Average square atomic displacement: A comparison of the lattice-dynamics, molecular-dynamics, and Monte Carlo results

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Molecular-dynamics (MD) and Monte Carlo (MC) calculations of the mean-square displacement (MSD) have been carried out for a fcc nearest-neighbor Lennard-Jones model for a wide range of temperatures and lattice spacings. The lattice-dynamics (LD) calculations of the harmonic and the lowest-order anharmonic (cubic and quartic) contributions to the mean-square displacement were performed for the same potential model as in the MD and MC calculations. The dependence of MSD on sample size (N) has been examined in detail in MC calculations and the results are presented for a 256-atom sample as well as the extrapolated sample of the infinite size. The MD results are given only for the 256-atom sample size. The LD results for the harmonic and quartic contributions to MSD were obtained for almost completely converged Brillouin-zone (BZ) sums, whereas the cubic BZ sums were uncertain by 2%. It is estimated that the N=256 sample size used in MD calculations produces a result which is somewhere between 10% and 20% smaller than the value converged with respect to N. However, the general temperature dependence of MSD is the same in MD, MC, and LD results for all temperatures at the highest lattice spacings examined, while at higher volumes and high temperatures the results differ. This indicates the importance of higher-order (e.g., λ^4) perturbation-theory contributions in these cases. These results represent the best picture vet obtained for the MSD from the first such calculation for a rare-gas crystal by the MD, MC, and LD methods.

I. INTRODUCTION

A knowledge of the average square atomic displacement $\langle u^2 \rangle$ in a crystal is fundamental in determining the Debye-Waller factor which appears in the intensity of xray and neutron scattering and in the Mössbauer fraction. It also plays a role in theories of melting, through the Lindemann criterion, and is a guide to the magnitude of the convergence parameter λ of anharmonic perturbation theory. The experimental determination of $\langle u^2 \rangle$ is difficult in the most favorable cases, and for the rare-gas solids the only recent results of which we are aware are those of Windecker¹ on krypton, which are limited to a related quantity Θ'_M (derived from the temperature dependence of the x-ray intensities).

In a recent publication² one of us has calculated $\langle u^2 \rangle$ for Li and Rb employing the lowest order (λ^2) latticedynamics anharmonic perturbation theory and the molecular-dynamics (MD) method. The latter procedure presumably give the exact numerical answer for $\langle u^2 \rangle$ for a given potential function whereas the lattice-dynamical calculation is a term-by-term calculation of the contributions to $\langle u^2 \rangle$ from the expanded potential function (V). To $O(\lambda^2)$ there are four anharmonic contributions to the Debye-Waller factor. Two of these are of $O(T^2)$ and the other two of $O(T^3)$, the latter contributions being just about negligible. Then to $O(\lambda^2)$ and $O(T^2)$, which includes the contributions from the cubic and quartic terms in the Taylor-series expansion of V, the agreement between the MD and lattice-dynamical results for $\langle u^2 \rangle$ was quite good for all the temperatures in the interval $\Theta_D < T < T_m$, indicating the adequacy of the anharmonic calculation in the lowest order of perturbation theory.

For the rare-gas solids, the earliest calculation was by Goldman,³ who estimated the average anharmonic correction to quasiharmonic lattice-dynamics results. Kanney⁴ made a calculation using the ISC correction to the self consistent phonon theory value. The accuracy of her values was limited by the coarse meshes used in the Brillouin-zone sums. One of us used a cell-cluster technique⁵ to obtain a fairly similar set of results, but this method is less suited to the calculation of this property than to other thermodynamic quantities because the long-wavelength modes are not well described. An interesting feature of these results is that the successive estimates of $\langle u^2 \rangle$ are all larger than the preceding values, and this trend is continued in the results given here.

A full calculation of all of the terms arising in anharmonic perturbation theory has not been performed, and we wished to compare such a calculation with the two simulation techniques, the Monte Carlo and moleculardynamics methods. Each of these is in principle exact for a given potential, but the molecular-dynamics method involves the calculation of a time average while in the Monte Carlo method an ensemble average is formed.

The purpose of this paper is to calculate the average square of the atomic displacement $\langle u^2 \rangle$ for a Lennard-Jones (LJ) rare-gas solid by three different methods: (a)

the lowest order (λ^2) anharmonic perturbation theory (PT) (λ is the Van Hove ordering parameter), (b) the molecular dynamics (MD) method, and (c) the Monte Carlo (MC) method. For a meaningful comparison of the numerical results for $\langle u^2 \rangle$, we employ the same model potential [nearest-neighbor (NN) LJ interaction] in all the three methods. We believe it to be the first calculation of $\langle u^2 \rangle$ where such a comparison has been reported in the literature.

A comparison of the λ^2 PT results for $\langle u^2 \rangle$ with those of the MD and MC methods will indicate the importance of the omitted contributions from the term-by-term calculation used in the λ^2 PT. The first set of the omitted terms from the λ^2 PT are of $O(\lambda^4)$. It has been noted before (in the context of thermodynamic properties of raregas solids) that the λ^2 perturbation theory breaks down⁶ beyond $\frac{1}{3}T_M$ and the λ^4 perturbation theory⁷ holds up to 40% of T_M .

The layout of this paper is as follows. Section II contains a summary of the lattice-dynamics calculations and a discussion of the dependence on sample size of MC and MD calculations is presented in Sec. III. The MC and MD calculations are presented in Sec. IV, and finally the results and discussion are presented in Sec. V.

II. A SUMMARY OF LATTICE-DYNAMICS CALCULATIONS

There are four contributions to $\langle u^2 \rangle$ in the lowest order of perturbation theory. Three of these contributions arise from the harmonic, cubic (C), and quartic (Q) terms in the crystal Hamiltonian, respectively. The fourth contribution arises from the thermal expansion effect of the harmonic contribution. The harmonic and its thermal expansion effect can be evaluated as one single contribution in the quasiharmonic (QH) approximation. Representing these contributions to $\langle u^2 \rangle$ by appropriate subscripts, we have the following expressions⁸ in the classical hightemperature limit $(T > \Theta_D)$, where Θ_D is the Debye temperature:

$$\langle u^2 \rangle_{\rm QH} = \frac{k_B T}{NM} \sum_{\mathbf{q}, j} \frac{1}{\omega^2(\mathbf{q}, j)} , \qquad (1)$$

$$\langle u^{2} \rangle_{Q} = -\frac{(k_{B}T)^{2}}{2N^{2}M} \sum_{\mathbf{q}_{1},\mathbf{q}_{2}} \sum_{j_{1},j_{2}} \frac{\Phi(\mathbf{q}_{1},j_{1};-\mathbf{q}_{1},j_{1};\mathbf{q}_{2},j_{2};-\mathbf{q}_{2},j_{2})}{\omega^{2}(\mathbf{q}_{1},j_{1})\omega^{4}(\mathbf{q}_{2},j_{2})} , \qquad (2)$$

$$\langle u^{2} \rangle_{C} = \frac{(k_{B}T)^{2}}{2N^{2}M} \sum_{\mathbf{q}_{1},\mathbf{q}_{2},\mathbf{q}_{3}} \sum_{j_{1},j_{2},j_{3}} \Delta(\mathbf{q}_{1}+\mathbf{q}_{2}+\mathbf{q}_{3}) \frac{|\Phi(\mathbf{q}_{1},j_{1};\mathbf{q}_{2},j_{2};\mathbf{q}_{3},j_{3})|^{2}}{\omega^{2}(\mathbf{q}_{1},j_{1})\omega^{2}(\mathbf{q}_{2},j_{2})\omega^{4}(\mathbf{q}_{3},j_{3})}$$
(3)

The various symbols in Eqs. (1)-(3) are as follows: M is the atomic mass, k_B is the Boltzmann constant, T is the temperature, N is the number of unit cells in the crystal, $\omega(\mathbf{q}, j)$ is the phonon frequency for the wave vector \mathbf{q} and branch index j, and ϕ 's are the Fourier transforms defined by

$$\Phi(\mathbf{q}_{1}, j_{1}; \mathbf{q}_{2}, j_{2}; \dots; \mathbf{q}_{n}, j_{n}) = \frac{1}{2M^{n/2}} \sum_{l} \sum_{\alpha, \beta, \dots, \gamma} \phi_{\alpha\beta, \dots, \gamma} \phi_{\alpha\beta, \dots, \gamma}(l) e_{\alpha}(\mathbf{q}_{1}, j_{1}) e_{\beta}(\mathbf{q}_{2}, j_{2}) \times \dots \times e_{\gamma}(\mathbf{q}_{n}, j_{n}) \prod_{i=1}^{n} (1 - e^{-i\mathbf{q}_{i}\cdot\mathbf{r}_{l}}) , \qquad (4)$$

where the prime on the *l* summation indicates the omission of the origin point; $\alpha, \beta, \ldots, \gamma$ each take the value of x, y, z; \mathbf{r}_l is the direct lattice vector $\left[=\frac{1}{2}a_0(l)\right]$; $\phi_{\alpha\beta}\ldots_{\gamma}$ is the Cartesian tensor derivative of the two-body potential $\phi(|\mathbf{r}_l|)$; $e_{\alpha}(\mathbf{q}, \mathbf{j})$ are the α components of the eigenvector. The Δ function in Eq. (3) is unity if $\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3 = \mathbf{0}$ or τ (reciprocallattice vector) and zero otherwise.

Since the Debye-Waller factor sums are the same as those arising in the above calculation of $\langle u^2 \rangle$ [see Eqs. (9)–(11) of Ref. 2], we will omit presenting here the details and simply summarize the final expressions² used in the calculation of $\langle u^2 \rangle_{QH}$ and $\langle u^2 \rangle_Q$, viz.,

$$\langle u^2 \rangle_{QH} = \frac{k_B T}{3NM} [S_{xx}(0) + S_{yy}(0) + S_{zz}(0)],$$
 (5)

$$\langle u^2 \rangle_Q = \frac{(k_B T)^2}{N^2 M} \sum_{l}' \sum_{\alpha, \beta, \gamma, \delta} \phi_{\alpha\beta\gamma\delta}(|l|) [S_{\alpha\beta}(0) - S_{\alpha\beta}(l)] [T_{\gamma\delta}(0) - T_{\gamma\delta}(l)], \qquad (6)$$

where $S_{\alpha\beta}(l)$ and $T_{\gamma\delta}(l)$ are obtained from the following general tensor $I^n_{\alpha\beta}(l)$ when n = 2 and n = 4, respectively:

$$I_{\alpha\beta}^{n}(l) = \sum_{\mathbf{q},j} \frac{e_{\alpha}(\mathbf{q},j)e_{\beta}(\mathbf{q},j)}{\omega^{n}(\mathbf{q},j)} \cos(\mathbf{q} \cdot \mathbf{r}_{l}) .$$
(7)

The above tensors can be calculated by reducing the whole Brillouin zone (BZ) sum to that of the irreducible $\frac{1}{48}$ th

portion of BZ. The necessary equations have been derived previously, and are given in Shukla and Wilk.⁹

The numerical values of the BZ sums depend on the number of wave vectors used in the calculations. The convergence with increasing number of wave vectors is not very rapid for the $S_{xx}(0)=S_{yy}(0)=S_{zz}(0)$ tensor although the difference, $S_{\alpha\beta}(0)-S_{\alpha\beta}(l)$ tensor arising in

Eq. (6) converges rapidly. The convergence of the other difference tensor $T_{\gamma\delta}(0) - T_{\gamma\delta}(l)$ in Eq. (6) is not very good even with increasing number of wave vectors in BZ. The convergence can be improved by using a shifted mesh of points rather than a simple cubic mesh. This is so, because the shifted mesh produces points closer to the origin and that is where the weighting of the contributions from different regions of q in BZ is heavy. The tensors $S_{\alpha\beta}(l)$ and $T_{\gamma\delta}(l)$ were computed for a step length L as high as 100 and then the final numerical values were obtained by graphical extrapolation. The calculation of $\langle u^2 \rangle_C$ was performed by the scanning method which is described in Ref. 2.

III. DEPENDENCE ON SAMPLE SIZE

The mean-square displacement and hence the Debye-Waller factor are much more dependent on the sample size than are most thermodynamic quantities. This dependence arises because long-wavelength vibrations of the crystal make a disproportionately large contribution to this particular property, and the presence of these modes depends sensitively on the size of the crystal. Fortunately, the dependence on sample size appears to show a universal behavior so that results obtained using two or more sample sizes can be corrected to give rather accurate results for the infinite sample. A simple approach to the evaluation of the mean-square displacement using quasiharmonic lattice dynamics is to carry out the single Brillouin zone summation over a simple cubic mesh of wave vectors whose components are integral multiples of $2\pi/(La_0)$, where L is an integer, and omitting completely the wave vector (0,0,0). If this is done, the calculated mean-square displacement is found to vary very closely linearly with 1/L. This trend holds over values of L from 2 or 3 up to 100 or more, and, obviously, can be used to give an accurate value extrapolated to 1/L equal to zero, corresponding to the infinite crystal.

This procedure was employed in the calculation of $\langle u^2 \rangle_{\rm QH}$ and $\langle u^2 \rangle_Q$. For the calculation of $\langle u^2 \rangle_C$ it was not practicable to use *L* values as high as 100 but we have some estimate for the change of values in going from L = 5 (500 wave vectors) to L = 10 (4000 wave vectors). The values change by 7–8%. For our final runs we have used L = 10 in the calculation of $\langle u^2 \rangle_C$. If one could obtain a fully converged answer for $\langle u^2 \rangle_C$ we estimate it will be larger than the L = 10 value by 2%.

Our Monte Carlo results obtained with samples of various sizes show the same behavior. In Fig. 1 are shown a typical set of values of the mean-square displacement for systems of 32, 108, and 256 atoms, corresponding to Lvalues of 2, 3, and 4. The values are plotted as a function of 1/L and lie within the statistical uncertainties on a straight line. Hence, we can deduce the value for an infinite-sized system, or, for that matter, for any other finite-sized system. Note that the correction is not small. Even the 256-atom sample gives results which are too small by approximately 17%.

A similar kind of analysis for MD was not carried out. The results presented later are all for a system of 256 particles. However, we have some estimates of $\langle u^2 \rangle$ when



FIG. 1. Mean-square displacement as a function of the inverse of the linear sample size calculated for a reduced temperature of 0.5 by the Monte Carlo method. Statistical uncertainties are smaller than the plotted circles.

the number of particles was increased from 256 to 500 (corresponding to L equal to 4 and 5, respectively). The value of $\langle u^2 \rangle$ increased by 8.5%.

IV. MONTE CARLO AND MOLECULAR-DYNAMICS CALCULATIONS

A. Monte Carlo method

In a recent paper¹⁰ one of us gave values for a variety of thermodynamic and elastic properties for the Lennard-Jones solid, calculated for six temperatures at volumes which corresponded essentially to the zero-pressure equation of state. We have calculated the mean-square displacement for the same six temperature-volume combinations. The calculations were performed for 32- and 108- atom systems at all temperatures, and at the highest temperature an additional run was made for a 256-atom sample. The runs were made over 960 000, 2 160 000, and 7 680 000 configurations respectively for the 32-, 108-, and 256-atom samples. In each case the atoms were started from their equilibrium positions and a preliminary run of 1000 attempted moves per atom was made before the averaging was started.

The atoms were moved individually, and no attempt was made to hold the center of mass (c.m.) of the system fixed. Therefore, in order to compute the mean-square displacement from equilibrium, a running value was maintained for the displacements $x_{c.m.}$, $y_{c.m.}$, and $z_{c.m.}$ of the center of mass, and the quantities actually averaged were $(x - x_{c.m.})^2$ etc. The averages for the three Cartesian components always agreed within their statistical uncertainties, and the three were added to give a total meansquare displacement with an uncertainty typically of 0.4%. As indicated earlier, the results for the different values of L could be extrapolated to correspond either to the infinite crystal or, for comparison with MD, to the 256-atom sample.

B. Molecular-dynamics method

The MD calculations were done for N = 256 particles $(L = 4a_0)$ except for one run using $N = 500(L = 5a_0)$. Initially, the particles were placed in a cube containing $4 \times 4 \times 4$ fcc unit cells and given random velocities. Periodic boundary conditions were employed to minimize surface effects. The time step was $\Delta t = 0.001\tau$ $[\tau = a_0(M/\epsilon)^{1/2}]$ and the integrations were carried out for 6000 times steps employing Beeman algorithm given in Refs. 11 and 12 to integrate the equations of motion. This produced energy fluctuations of the order of 10 ppm

0.002
0.0234
1%
0.6%
2.5

(parts per million) and an average loss of energy of 2 ppm per time step.

The reliability of MD results depends on three parameters: the time increment Δt , the number of integration steps, *n*, and the number of simulated particles, *N*. The influence of the first two (Δt and *n*) can be easily determined by comparing runs with different parameter settings but the *N* dependence is much harder to assess.

The effect of n and Δt was explored in several runs using 0.01, 0.005, and 0.002 for Δt and up to 6000 integration steps (n). The results are as follows:

0.005	0.01
0.0232	0.0224
2000-3000	1000-2000
2%	4%
2%	2.5%

Never stabilized

It can be seen that with the longer time steps the energy loss is drastically increased compared to the case $\Delta t = 0.002$. Moreover, the C_v estimate never stabilized near a value of 3 during the whole simulation. From these tests it was concluded that the choices $\Delta t = 0.002$ and n = 3000 would produce results converged to about 1% with respect to n and probably 1-2% with respect to Δt . The former conclusion was confirmed when comparing results of subsequent runs, where the final configuration of one simulation was taken as the initial configuration for the next run. The results generally differed by less than 1%.

The errors quoted above in the summary of the MD results are estimated from the fluctuations during the last 1000 time steps. They do not reflect the error introduced by the choices of Δt and N. 5000 to 6000 time steps were required to stabilize the MSD results to less than 1% for the chosen time increment $\Delta t = 0.002$. The convergence with respect to Δt is estimated to be within 2-4%.

The dependence of the simulation results on N can be investigated in two ways. Simulations can be run using different numbers of particles, and the MD results can be compared with LD for lower temperatures, where the higher order PT contributions are exceedingly small. The first possibility is far more complicated and time consuming than the aforementioned comparisons between different Δt and n values. This is because a simulation using a different number of particles must always start from scratch, while Δt and n can be changed during the simulation. For this reason, only one such comparison was made. The MSD calculation for $r = r_0$, the minimum of the central force potential $V, k_B T/\epsilon = 0.48$ was done for N = 256 and for N = 500. The results in reduced units were MSD/T = 0.07030 for n = 256 and MSD/T = 0.07628 for N = 500, the latter being about 8.5% larger. This indicates that the converged result (with respect to N) would be at least 10% higher than the value for N = 256.

This observation is confirmed by the comparisons with LD. At the lowest temperature $(k_BT/\epsilon=0.12)$ the anharmonic contribution to MSD at $r=r_0$ is only 2.5% of the harmonic value. It is safe to assume that any anharmonic contributions of $O(\lambda^4)$ would be much less than 1%. The LD value should, therefore, be within less than 1% of the fully converged answer. However, the MD result in this case differs from the LD value by 16%. This discrepancy can be explained as the effect of the finite value of N and it can serve as an estimate of the total error of the MD calculations.

V. RESULTS AND DISCUSSION

In Table I are listed the values of $\langle u^2 \rangle$ calculated by the three methods described above, for the six tempera-

TABLE I. Mean-square displacement results.

Temperature (ϵ/k_B)		$\langle u^2 \rangle \langle \sigma^2 \rangle$	/1000)	
	MD(256)	MC(256)	MC (∞)	LD
0.125	2.67	2.67	3.15	3.15
0.225	5.40	5.40	6.38	6.34
0.3	8.07	8.06	9.69	9.44
0.375	11.7	11.3	13.7	12.5
0.45	17.1	15.7	19.2	16.4
0.5	22.7	19.2	23.2	19.3



FIG. 2. Mean-square displacement as a function of temperature: solid line by lattice dynamics, dashed line by molecular dynamics, and dotted lines by Monte Carlo for 256-atom (lower) and infinite-atom (upper) samples.

tures at which our earlier MC calculations were performed. The temperatures are expressed in units of ϵ/k_B , where ϵ is the well depth of the Lennard-Jones potential, and $\langle u^2 \rangle$ is given in units of $\sigma^2/1000$, where σ is the position of the zero of the potential. In each case the calculation was carried out at, or interpolated to, the lattice spacing used earlier, which corresponds to zero pressure.

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The second and third columns list the values obtained by MD using 256 atoms, and by MC extrapolated to 256 atoms. There is excellent agreement at low temperatures, gradually worsening to 15% at the highest temperature. This is much greater than the combined statistical uncertainties of the two calculations, and we are presently unable to account for this discrepancy. In the fourth and fifth columns, the MC results extrapolated to the infinite crystal are compared with the lattice-dynamics (LD) results. Again, the low-temperature agreement is excellent, gradually worsening to about 16% at the highest temperature. Presumably this disagreement indicates the lack of convergence of the λ^2 perturbation theory. If the MD results were corrected to finite sample size, the disagreement with LD would be even worse. Our earlier cell-cluster results⁵ are not listed but are very similar to the LD results and hence slightly lower than the extrapolated MC values.

While the difference between the MD and MC values at high temperatures does remain a problem, we nevertheless believe that these results represent the best picture yet obtained for the mean square displacement in a rare-gas crystal. The overall pictures of $\langle u^2 \rangle$ given by the above three methods are very similar as can be seen in Fig. 2.

ACKNOWLEDGMENT

Ramesh C. Shukla would like to acknowledge the support of the Natural Sciences and Engineering Research Council of Canada.

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