Vibrational Normal Modes of Polymer Nanoparticle Dimers Using the Time-Averaged Normal Coordinate Analysis Method

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The recently developed time-averaged normal coordinate analysis method is employed to investigate the normal modes of polymer nanoparticle dimers. In addition to providing the first accurate calculation of vibrational frequencies and vibrational displacements in dimerized nanoparticles, the normal mode corresponding to the particle dimer vibration is observed for the first time. It is observed that the nanoparticle dimer vibration is only minimally coupled to the other internal motions of the particle, showing a true correspondence to the vibrational motion in diatomic species. Several other characteristic vibrations of the dimerized species are observed, which correspond to coupled indifferent modes of the monomer particles.

I. Introduction

There has been a great deal of interest in recent years on the production, analysis, and properties of monodisperse polymer particles, following experimental techniques that have allowed for uniform production of polymer particles of arbitrary size and construction. Much work has gone into experimental analysis[1−9] and theoretical study[10−22] of these particles and their properties.

In recent experimental studies, it has been demonstrated that large structures composed of individually attached polymer nanoparticles can be constructed using a particle positioning tool.[23] These structures are persistent for long time scales and are presently being investigated for novel material properties. Identifying the properties of these particle systems is of critical and fundamental importance in understanding the physical characteristics of the collective systems, and a great deal of effort has been dedicated to investigation of both individual and collective nanoparticle properties.

Understanding the vibrational frequencies of large systems is important for evaluation of thermodynamic properties, infrared and Raman spectra, and reaction mechanisms. Of particular importance is the low frequency modes, which are typically related to conformational changes. Frequently, large molecular systems, such as proteins, are observed in the presence of solvent, the motions of which are strongly coupled to the conformational motion of the molecule. In the present case under investigation, we simulate polymer spheres in the absence of solvent, under conditions similar to those under which they are experimentally observed.[1−9]

In recent molecular dynamics simulations, we have seen evidence of collective vibrational motion of polymer particle dimers;[24] however, the vibrational frequencies of the intraparticle stretching modes must be estimated from the periodicity of the oscillations of the center of mass separation. Such an estimation makes the ad hoc assumption that there is, in fact, dimer vibrational normal mode, without detailed examination of the vibrational behavior. An understanding of the origins of the vibrational frequencies and their detailed motion and the examination of other collective motions of the systems can lead to a better understanding of the system dynamics. In addition, there may be other characteristic motions and frequencies that may aid in characterization of the systems, but that are difficult to evaluate without computation of the normal modes of the system.

Essentially, there are two classes of normal modes in a collection of particles. There are normal modes that roughly correspond to motion of the individual particles, and there are normal modes that involve internal elasticity of the particles. In this simplified classification, however, we ignore a number of fundamental couplings between the two kinds of motions, but such a simplification presents a construct to frame the study of the normal modes. In the present calculations, we seek to investigate both kinds of normal modes and compare the frequencies for the interparticle modes to the estimated frequencies from our previous MD simulation. The analysis of the normal modes of the complete system, however, requires accurate determination of the eigenvalues (frequencies) and eigenvectors (normal modes) of a very large system. To accomplish this feat, we must resort to special techniques.

The process of the computation of normal modes of molecules is well-known and has been reviewed extensively elsewhere,[25−29] so we provide a brief summary here of the results that are important to the present study. The essence of normal-mode analysis is the solution of the secular equation,

$$|\mathbf{F} - \lambda \mathbf{I}| = 0 \tag{1}$$

where λ are the eigenvalues and $\mathbf{F}$ is the force constant matrix

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in mass-weighted Cartesian coordinates. The squares of the frequencies of vibration are given by the eigenvalues, λ. The force constant matrix is obtained from the second derivatives of the potential function, V,

$$\mathbf{F} = \mathbf{M}^{-1/2}(\nabla^2 V)\mathbf{M}^{-1/2} \qquad (2)$$

where $\mathbf{M}$ is a diagonal matrix composed of the masses. In a traditional NCA calculation for a large molecule, there are numerous negative eigenvalues, which correspond to imaginary frequencies, which are in contrast to the assumption that the system is at a local minimum.

Recently, our laboratory has developed a technique for obtaining the normal modes of large systems composed of thousands of atoms.[15,16,18,21] In contrast to previously employed techniques,[25,26] the present method relies on a time-averaging procedure to smooth positional variations in the Hessian matrix. The averaging procedure ensures the Hessian matrix to be positive semidefinite and eliminates the occurrence of negative eigenvalues. The negative eigenvalues are physically unrealistic and are at odds with the fundamental assumption of normal-mode analysis: that the system lies at a harmonic local minimum of the potential energy surface where all of the second derivatives must be positive. The eigenvalues obtained from the diagonalization of the Hessian matrix represent the squares of vibrational frequencies, and negative eigenvalues represent unbound motions. When the method has previously been employed,[15,16,18,21] it has successfully produced the spectrum of large systems, faithfully finding six eigenvalues that are essentially zero, corresponding to the indifferent modes[30] (translations and rotations), with the remainder of the modes being assigned to true vibrations of the system.

The following paper is organized as follows: in section II we describe the theoretical methods employed in the present calculations, and the methods by which the calculations were performed. In section III we present and discuss the results.

II. Computation

The complete calculation occurs in several steps. The first step is the construction of the particle dimers by molecular dynamics simulation, followed by annealing of the particle dimers to a local minimum via a molecular mechanics procedure. The minimized configuration is used to generate a trajectory-averaged Hessian matrix, which is diagonalized using sparse matrix techniques to yield the eigenvalues (frequencies) and eigenvectors (displacements) of the molecular normal modes. Finally, the eigenvectors are searched to evaluate their character as consisting largely of inter- or intraparticle motions. Each of these procedures is discussed in some detail in the following sections. For the purpose of this study, we have restricted ourselves to polymer particles of 60 chains of 100 monomer units, with an initial temperature of 5 K.

A. Molecular Dynamics. For the purposes of the present study, we have examined motions and interaction forces between individual polymer particles both before and after interactions take place. The details of the geometric statement function approach developed in this group are described more fully elsewhere.[31]

Polymer particles have been treated with a molecular dynamics approach,[32,33] integrating Hamilton's equations of motion in time,

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \qquad (3)$$

$$-\dot{p}_i = \frac{\partial H}{\partial q_i} \qquad (4)$$

where H is the Hamiltonian of the system and the q_i and p_i represent the coordinates and their conjugate momenta. In the present case, we have treated coordinates and momenta in the Cartesian frame, where the total kinetic energy is diagonal. Integration of the equations of motion was accomplished by use of novel symplectic integrators developed in our laboratory.[34]

As a simplification we have collapsed the CH_2 and CH_3 units of the polyethylene chain into a single monomer of mass 14.5 amu. If the internal structure of these groups is neglected, the number of coordinates and thus the number of equations of motion for the system are greatly reduced. The model has been shown to be useful to study the low-temperature behavior of the system where the effects of the hydrogens have little effect on the heat capacity and entropy of the system.[35]

The Hamiltonian for the system is specified as[9,35]

$$H = T + \sum V_{2b} + \sum V_{3b} + \sum V_{4b} + \sum V_{nb} \qquad (5)$$

where T is the kinetic energy component, expressed in terms of Cartesian coordinates, the terms V_{2b}, V_{3b}, and V_{4b} represent the two-, three-, and four-body terms for monomer units in an individual polymer strand, and V_{nb} is the nonbonded interaction between individual monomer units separated by four or more monomer units along the chain, and within a spherical cutoff of 10 Å. The functional forms of the potentials are given by[35−39]

$$V_{2b} = D\{1 - \exp[-\alpha(r_{ij} - r_e)]\} \qquad (6)$$

$$V_{3b} = \frac{1}{2}\gamma(\cos\theta - \cos\theta_e)^2 \qquad (7)$$

$$V_{4b} = 8.77 + a\cos\tau + b\cos^3\tau \qquad (8)$$

$$V_{nb} = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \qquad (9)$$

with the values of the constant terms given in Table 1. The distances between the various monomer units, r_{ij} are given by the standard Cartesian relation,

$$r_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2} \qquad (10)$$

In the present case, initial conditions for the trajectories comprised the coordinates of individual amorphous polymer particles, which had previously been obtained by an annealing.[14] Momenta were chosen randomly in the radial coordinate so as not to excite internal angular momentum. The randomly chosen momenta were rescaled so as to produce the appropriate temperature for the simulation,

$$\sum_i \frac{1}{2m_i} p_i^2 = \frac{3}{2}k_B T \qquad (11)$$

The thermalized particles were then offset in the z-coordinate so that their minimum edge to edge distance was 5.75 Å. The molecular dynamics simulation was allowed to run for a minimum of 100 ps to allow the particles equilibrate and relax to their final configuration.

B. Potential Minimization. After creation of the particle dimer, it is necessary to establish suitable equilibrium positions for each of the monomer units in the structure, finding the local

TABLE 1: Potential Parameters for Polyethylene Particle Systems

Two-Body Bonded Constants[a]
$D = 334.72$ kJ/mol
$r_e = 1.53$ Å
$\alpha = 199$ Å^{-1}

Three-Body Bonded Constants[b]
$\gamma = 130.122$ kJ/mol
$\theta_e = 113°$

Four-Body Bonded Constants[a]
$a = -18.4096$ kJ/mol
$b = 26.78$ kJ/mol

Two-Body Nonbonded Constants[a]
$\epsilon = 0.4937$ kJ/mol
$\sigma = 4.335$ Å

[a] References 38 and 39. [b] References 36 and 37.

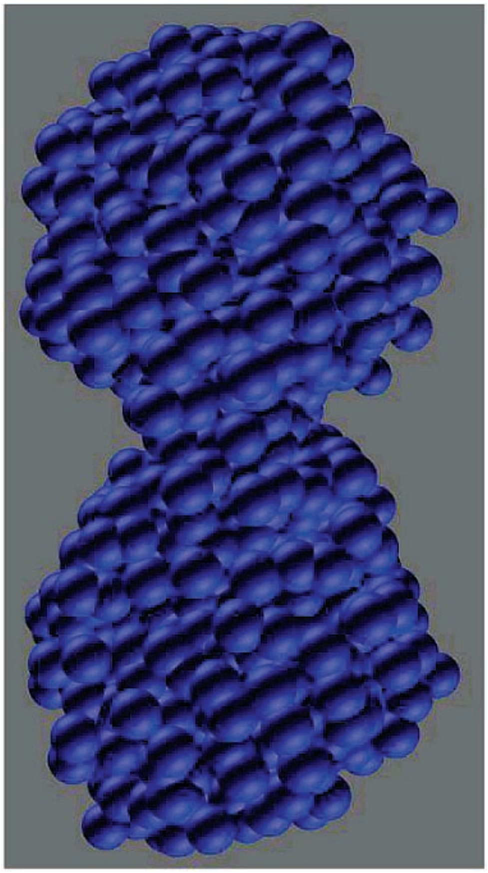

Figure 1. Structure of polymer particle dimer composed of 60−100 monomer unit chains.

potential minimum. The method employed in the present approach is a hybrid molecular dynamics−molecular mechanics simulation using the Broyden, Fletcher, Goldfarb, and Shannon (BFGS) quasi Newton minimization algorithm and simulated annealing via classical trajectories (a short trajectory in which the momenta are periodically quenched to zero). The resulting 6000 monomer unit particle dimers are shown in Figure 1.

C. Hessian Matrix Evaluation. The usual method for normal coordinate analysis is to choose a single configuration and to evaluate and diagonalize the Hessian matrix for this configuration. Because finding the exact minimum of the potential is difficult, such an approach invariably leads to obtaining the Hessian away from the minimum, leading to numerous negative eigenvalues. In a recent development, it was discovered that the matrix elements of the Hessian for coordinates obtained by sampling over a classical trajectory randomly fluctuate about the average value, which is then employed instead of the Hessian at a fixed configuration. The accurate integration of the trajectories is rendered particularly rapidly due to expressions for analytic derivatives that have evolved in our laboratory.[40,41]

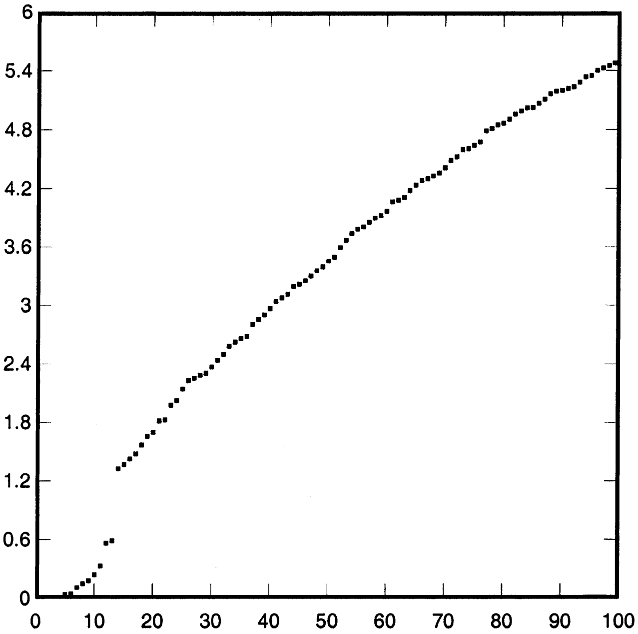

Figure 2. First 100 vibrational frequencies (in cm^{-1}) of particle dimer pair composed of 6000 monomer unit particles.

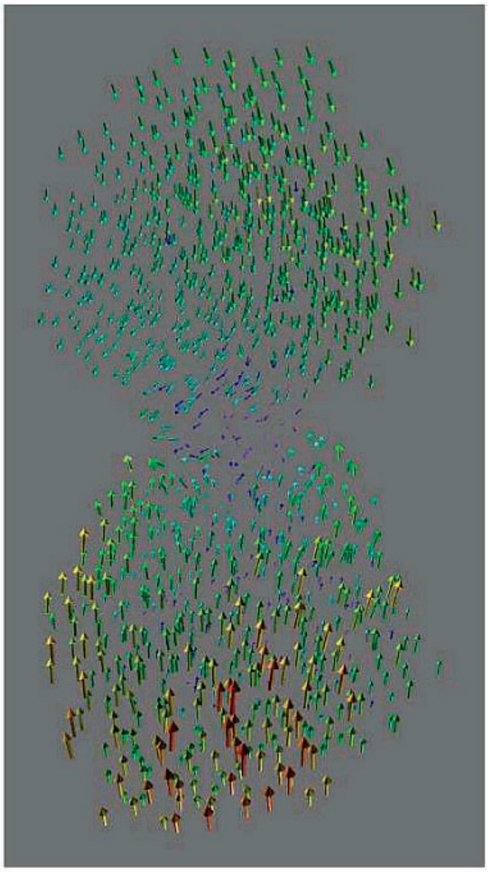

Figure 3. Dimer stretching modes of 6000 monomer unit particle dimers, mode 10.

D. Sparse Matrix Diagonalization. We have used ARPACK to compute the lowest vibrational modes of the sparse matrix representing the time-averaged Hessian matrix. The ARPACK

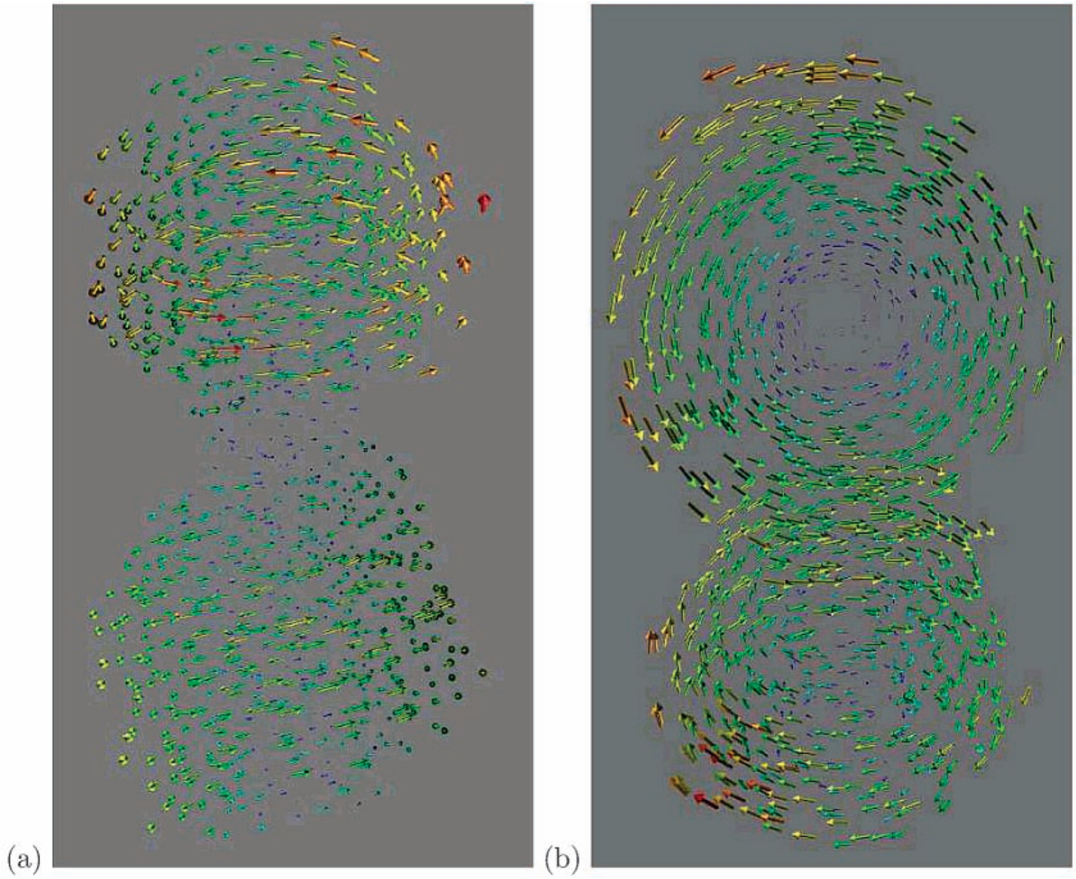

Figure 4. Bitoroidal modes of 6000 monomer unit particle dimers, mode 8: side view (a) and top view (b).

software is based on a variant of the Arnoldi process and for symmetric matrixes is equivalent to the Lanczos algorithm. The details of the computations employed in our computations have been described and reviewed extensively elsewhere.[15,16,18,21]

E. Eigenvector Searching. To characterize the vibrational modes as correlating to particle dimer motion or to internal motion a simple procedure was developed to screen for eigenvectors that were composed of large changes in the center of mass separation of the two particles. For each particle the Cartesian displacements Δx, Δy, and Δz were summed over all of the constituent monomer units. A concerted motion of all of the monomer units in the nanoparticle in a single direction results in a large cumulative displacement, whereas nominally internal motions in an individual particle conserve the particle center of mass and the displacements sum to zero. Using this screen as a diagnostic tool allows for rapid evaluation of classes of eigenvectors involving concerted particle motion for more detailed inspection.

The eigenvectors corresponding to the lowest 100 frequencies were explicitly visualized to observe characteristic behaviors. As expected, the first six modes correspond to the overall translations and rotations,[28,30] the next six to “coupled monomer indifferent modes”, as described below. Modes corresponding to higher vibrational frequencies did not have any readily discernible characteristic behavior, with the exception of modes in which the majority of the motion was restricted to a single particle (local or “spectator” vibrations).

III. Results and Discussion

It is observed that the molecular dynamics simulation produces particle dimers very similar in structure to those that are experimentally observed, Figure 1, although the simulated particle dimers are smaller in overall size. Experimental investigation of the interfacial region has not yet been made, but calculations of the particles in the present system show that there is not a significant amount of intertwining of the chains of the individual particles. Essentially, the present configuration consists of two individual particles in close contact, with a modest amount of deformation to minimize the exposed surface area of the particle dimer and subject to the constraint of minimization of large scale chain migration.

The vibrational frequencies show the usual characteristic behavior of having six near zero values, corresponding to the pure translations and vibrations. The remaining eigenvalues correspond to true vibrations of the dimer pair. The vibrational frequencies are shown in 2.

The investigation of the structure of the displacements in the eigenvectors leads to the identification of several normal mode types that are characteristic of particle structures. First is the dimer stretching mode represented in Figure 3, which is analogous to the vibrational stretch of a diatomic molecule, mode 10 in the 6000 monomer unit dimer, which was identified through the search algorithm previously described. The normal modes identified in this way were verified by explicit visualization of the eigenvectors of the normal modes, Figure 3.

Correlation of the dimer vibration frequency to the center of mass separation vibration appears to be reasonable. In a separate calculation, the dimer vibrational eigenvector for a 3000 monomer unit dimer, was found to have a frequency of about 0.8 cm^{-1}.[42] This compares quite favorably with the our previous simulation studies that estimated the vibrational frequency from the periodic oscillations of the center of mass separation of the particles, where the vibrational frequency was found to be approximately 1 cm^{-1}.[24]

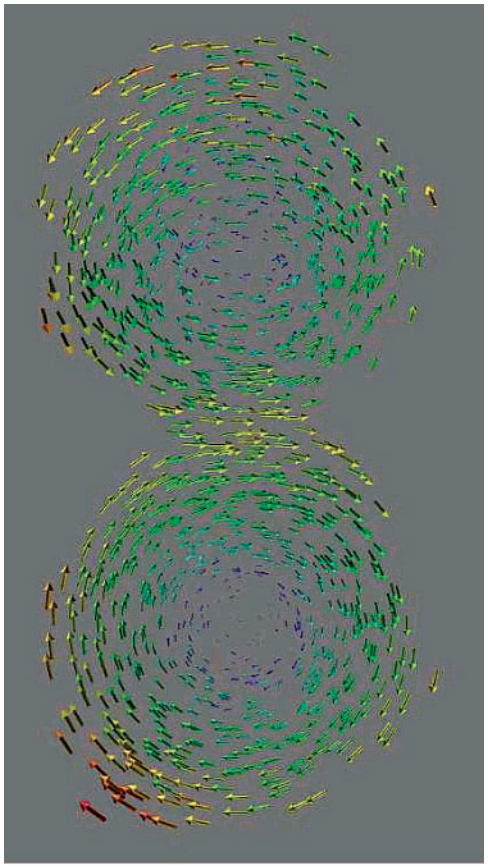

Figure 5. Symmetric "gear mode" of a 6000 monomer unit particle dimer, mode 7.

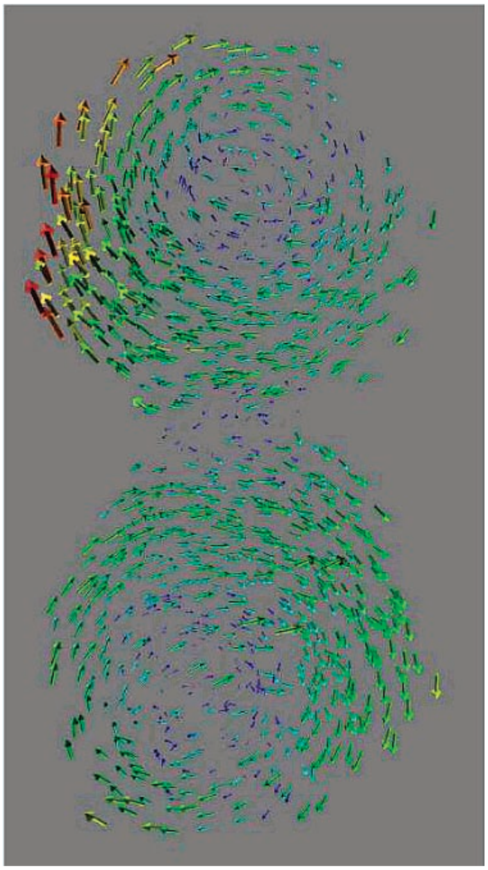

Figure 6. Asymmetric "gear mode" of a 6000 monomer unit particle dimer, mode 12.

There are additional vibrational modes that appear to be characteristic of the particle dimers that are not found in the spectrum of diatomic molecules. These characteristic modes are those which couple the internal motion of the individual particles making up the dimer. A diatomic molecule has no internal motion for the constituent atoms, whereas the individual polymer particles express a wide variety of normal mode types. In particular, we consider the indifferent normal modes,[30] those which correspond to the overall translations and rotations of the individual polymer particles, and how they couple to form new normal modes in the particle dimers. We classify the joint normal modes by an approximate scheme in which we couple the indifferent normal modes (specifically those with a zero frequency, i.e., the translations and rotations) of the same type for the single particles. For simplicity we apply this scheme to the particles composed of 60−100 monomer unit chains and reference the normal mode numbers for that system.

The scheme we establish for the coupling is to essentially write a basis for the eigenvector of each individual particle, $\mathbf{e}_1$ and $\mathbf{e}_2$, and to write the symmetric and antisymmetric combinations of the motion,

$$\mathbf{e}_s = (\alpha\mathbf{e}_1, \beta\mathbf{e}_2) \tag{12}$$

$$\mathbf{e}_a = (\alpha\mathbf{e}_1, -\beta\mathbf{e}_2) \tag{13}$$

remembering that the two vectors $\mathbf{e}_1$ and $\mathbf{e}_2$ belong to orthogonal vector spaces, and α and β are greater or equal to zero. The linear combination may be made with arbitrary coefficients, with the restriction that at least one eigenvector must have a nonzero component. Under such a scheme, we now classify the overall motions as approximately coupled motions of individual particles. Naturally, one could take additional components from each of the vector spaces, and this corresponds to the true solutions of the normal modes; however, it appears that for the lowest frequency modes the contributions come from one principal component.

Without loss of generality, we can assign a Cartesian coordinate system to the particles, with the z-axis being aligned along the line connecting the centers of mass. If we couple the z translations for the individual particles symmetrically, we find a overall translation in the z direction (mode 1). The antisymmetric combination corresponds (approximately) to the pseudodiatomic vibrational mode (mode 10). Similar analysis for the x and y translations produces normal modes that correspond to overall translations in the x and y directions (modes 2 and 3), and (approximately) to the "diatomic" rotations about the x and y axes (modes 4 and 5). The coupling of the individual particle rotations about the z-axis produces a true rotation about the z-axis (mode 6) and the lowest frequency vibrational mode, which we have designated as a "bitoroidal" mode, in which the two particles have pseudorotations about the z-axis on opposite directions (mode 8), Figure 4. We note in the figure that the coupling is not perfectly on axis, likely due to the effect of the polymer strands making up the structure, but the characteristic nature of the vibration is clear.

The coupling of the x and y rotational motions produces characteristic eigenmodes that are unique to structures composed of particle composites. The two particles can rotate in the same direction (e.g., clockwise) with respect to the x- or y-axis, which produces an antisymmetric "gear mode" (modes 11 and 12) (Figure 6), or in opposite directions to produce a symmetric "gear mode" (modes 7 and 9) (Figure 5). These motions are not truly gear rotations, as they are restricted in the extent of

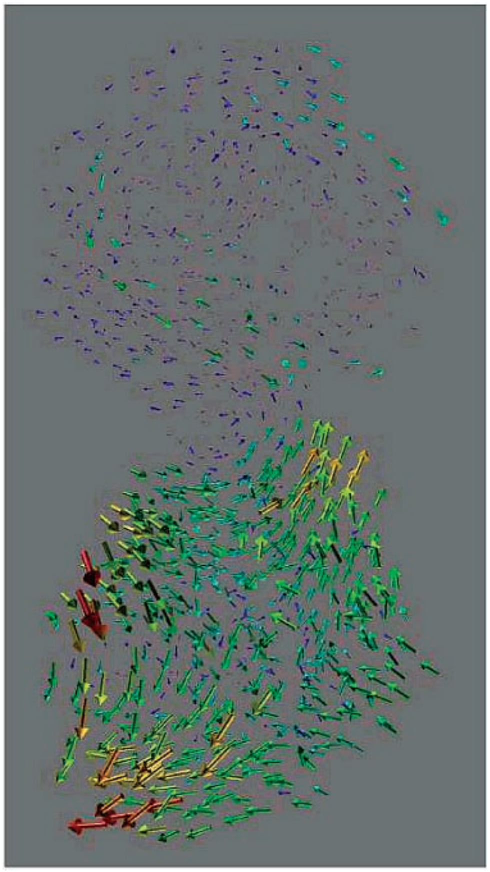

Figure 7. Single particle spectator mode in a 6000 monomer unit particle dimer, mode 24.

rotation by the potential force, and they oscillate about the equilibrium position. Nonetheless, this approximate classification scheme appears to correctly characterize the classes of motion.

These approximate characterizations are quite likely to be dependent on the extent of the interparticle coupling of the interfacial region. Clearly, particles with large surface contact regions will be more strongly coupled, and this classification scheme, which essentially amounts to a perturbation treatment will fail. Nonetheless, this picture does provide significant physical insight into the nature of the motion.

Normal modes corresponding to higher vibrational frequencies are more difficult to classify and involve large scale motion of monomer units in both particles. It is likely that these motions can be considered in terms of coupled vibrational modes of similar character in the individual particles, at least in the case of lower frequency vibrations, but we have not attempted to do so. There are also a number of normal modes, for instance mode 24 in Figure 7, which appear to consist of large displacements in one particle, with minimal displacements in the other; essentially, the second particle is reduced to “spectator” status. Of the remaining 88 of the 100 lowest frequency normal modes not corresponding to approximate coupled individual motion, approximately 25% (23 modes) correspond to approximate local (spectator) vibrational modes.

IV. Conclusion

The vibrational eigenvectors of coupled polymer spheres are determined for the first time using the time-averaged normal coordinate analysis method. Several modes are characterized, including modes that correspond to internal torsion about the interparticle axis, coupled single particle rotations, and an approximate dimer stretching vibration. In addition, there appear to be a large number of modes that correspond, in an approximate sense, to decoupled particle vibrations, where one particle undergoes large displacements while the other is stationary.

We have adopted a simple scheme for classifying the normal modes of the coupled particle system, based on an extension of the motions of individual particles. Although the approximate scheme is not derived within a rigorous group theoretic treatment (there is no simple point group that can be applied to the coupled polymer spheres), the scheme appears to correctly predict the motions of the coupled indifferent (zero frequency) modes of the individual particles.

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References and Notes

(1) Kung, C.-Y.; Barnes, M.; Sumpter, B. G.; Noid, D. W.; Otaigbe, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39*, 610.

(2) Barnes, M. D.; Kung, C.-Y.; Sumpter, B. G.; Noid, D. W.; Otaigbe, J. *Opt. Lett*. **1999**, *24*, 121.

(3) Barnes, M. D.; Ng, K. C.; Fukui, K.; Sumpter, B. G.; Noid, D. W. *Mater. Today* **1999**, *2*, 25.

(4) Barnes, M. D.; Ng, K. C.; Fukui, K.; Sumpter, B. G.; Noid, D. W. *Macromolecules* **1999**, *32*, 7183.

(5) Ford, J. V.; Sumpter, B. G.; Noid, D. W.; Barnes, M. D. *Chem. Phys. Lett.* **2000**, *316*, 181.

(6) Ford, J. V.; Sumpter, B. G.; Noid, D. W.; Barnes, M. D. *J. Phys. Chem. B* **2000**, *104*, 495.

(7) Ford, J. V.; Sumpter, B. G.; Noid, D. W.; Barnes, M. D. *Polymer* **2000**, *41*, 8075.

(8) Ford, J. V.; Sumpter, B. G.; Noid, D. W.; Barnes, M. D.; Otaigbe, J. U. *Appl. Phys. Lett*. **2000**, *77*, 2515.

(9) Otaigbe, J.; Barnes, M.; Fukui, K.; Sumpter, B. G.; Noid, D. W. *Adv. Polym. Sci.* **2001**, *154*, 1.

(10) Fukui, K.; Sumpter, B. G.; Barnes, M.; Noid, D. W.; Otaigbe, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39*, 612.

(11) Fukui, K.; Sumpter, B. G.; Barnes, M. D.; Noid, D. W.; Otaigbe, J. *Macromol. Theory Simul.* **1999**, *8*, 38.

(12) Fukui, K.; Sumpter, B. G.; Runge, K.; Kung, C. Y.; Barnes, M.; Noid, D. W. *Chem. Phys.* **1999**, *244*, 339.

(13) Fukui, K.; Sumpter, B. G.; Barnes, M. D.; Noid, D. W. *Comput. Theor. Polym. Sci.* **1999**, *9*, 245.

(14) Fukui, K.; Sumpter, B. G.; Barnes, M. D.; Noid, D. W. *Polym. J.* **1999**, *31*, 664.

(15) Noid, D. W.; Fukui, K.; Sumpter, B. G.; Yang, C.; Tuzun, R. *Chem. Phys. Lett.* **2000**, *316*, 285.

(16) Fukui, K.; Noid, D. W.; Sumpter, B. G.; Yang, C.; Tuzun, R. *J. Phys. Chem. B* **2000**, *104*, 526.

(17) Sumpter, B. G.; Barnes, M. D.; Fukui, K.; Noid, D. W. *Mater. Today* **2000**, *2*, 3.

(18) Fukui, K.; Sumpter, B. G.; Yang, C.; Noid, D. W.; Tuzun, R. E. *J. Polym. Sci.: Polym. Phys.* **2000**, *38*, 1812.

(19) Fukui, K.; Sumpter, B. G.; Barnes, M. D.; Noid, D. W. *Macromolecules* **2000**, *33*, 5982.

(20) Sumpter, B. G.; Fukui, K.; Barnes, M. D.; Noid, D. W. In *Computational Studies, Nanotechnology, and Solution Thermodynamics of Polymer Systems*; Kluwer Academic/Plenum Publishers: New York, 2001.

(21) Fukui, K.; Sumpter, B. G.; Yang, C.; Noid, D. W.; Tuzun, R. E. *Comput. Theor. Polym. Sci.* **2001**, *11*, 191.

(22) Vao-soongern, V.; Ozisik, R.; Mattice, W. L. *Macromol. Theory Simul.* **2001**, *10*, 553.

(23) Barnes, M. D.; Mahurin, S.; Mehta, A.; Sumpter, B. G.; Noid, D. W. Submitted for publication.

(24) Hathorn, B. C.; Sumpter, B. G.; Barnes, M. D.; Noid, D. W. *Macromolecules* **2002**, *35*, 1102.

(25) Brooks, B.; Janezic, D.; Karplus, M. *J. Comput. Chem. Phys.* **1995**, *16*, 1522.

(26) van Vlijmen, H. W. T.; Karplus, M. *J. Phys. Chem. B* **1995**, *103*, 3039.

(27) Painter, P. C.; Coleman, M. M.; Koenig, J. L. *The Theory of Vibrational Spectroscopy and its Applications to Polymeric Materials*; Wiley: New York, 1982.

(28) Wilson, E. B.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; Dover: New York, 1955.

(29) Meister, A. G.; Cleveland, F. F. *Am. J. Phys.* **1946**, *14*, 13.

(30) Goldstein, H. *Classical Mechanics*, 2nd ed.; Addison-Wesley: Reading, MA, 1980.

(31) Noid, D. W.; Sumpter, B. G.; Wunderlich, B.; Pfeffer, G. A. *J. Comput. Chem.* **1990**, *11*, 236.

(32) Hoover, W. G. *Annu. Rev. Phys. Chem.* **1983**, *34*, 103.

(33) Klein, M. L.; Annu. *Rev. Phys. Chem.* **1985**, *36*, 525.

(34) Gray, S. K.; Noid, D. W.; Sumpter, B. G. *J. Chem. Phys.* **1994**, *101*, 4062.

(35) Sumpter, B. G.; Noid, D. W.; Wunderlich, B. *J. Chem. Phys.* **1990**, *93*, 6875.

(36) Weber, T. A. *J. Chem. Phys.* **1978**, *69*, 2347.

(37) Weber, T. A. *J. Chem. Phys.* **1979**, *70*, 4277.

(38) Sorensen, R. A.; Liam, W. B.; Boyd, R. H. *Macromolecules* **1988**, *21*, 194.

(39) Boyd, R. H. *J. Chem. Phys.* **1968**, *49*, 2574.

(40) Tuzun, R. E.; Noid, D. W.; Sumpter, B. G. *Macromol. Theory Simul.* **1996**, *5*, 771.

(41) Tuzun, R. E.; Noid, D. W.; Sumpter, B. G. *J. Comput. Chem.* **1997**, *18*, 1804.

(42) For conciseness in presentation, we have not given the detailed results on the 3000 monomer unit particle dimers and have focused our presentation to the 6000 monomer unit particle dimers. We report the "stretching" frequency of the 3000 monomer unit dimer here because it is the only case where a comparable value is available from the periodic behavior in the center of mass separation in a numerical simulation.