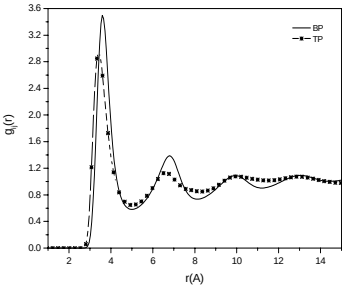


*Fig. 1. Pair Distribution Function for BaO at 1600K.*

In Fig 2a, we present our velocity autocorrelation functions which are obtained by TP and BP for liquid BaO at 1600K. The results of TP shows the backscattering minimum typical of high density systems at times around t=0.25ps followed by rather small oscillations around zero. But for BP, it makes backscattering minimum at times around t=0.18ps followed by bigger oscillations around zero. In Fig 2b we present our memory functions, the binary and mode-coupling contributions for BaO at 1600K. It is observed that the behaviour of the memory function for short time is clearly dominated by the binary contribution. The binary contribution has decay to zero. (For TP approximately t>0.4ps and for BP approximately t>0.6ps).

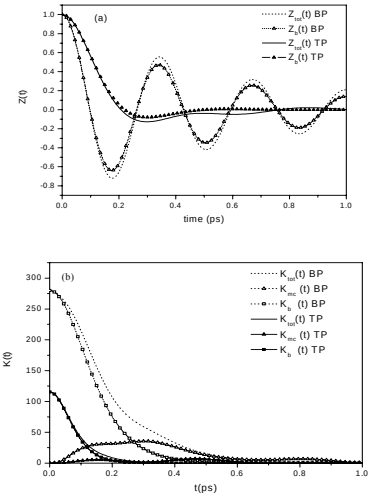


*Fig. 2. (a) Velocity autocorrelation functions (b) memory functions of BaO at 1600K using TP and BP.*

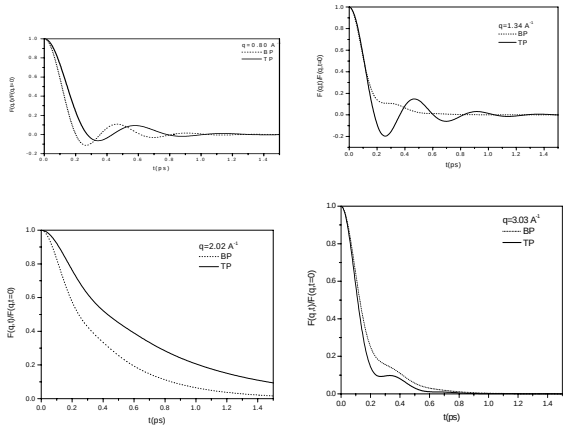


*Fig. 3. The intermediate scattering functions for BaO at 1600K using TP and BP.*

The normalized intermediate scattering functions obtained by the presented formalism are shown in Fig.3. It is observed that F(q,t) exhibits an oscillatory behavior for small q, which persists until around $q \approx 2q_p/3$. The $q_p$ is the position of the main peak of the static structure factor which is about 2.02 $A^{-1}$ for BaO. The amplitude of oscillations of F(q,t) is stronger for the smaller q values and the oscillations take place around a globally decaying positive tail. For $q \leq 1.34A^{-1}$, F(q,t) has an oscillatory behavior for TP, whose period is 0.56ps and 0.46ps for $q=0.80A^{-1}$ and $q=1.34A^{-1}$ respectively. It is found that the smaller wave vectors shows the longer oscillatory period.

For BP F(q,t) has an oscillatory behavior at $q=0.80A^{-1}$ which period is 0.46ps. At $q=2.02A^{-1}$, F(q,t) decreases monotonically with time for both TP and BP. However, the half width at half maximum (HWHM) of F(q,t) is larger than those of other q values. The reason of this behavior is known it is at the main peak of S(q). At $q=3.03A^{-1}$, the decrease of F(q,t) is also monotonic though a shoulder are observed at $q=0.25A^{-1}$ for TP and $q=0.3A^{-1}$ for BP.

In Fig. 4a, we present our results for the MSD obtained by TP and BP for BaO at different temperatures. We can see that results are different to each others. But their behaviors as linearity are same, from high temperature to low temperature and low density to higher density the particular mobility to get difficult. Fig. 4b shows the calculated diffusion coefficients using TP and BP by comparing with the results those obtained from surface diffusion calculations by Harris and co-workers [23].

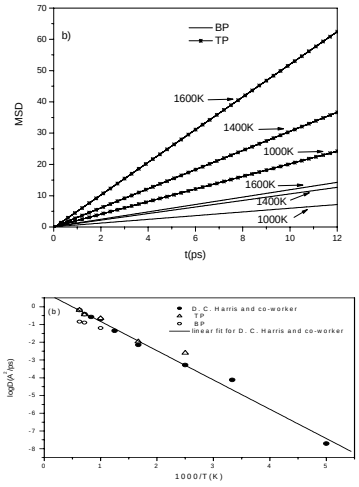


*Fig. 4. (a) Mean-Square Displacements for BaO at different temperature using TP and BP (b) The presently obtained diffusion constants comparing with surface diffusion data.*

It is clear in Fig. 4b that the diffusion coefficient *D* evaluated from the relation between the mean square displacement and time is well predicted. The value of *D* increases with increasing temperature. The temperature dependence of our diffusion coefficient data exhibits the Arrhenius-type behaviour.

## 4. Conclusions

First, the presented semi-empirical three body TP potential provides a realistic description of the pair interactions in molten BaO. These calculations were performed for the functions not only fit to solid data but also liquid state properties. The VMHNC integral equation theory is carried out in structural calculations. We conclude that an empirical three body TP potential with the VMHNC method reproduces well the structural, atomic dynamics properties of molten BaO than the presented ionic potential of Buckingham. We may note that the theory used in our dynamic calculations have extended for metallic systems. Thus the presented formalism can be revised for the ionic type potentials which is capable of providing a good description of molten BaO. This method can be easly applied to the other alkaline earth oxides. The validity of these potentials can be resulted after that. This work will progress on this line.

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