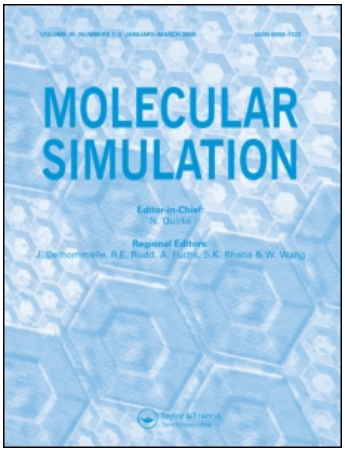

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Computer Simulation of Liquid Methanol II. System Size Effects

J. Casulleras[a]; E. Guardia[a]
[a] Department de Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya, Barcelona, Spain

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COMPUTER SIMULATION OF LIQUID METHANOL II. SYSTEM SIZE EFFECTS

J. CASULLERAS and E. GUARDIA

Departament de Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya, Pau Gargallo 5, 08028 Barcelona, Spain

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A series of molecular dynamics simulations of liquid methanol has been carried out on a supernode transputer array. Four system sizes from 125 to 512 molecules have been considered, in order to study the effect of system size on the calculated structural, orientational and dynamic properties. The dielectric constant and the dielectric relaxation time are compared with experimental data.

KEY WORDS: Molecular dynamics, methanol, system size effects, dielectric constant, dielectric relaxation time.

INTRODUCTION

Computer simulation has become an essential tool for the study of liquid systems. Although the spectacular development of computer power has made possible the study of systems of increasing complexity [1], molecular dynamics (MD) simulations are still limited to no more than a few thousand particles. Therefore, on a macroscopic scale, the size of the system that can be studied is extremely small. This is probably the main technical limitation of MD and it must be taken into account, for instance, when simulation results are used to test models by comparison with experimental data.

System size effects may be specially important in the case of systems with long range interactions such as polar liquids. Most of the previous papers that have assessed this problem are devoted to the study of the system size influence on structural and orientational properties in liquid water [2–4]. The aim of the present work is to extend these previous studies to another substance, liquid methanol, and to include the analysis of the influence of system size on dynamic as well as dielectric properties. To this end, we performed a series of four MD simulations of liquid methanol at normal room temperature conditions, with a number of molecules in the simulation box equal to 125, 216, 343, and 512, respectively. Particular attention has been given to the analysis of the dependence of dielectric properties on the system size, since this work is part of a project concerned with the study of dielectric relaxation in hydrogen bonded liquids by means of computer simulation.

COMPUTATIONAL DETAILS

We carried out MD simulations of liquid methanol at approximately room temperature conditions ($T = 298$ K and $\rho = 0.01478$ molecules/Å^3). The system was made

Table 1 Intermolecular potential parameters

atom	$q(e)$	$\varepsilon(k_B)$	$\sigma(\AA)$
C	+0.265	104.17	3.775
O	−0.700	85.55	3.071
H_0	+0.435	0.	0.

up of N molecules in a cubic box of side length L with periodic boundary conditions. Four simulations were made with $N = 125$, 216, 343, and 512, respectively, which corresponds to an increase in L from 20.4 Å to 32.6 Å. The OPLS potential due to Jorgensen [5] was assumed for the methanol–methanol interactions. This intermolecular potential is based on a rigid three-site model. The methanol monomer is represented by the methyl group centered on carbon (C) and the oxygen (O) and hydroxyl hydrogen (H_0) atoms. The bond lengths and angles are $r(C\text{–}O) = 1.430$ Å, $r(0\text{–}H_0) = 0.945$ Å and $\angle COH_0 = 108.5$ deg. The charge assignments yield a dipole moment $\mu = 2.22$ D. The interaction energy between molecules a and b (U_{ab}) is given by

$$U_{ab} = \sum_{i}^{\text{on } a} \sum_{j}^{\text{on } b} \left[\frac{q_i^a q_j^b}{r_{ij}} + \frac{A_{ij}}{r_{ij}^{12}} - \frac{C_{ij}}{r_{ij}^{6}} \right] \tag{1}$$

Combining rules are used such that $A_{ij} = (A_{ii}A_{jj})^{1/2}$ and $C_{ij} = (C_{ii}C_{jj})^{1/2}$. The A and C parameters may be expressed in terms of the Lennard-Jones σ's and ε's as $A_{ii} = 4\,\varepsilon_i\sigma_i^{12}$ and $C_{ii} = 4\,\varepsilon_i\sigma_i^{6}$. The site charges and Lennard-Jones parameters are listed in Table 1. This potential describes correctly many structural and dynamic properties of liquid methanol [5, 6].

To perform the simulations we employed the leap-frog Verlet integration algorithm proposed by Berendsen *et al.* [7] with a time-step of 0.0025 ps and a velocity scaling time constant of 0.05 ps. The SHAKE procedure [8] was used to keep the interatomic distances fixed. The short range forces were truncated by means of a spherical molecular based cut-off with a radius equal to $L/2$. To handle with the long range coulombic interactions we used the Ewald summation method [9]. We took $\alpha = 5.5/L$. The real space sum was truncated according to the same criterion as the short range forces and the summation in reciprocal space was restricted to lattice vectors $\mathbf{h}$ having $|\mathbf{h}| \leqslant 5$. With this choice, the error introduced in the determination of the total force acting on a given particle was less than a few parts in 10^4 (see the Appendix for more details).

Each run consisted of an initial equilibration period of 15 ps and a production period of 75 ps–150 ps (see Table 2). The runs corresponding to $N = 125$ and $N = 343$ where afterwards extended (see Table 3) in order to obtain accurate dielectric properties. All the calculations were carried out on a supernode transputer array with the parallel algorithm described in a previous paper [10]. They required 40 days of array processor time, and would have required 23 months of a dedicated VAX8600.

RESULTS AND DISCUSSION

Structure

The structure of a molecular liquid is usually described in terms of site–site distribution functions which are measured experimentally in scattering experiments [11].

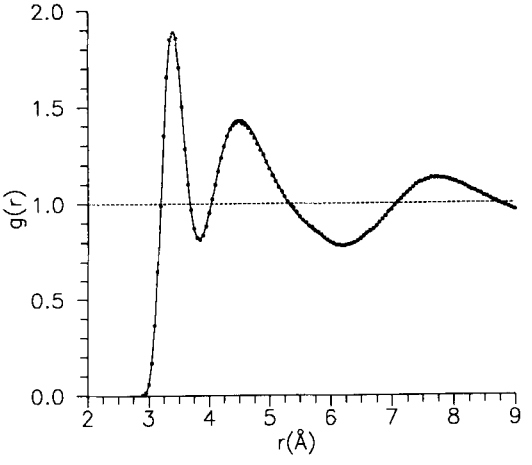

Figure 1 Center of mass radial distribution function. ○○○ $N = 125$, —— $N = 512$.

In the case of the methanol model assumed in this work, this should require the calculation of six radial distribution functions. Now then, the existence of previous works which show that for liquid water there are not appreciable effects of system size on the radial distribution functions [2, 4], suggested us to limit our analysis to the center of mass radial distribution function ($g(r)$).

Figure 1 shows the $g(r)$ functions computed for 125 and 512 molecules. The two functions are almost identical and they corroborate our initial assumption that the packing of neighboring molecules in polar liquids is not affected by system size for $N \geqslant 100$. Although the $g(r)$ are the same, there exist notable differences in the orientational ordering of methanol molecules as will be seen in the section devoted to the analysis of dielectric properties.

Translational and orientational motion

In order to investigate the influence of the system size on translational motion in liquid methanol we have calculated the molecular center of mass velocity auto-correlation function (VAF) and self diffusion coefficient (D).

As can be seen in Figure 2, the VAF obtained for the different values of N have an identical short time decay. For $N = 125$ and $N = 216$ minor differences can be appreciated at intermediate times which indicate that the phenomenon of back-scattering is slightly more important in the case of the smaller systems.

The molecular self-diffusion coefficient may be evaluated from the long time slope of the center of mass mean square displacement (MSD) by means of the expression [12]

$$D = \lim_{t \to \infty} \frac{1}{6t} \langle |\mathbf{r}_{cm}(t) - \mathbf{r}_{cm}(0)|^2 \rangle \tag{2}$$

Figure 3 displays the MSD corresponding to the different values of N. The values of D quoted in Table 2 were obtained from equation (2), using the time range between 3 ps and 10 ps. As has been reported for Lennard–Jones systems [13, 14], there is a systematic increase of D as N increases. Moreover, the increment of D becomes even

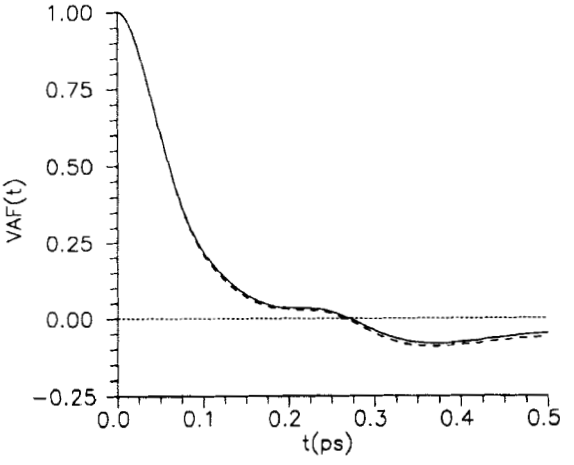

Figure 2 Center of mass velocity autocorrelation function. - - - $N = 125$, ——$N = 512$.

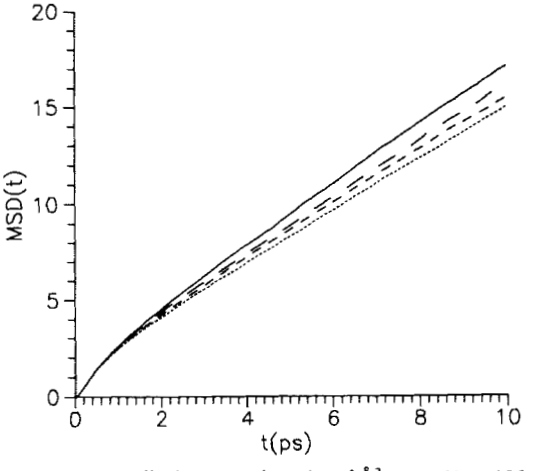

Figure 3 Center of mass mean square displacement in units of Å^2. - - - $N = 125$, — - - $N = 216$, — — $N = 343$, ——$N = 512$.

Table 2 Self-diffusion coefficients and reorientational times

N	L (Å)	*Number of equilibrium steps*	$D/10^{-5}$ (cm^2/s)	$\tau_1(ps)$	$\tau_2(ps)$
125	20.4	60000	2.23	9.4	4.5
216	24.5	45000	2.30	8.8	4.0
343	28.5	36000	2.42	8.9	4.2
512	32.6	30000	2.59	9.3	4.3

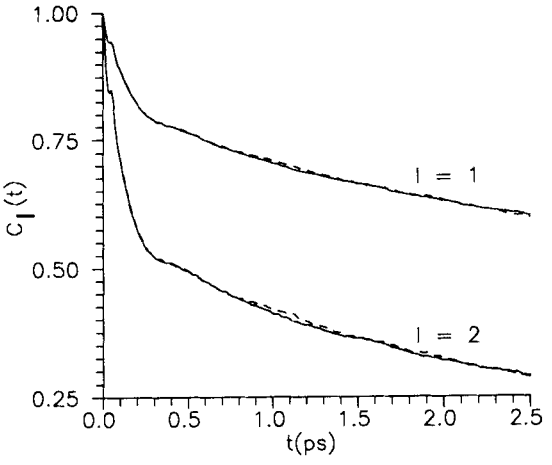

Figure 4 Reorientational correlation functions. - - - $N = 216$, —— $N = 512$.

more important as system size increases. This result suggests that, as far as transport properties are concerned, a system made up of 512 molecules is still far away from the thermodynamic limit.

Reorientational motions in molecular liquids are usually investigated by means of a set of time-correlation functions defined as [15]

$$C_l(t) = \langle P_l(\mathbf{u}(t) \cdot \mathbf{u}(0)) \rangle \tag{3}$$

where P_l is the lth Legendre polynomial and $\mathbf{u}$ is a unit vector that characterizes the orientation of the molecules. We considered the unit vector in the direction of the molecular dipole moment and we calculated the reorientational correlation functions for $l = 1$ and $l = 2$.

At short times, the $C_l(t)$ functions show an oscillation which is characteristic of strongly associated liquids. At long times, however, they display a Debye-like, exponential decay (see Figure 4). As in the case of translational motion, we have not detected any appreciable influence of system size on the short time reorientational motion. To analyse the long time regime the reorientational times (τ_l) have been calculated by assuming

$$C_l(t) \propto \exp(-t/\tau_l) \tag{4}$$

The values of τ_l were obtained using the time range between 1.0 ps and 2.5 ps. As Table 2 shows, the statistical uncertainties in the determination of τ_l dominate over systematic system size effects and, as a consequence, there is not a clear trend with N. In summary, over the range analysed in this work, there is not any significant influence of system size on the reorientational motion of methanol molecules.

Dielectric Properties

For a system with periodic boundaries and the long-range interactions treated by the Ewald method, the dielectric constant (ε) is given by [16]

$$\frac{\varepsilon - 1}{3} = yG_k \tag{5}$$

where $y = 4\pi\rho\mu^2/9k_BT$ is the dimensionless dipolar strength and G_k is the finite system Kirkwood g factor

$$G_k = \frac{\langle M^2 \rangle}{N\mu^2} \tag{6}$$

which measures the equilibrium fluctuations of the total dipole moment of the sample

$$\mathbf{M} = \sum_{i=1}^{N} \mu_i \tag{7}$$

Since G_k is a collective property, very long simulation runs are required in order to determine the dielectric constant with a reasonable precision [17]. To calculate ε for the four values of N would have demanded an amount of CPU time which is beyond our present computing facilities. As an alternative, we decided to carry out the calculation only for $N = 125$ and $N = 343$. To this end, the previously reported simulations corresponding to these values of N were extended up to 435 and 500 ps, respectively.

In Figure 5, the cumulative G_k factor is shown for the two simulations. Table 3 summarizes the calculated G_k and ε. The indicated errors are estimates based on the fluctuations during the last 200 ps of the simulations. Two comments may be made from our results. First of all, the convergence of G_k is markedly slower for the biggest system. As a consequence, the uncertainty in the reported values of ε is bigger for the case of $N = 343$. In spite of that, the results show a significant increment of the dielectric constant with system size. The same tendency was detected by Neumann *et al.* for the Stockmayer fluid [18]. However, the relative increment of ε is more important in the case of liquid methanol. Moreover, it is worth pointing out that the dielectric constant obtained with $N = 343$ is in very good agreement with experimental results [19].

To get some insight into the system size dependence of G_k we have analysed its radial decomposition $G_k(R)$, which is defined by the formula

$$G_k(R) = \frac{1}{N\mu^2} \left\langle \sum_{\substack{i,j \\ r_{ij} < R}} \mu_i \cdot \mu_j \right\rangle \tag{8}$$

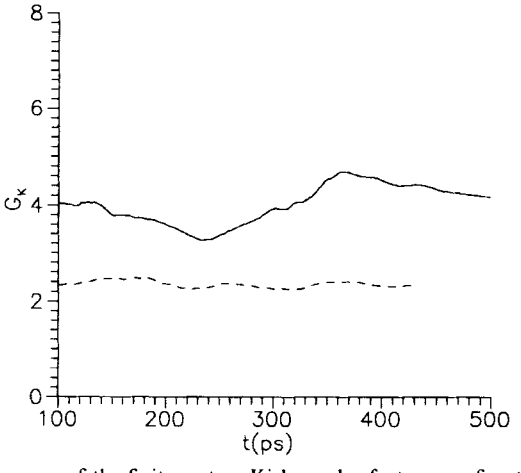

Figure 5 Cumulative average of the finite-system Kirkwood g factor as a function of the length of the simulation. - - - $N = 125$, —— $N = 343$.

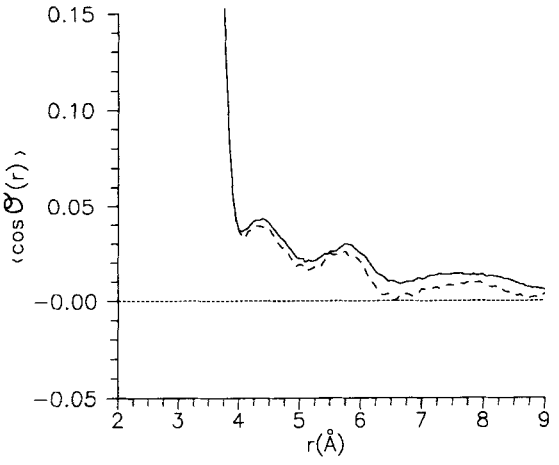

Figure 6 Correlation function between molecular dipoles as a function of the intermolecular separation. - - - $N = 125$, ——$N = 343$.

Table 3 Dielectric properties

N	*Number of equilibrium steps*	G_k	ε	$\tau_D(ps)$
125	174000	2.3 ± 0.1	18.0 ± 0.7	13.5 ± 1.0
343	200000	4.2 ± 0.5	32 ± 4	42 ± 4
experimental value [19]			31.9 ± 0.6	47 ± 1

Apart from a normalization factor, $G_k(R)$ is the average total dipole moment of a sphere of radius R around a reference molecule. For $R \to \sqrt{3}/2L$, $G_k(R)$ tends to the values given in Table 3. $G_k(R)$ is related to the angular correlation function $\langle \cos \vartheta(r) \rangle$, where ϑ is the angle between the dipole moments of two molecules which are separated by a distance r, through the expression

$$G_k(R) = 1 + \frac{4\pi\rho}{3} \int_0^R 3g(r)\langle \cos \vartheta(r) \rangle r^2 \, dr \tag{9}$$

Figure 6 shows that the qualitative behaviour of $\langle \cos \vartheta(r) \rangle$ is similar for both values of N. The large initial positive value of the dipole–dipole correlation function indicates that near neighboring molecules strongly prefer a parallel arrangement. The parallel alignment of molecular dipoles weakens but still persists at larger molecule–molecule separations. Even though the dipole correlations at large separations are small, these dipole pairs make a significant contribution to $G_k(R)$ because of the r^2 dependence in the integral of equation (9). The orientation of molecules in the first coordination shell appears to be insensitive to system size but at larger intermolecular distances the biggest system displays more orientational order.

In accordance with Figure 6, the $G_k(R)$ resulting from the two simulations present an important jump between 3.0 Å and 3.8 Å which corresponds to the contribution to the total dipole moment coming from the first shell of neighbors (see Figure 7).

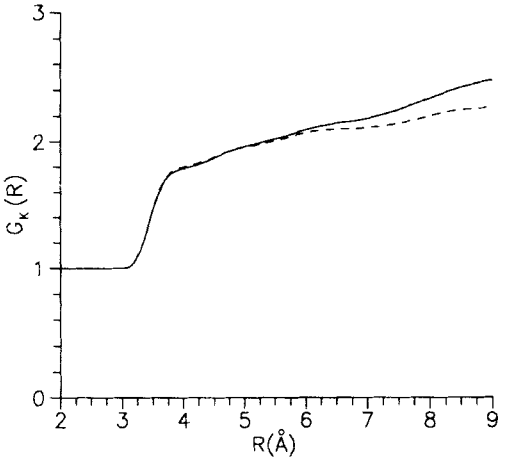

Figure 7 R dependent finite-system Kirkwood g factor. - - - $N = 125$, ——$N = 343$.

The contribution from successive shells is also positive but smaller. At $R \simeq 6$ Å (i.e., the second coordination shell) the influence of system size becomes evident and increases progressively as R increases. As a consequence there is an important increment of G_k (and so ε) with N which can be associated to the progressive increment of molecular order beyond the first coordination shell.

The relaxation of the collective orientational ordering can be studied through the total dipole moment autocorrelation function

$$\phi(t) = \frac{\langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle}{\langle \mathbf{M}^2(0) \rangle} \tag{10}$$

which is the collective analogue of the single particle reorientational function $C_1(t)$ (see equation (3)). From $\phi(t)$ the frequency-dependent dielectric constant can be obtained. Moreover, the exponential decay constant of this function gives the Debye dielectric relaxation time τ_D [20]

$$\phi(t) \propto \exp(-t/\tau_D) \tag{11}$$

The functions $\phi(t)$ obtained for the two values of N are shown in Figure 8. The relaxation times listed in Table 3 were obtained by fitting $\phi(t)$ to an exponential function from 2 ps to 5 ps. The estimated statistical uncertainties in τ_D are of 10%. In contrast to the single molecule reorientational time τ_1 which is not significantly influenced by system size (see Table 2), there is an important increment of the collective reorientational time τ_D as the system size increases. As in the case of ε, the dielectric relaxation time obtained with 343 molecules is in very good agreement with experimental results [19].

SUMMARY

The influence of system size on MD simulation of liquid methanol has been analysed for systems with 125 and 512 molecules. Molecular structure, translational and orientational motions and dielectric properties have been considered. We have not

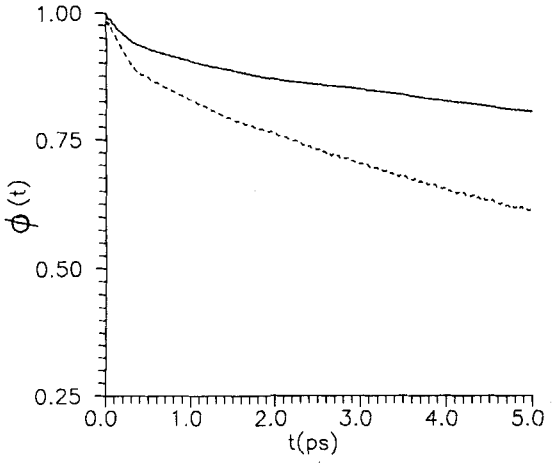

Figure 8 Total dipole moment autocorrelation function. - - - $N = 125$, ——$N = 343$.

detected significant system size effects on the molecular structure neither on the molecular reorientational times. Only small effects have been observed for the short and intermediate time translational motion, but there is a noticeable increment of the mobility of molecules in the long time regime as the size of the system increases. The dielectric constant and the dielectric relaxation time are also sensitive to the system size.

The agreement between the experimental data and the dielectric properties resulting from the system made up of 343 molecules is remarkable. However, longer simulations are necessary in order to make definite conclusions about the capability of the OPLS potential model to reproduce dielectric properties of liquid methanol. These simulations are now in progress and the results will be reported elsewhere soon [21].

Acknowledgments

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APPENDIX/ ERRORS IN THE EWALD SUMMATION METHOD

When the Ewald summation technique is used to deal with the long range forces, the total interaction energy (U) of the N molecules in the cubic box is given by [9]

$$U = \frac{1}{2}\sum_{a,b=1}^{N}\sum_{i,j=1}^{3}\left[q_i^a q_j^b \frac{\operatorname{erfc}(\alpha r_{ij})}{r_{ij}} + \frac{A_{ij}}{r_{ij}^{12}} - \frac{C_{ij}}{r_{ij}^{6}}\right] - \frac{1}{2}\sum_{a=1}^{N}\sum_{\substack{i,j=1\\(i\neq j)}}^{3} q_i^a q_j^a \frac{\operatorname{erf}(\alpha r_{ij})}{r_{ij}}$$

$$+ \frac{1}{2\pi L}\sum_{\mathbf{h}\neq 0}\frac{\exp\left(-\frac{\pi^2|\mathbf{h}|^2}{\alpha^2 L^2}\right)}{|\mathbf{h}|^2}\left\{\left[\sum_{a=1}^{N}\sum_{i=1}^{3} q_i^a \cos(2\pi/L\mathbf{h}\cdot\mathbf{r}_i)\right]^2\right.$$

$$\left. + \left[\sum_{a=1}^{N}\sum_{i=1}^{3} q_i^a \sin(2\pi/L\mathbf{h}\cdot\mathbf{r}_i)\right]^2\right\} - \frac{\alpha}{\sqrt{\pi}}\sum_{a=1}^{N}\sum_{i=1}^{3}(q_i^a)^2 + \frac{2\pi N\mu^2}{3L^3} \qquad (12)$$

where α is an arbitrary parameter that regulates the convergence of both the complementary error function and the reciprocal space summations.

In the simulations reported in this work, the real space summation was truncated by means of a spherical molecular based cut-off with a radius equal to $L/2$. The summation in reciprocal space was restricted to lattice vectors $\mathbf{h}$ having $|\mathbf{h}| \leqslant |\mathbf{h}|_{\max}$.

In order to determine the optimum choice of α and $|\mathbf{h}|_{\max}$ we carried out an analysis of the relative error (ε_F) introduced in the determination of the total force ($\mathbf{F}$) acting

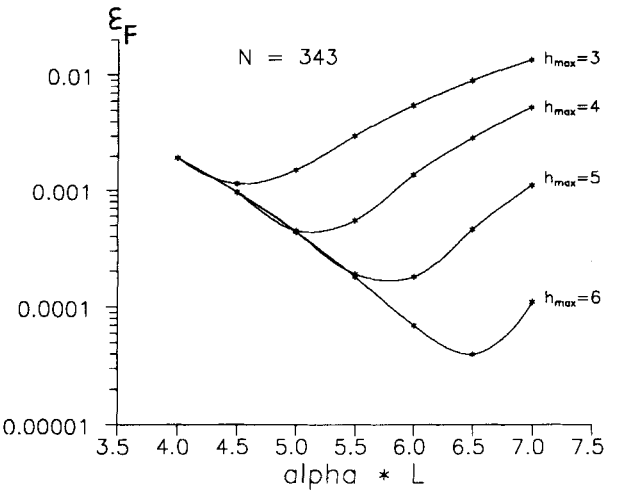

Figure 9 Relative error in the determination of the total force acting on a given particle as a function of αL and $|\mathbf{h}|_{max}$.

on a given particle as a function of these two parameters. ε_F was defined as

$$\varepsilon_F = \frac{|\mathbf{F} - \mathbf{F}_{exact}|_{maximum}}{|\mathbf{F}_{exact}|_{mean}} \tag{13}$$

and the "exact" value was calculated with $\alpha = 10/L$ and $|\mathbf{h}|_{max} = 13$.

Figure 9 shows the computed ε_F as a function of αL and $|\mathbf{h}|_{max}$ for $N = 343$. The curves clearly illustrate the fact that α has opposite effects in the convergence rates of the real and reciprocal space summations. At low values of α, ε_F is mainly due to the error in the evaluation of the complementary error function sum and it is nearly independent of $|\mathbf{h}|_{max}$. As α increases, the contribution to ε_F due to the real space summation disappears and the main source of error is the reciprocal space summation. The minima displayed by ε_F indicate that there is an optimum choice of α for any value of $|\eta|_{max}$. Furthermore, we have observed that, for a given value of αL and $|\mathbf{h}|_{max}$, ε_F diminishes slightly as the system size increases.