

TABLE I. The bandwidths of the conduction and valence bands, the effective masses of the electron and the positive hole, and the constants  $\sigma_{0e}$  and  $\sigma_{0h}$ , respectively, of complicated periodic DNA models.

	$\Delta W_c$	$\Delta W_v$	$m_e^*$	$m_h^*$	$\sigma_{0e}$	$\sigma_{0h}$	$\sigma_0 = \sigma_{0e} + \sigma_{0h}$
poly $\begin{pmatrix} \text{A-T} \\ \text{G-C} \end{pmatrix}$	0.016	0.051	209	65	$3.50 \times 10^3$	$1.60 \times 10^4$	$1.64 \times 10^4$
poly $\begin{pmatrix} \text{A-T} \\ \text{C-G} \end{pmatrix}$	0.001	0.006	5260	549	$2.39 \times 10^4$	$1.71 \times 10^5$	$1.95 \times 10^5$
poly $\begin{pmatrix} \text{A-T} \\ \text{T-A} \end{pmatrix}$	0.003	0.081	1320	41	$8.43 \times 10^1$	$6.72 \times 10^5$	$6.72 \times 10^5$
poly $\begin{pmatrix} \text{G-C} \\ \text{C-G} \end{pmatrix}$	0.002	0.021	2000	158	$2.61 \times 10^3$	$2.29 \times 10^5$	$2.32 \times 10^5$

and  $u_{e,i}$  and  $k_{e,i}$  stand for the complex eigenvector and the  $k$  value, respectively, belonging to the lower limit of the conduction band.

In Table I, we give the widths (in eV) of the conduction and valence band ( $\Delta W_c$  and  $\Delta W_v$ ), the corresponding effective masses  $m_e^*$  and  $m_h^*$  (in electronic masses) and the constants  $\sigma_{0e}$  and  $\sigma_{0h}$  in  $\Omega^{-1} \cdot \text{cm}^{-1}$ .

We can see that all the values  $\sigma_0$  fall in the range  $10^4$ – $10^5 \Omega^{-1} \cdot \text{cm}^{-1}$ . While the individual values of  $\sigma_{0e}$  are in the orders  $10^1$ – $10^5 \Omega^{-1} \cdot \text{cm}^{-1}$ , those of  $\sigma_{0h}$  lie in the range  $10^4$ – $10^5 \Omega^{-1} \cdot \text{cm}^{-1}$ . This agrees with the fact that the width of the conduction band is, in all four cases, considerably smaller than that of the valence bands. We have obtained, however, for

$$\text{poly} \begin{pmatrix} \text{A-T} \\ \text{C-G} \end{pmatrix}$$

which has a very narrow conduction and valence band, quite large  $\sigma_0$  constants, which is in contradiction with general physical considerations. This indicates, as we have mentioned already previously,<sup>2</sup> that the deformation potential approximation breaks down in the case of very narrow bands. To overcome this difficulty work is in progress to calculate the conductivity of periodic DNA models with narrow bands using the deformable ion approximation which treats the electron-phonon interaction in a more correct way.

<sup>1</sup> See J. Ladik and G. Biczó, "Erratum [42, 1658 (1965)]," J. Chem. Phys. (to be published).

<sup>2</sup> W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Co., Inc., New York, 1950), p. 278.

<sup>3</sup> J. Ladik, G. Biczó, and G. Elek, J. Chem. Phys. 44, 483 (1966).

<sup>4</sup> K. Komatsu and T. Nagayama, J. Phys. Soc. Japan 6, 438 (1951).

<sup>5</sup> For details see J. Ladik and K. Appel, J. Chem. Phys. 40, 2470 (1964).

## *N* Dependence in Monte Carlo Studies of the Square-Well System\*

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Extensive Monte Carlo calculations by Rotenberg<sup>1</sup> on a square-well system have yielded two sets of "van der Waals" loops for low-temperature isotherms in the  $p$ - $V$  plane, one at densities higher than the hard-sphere transition region and the other at lower. The high-density loops result in large negative pressures and the suggestion of an anomalous critical point in the presumed melting transition of square-well molecules. As noted by Rotenberg, these negative pressures are an artifact of the periodic boundary conditions coupled with the small number  $N$  of molecules used in the calculations. We report here some Monte Carlo calculations showing a marked dependence of the pressure and energy upon system size.

The square-well potential is characterized by a well depth  $\epsilon$  and a range  $K\sigma$ , where  $\sigma$  is the hard-core diameter. It is convenient to use reduced units for volume and temperature,  $\tau = V/V_0$  and  $\theta = kT/\epsilon$ , where  $V_0 = N\sigma^3/\sqrt{2}$  is the fcc close-packed volume of the hard cores. The pressure  $p$  is then given by<sup>2</sup>

$$pV/NkT = 1$$

$$+ (2\pi\sqrt{2}/3\tau) [g(1+) - K^3(1 - e^{-1/\theta})g(K-)],$$

where  $g(a+)$  and  $g(a-)$  denote the values of the radial distribution function  $g(\zeta)$  as  $\zeta = r/\sigma$  approaches  $a$  from above and below, respectively.

The usual Monte Carlo procedure of Metropolis *et al.*<sup>3</sup> was used to calculate the radial distribution function and the average potential energy  $U$  for periodic systems of 256, 500, and 864 molecules in a cubical volume  $V$  at  $K = 1.5$ ,  $\tau = 1.185$ , and  $\theta = 0.5$ . One molecule was held fixed throughout the calculations and the others given

TABLE I. Summary of Monte Carlo results ( $\pm$  standard deviation) for square-well systems with  $K=1.5$ ,  $\tau=1.185$ , and  $\theta=0.5$ .

$N$	Moves/( $N-1$ )	$g(K^-)e^{-1/\theta}$	$g(K^+)$	$U/NkT$	$pV_0/NkT$
256	50 500	$0.3861 \pm 0.0005$	$0.3858 \pm 0.0011$	$-16.0967 \pm 0.0021$	$-2.821 \pm 0.042$
500	25 500	$0.3358 \pm 0.0004$	$0.3356 \pm 0.0004$	$-16.3295 \pm 0.0073$	$-0.463 \pm 0.035$
864	22 600	$0.3047 \pm 0.0005$	$0.3054 \pm 0.0005$	$-16.5437 \pm 0.0045$	$1.095 \pm 0.022$

attempted displacements in cyclical order. The results are displayed in Table I, where the realization, or sample sequence, lengths given in the second column are the total number of attempted moves per molecule (excluding the fixed one) in the realization. Up to as many as 2600 initial attempted moves per molecule were omitted from the estimates of  $g(\zeta)$  and  $U$  as being associated with a transient decay away from the face-centered-cubic initial configuration.

Inasmuch as  $g \exp(u/kT)$ , where  $u$  is the interparticle potential, is a continuous function of  $\zeta$ , the calculated values of  $g$  at  $K$ , from the left and from the right, serve as a check on the convergence of the Markov chain. The agreement between columns three and four in Table I is seen to be very good. These values of  $g$ , as well as of  $g$  at contact, were obtained by extrapolation of least-squares fits to the computed points, as in the case of simple hard-core potentials.<sup>4</sup> The computed radial distribution functions for the 256- and 864-molecule systems are shown in Fig. 1, where it is clear

that with increasing  $N$  the first peak in  $g$  increases while the second decreases (and is shifted left), both changes tending to increase the pressure obtained from the equation displayed above.

The reduced pressure is seen to be especially sensitive to system size, with negative pressures resulting from the smaller values of  $N$ . This was also found by Rotenberg, who obtained for a 256-molecule system  $pV_0/NkT \approx -3.88$  (as read from Fig. 2 of Ref. 1). The discrepancy between this value and the corresponding result in Table I is large, but probably not inconsistent with Rotenberg's statement regarding the length of his runs and the precision of his results. A linear extrapolation in  $N^{-1}$  of the 500- and 864-molecule results gives the estimate  $pV_0/NkT=3.24$  for an infinite system, which should evidently not be regarded as a precise result.

These results suggest some caution in interpreting the significance of the high density "van der Waals" loops in Rotenberg's 256-molecule calculations.

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<sup>1</sup> A. Rotenberg, J. Chem. Phys. 43, 1198 (1965).

<sup>2</sup> The derivation of this equation for finite, periodic systems may be found in W. W. Wood, "Monte Carlo Studies of Simple Liquid Models," in *The Physics of Simple Liquids*, H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke, Eds. (North-Holland Publ. Co., Amsterdam, to be published).

<sup>3</sup> N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. 21, 1087 (1953); W. W. Wood and F. R. Parker, *ibid.* 27, 720 (1957).

<sup>4</sup> See, e.g., W. W. Wood, Los Alamos Scientific Laboratory Rept. LA-2827, 1963, Chap. 9. (Available from Office of Technical Services, U.S. Dept. of Commerce, Washington, D.C.)

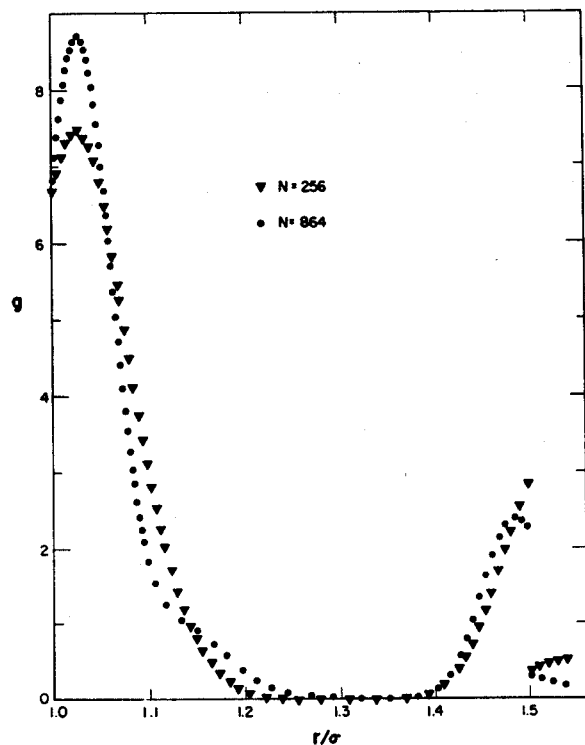


FIG. 1. Radial distribution functions of two different-sized square-well systems, both with  $K=1.5$ ,  $\tau=1.185$ , and  $\theta=0.5$ , obtained by Monte Carlo techniques.

## Interpretation of Spectra

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With the increasing interest in hydrogen-bonded substances, and, in particular, water, which have infrared and Raman spectra characterized by broad, overlapping bands, several authors<sup>1,2</sup> have attempted to extricate the concealed structure using numerical or mechanical methods, by fitting several Gaussian components to the experimental contours. The following simple counter example shows, that, within the experimental errors and the uncertainty in the actual com-