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Computational simulation of polymer particle structures: vibrational normal modes using the time averaged normal coordinate analysis method

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Abstract

The structures composed of individual polymer nanoparticles are simulated using a molecular dynamics technique. Structures composed of model polyethylene particles consisting of between 3000 and 24,000 monomer units are paired into dimers in a molecular dynamics simulation. The vibrational motion of the polymer particle structures corresponding to the stretching vibration between particles is studied using the time averaged normal coordinate analysis method. The data are fit to an empirical formula based on the expected scaling of the force constants with the surface contact area, yielding a formula which could be extrapolated to large particle structures which can be experimentally generated.

Keywords: Vibrational normal modes; Time averaged normal coordinate analysis; Dimer

1. Introduction

Molecular dynamics (MD) has shown great use in studying material properties of polymer systems. The material properties can be formulated at the microscopic molecular level, and through simulation and extension to macroscopic systems, the effects of bulk properties can be investigated. The deduced bulk properties can then be compared to experimentally available measurements.

Essentially, any molecular dynamics simulation consists of establishing an initial set of positions and momenta for all the bodies in a system, and integrating Hamilton's equations of motion to observe the evolution in time of the coupled bodies in the system. Recent evolution of the molecular dynamics technique in our laboratory (the geometric statement function approach with simplistic integration) has greatly increased the efficiency of the propagation of the equations of motion, allowing the treatment of very large polymer systems [1–4].

Recently, we have utilized molecular dynamics as a tool to circumvent difficulties which arise in the numerical analysis of normal coordinates of large systems [5–8]. The normal coordinates of a system give the vibrational displacements, and the corresponding eigenvalues give the squares of the vibrational frequencies. Even in the region of a local minimum, conventional normal mode analysis yields a large number of negative eigenvalues, corresponding to imaginary frequencies. Such difficulty arises from computational evaluation of an exact local minimum on a very high dimensional surface with a complicated potential energy function. We have found that, instead of evaluating the required Hessian matrix at a single numerically computed point, which does not represent an exact local minimum, averaging the Hessian matrix elements over a molecular dynamics trajectory in the vicinity of this local minimum yields a matrix which is positive semi-definite. The matrix yields the desired, physically realistic, positive eigenvalues, with six near zero eigenvalues which correspond to indifferent modes (translations and rotations) [9]. The vibrational frequencies so obtained are related to a wide variety of physical properties of the system, including such direct measurables as the heat capacity [10].

In the present investigation, we build on previous work from our laboratory, where individual polymer particles were simulated to compare with experimental studies of polymer particles. In the present work, we extend the previous studies to simulate interactions of individual

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polymer particles as a prelude to large scale simulations of structures composed of polymer particles which can be experimentally constructed [11].

As opposed to previous studies which encompassed the interactions and deformations of individual particles during the collision process [12–14], we focus here on the vibrational normal modes of the agglomerates. The vibrational structure gives information about the rigidity of the structures, and the concerted motion of the particles. There has been substantial interest in related structures, based on dimerized fullerenes and their analogues [15]. The present structures differ from these in the fact that the particles are not 'hollow' structures, and thus have substantially more atoms, and the systems are 'soft' and more prone to deform, due to a lack of a definitive chemically linked structure.

In particular, the vibrational normal modes of the particle dimers are related to the force constants for interaction between the particles. These force constants are then compared to simple models for interparticle forces based on a continuum model which is based on the interaction between two planar surfaces [16].

In Section 2, we briefly describe the methodology by which our polymer particle dimers are constructed. In Section 3, we develop the treatment of interparticle vibrations and briefly outline the time averaged normal coordinate analysis method which includes the internal elasticity of the particles, which we term the 'exact' solution for the complete normal coordinates of the system. Lastly, in Section 4, we discuss our results and provide a convenient expression by which the present results can be extrapolated to larger systems.

2. Structure generation and analysis

Our method for generating structures for simulation is similar to the experimental method by which they are produced, where pre-formed spherical particles are brought into contact with a particle positioning apparatus [11]. For use in our simulations, we have generated a library of molecular structures of particles of several sizes [18] which we employ to generate particle superstructures. In practice, we can produce polymer particle dimers by selecting two particles of desired size, and placing them in close proximity (surface contact distances of about 10 Å). The momenta of the monomer units are then chosen randomly and scaled to produce a desired temperature (in this case 5 K). The momenta are chosen to align with the vector of displacement from the center of mass, so as to produce particles with no intrinsic angular momentum, and the motion of the center of mass was subtracted out. To each monomer unit's velocity, an additional 0.25 Å/ps is added in the direction of the line connecting the centers of mass of the two particles, so that the particles approach with a relative velocity of 0.5 Å/ps.

The particles have been treated with a molecular dynamics approach [19,20]. Integration of the equations of motion was accomplished by use of novel symplectic integrators developed in our laboratory [2].

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. By neglecting the internal structure of these groups, the number of coordinates and thus the number of equation 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 effect of the hydrogens have little effect on the heat capacity and entropy of the system [21].

The Hamiltonian for the system is specified as [21]

$$H = T + \sum V_{2b} + \sum V_{3b} + \sum V_{4b} + \sum V_{nb} \tag{1}$$

where T is the kinetic energy component, expressed in terms of Cartesian coordinates, and the terms V_{2b}, V_{3b} and V_{4b} represent the 2-, 3-, 4-body terms for monomer units in an individual polymer strand, and V_{nb} is the non-bonded 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 Refs. [21–25]

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

$$V_{3b} = \tfrac{1}{2}\gamma(\cos\theta - \cos\theta_e)^2 \tag{3}$$

$$V_{4b} = 8.77 + a\cos\tau + b\cos^3\tau \tag{4}$$

$$V_{nb} = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right], \tag{5}$$

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

Molecular dynamics simulations were run until the particles had partially coalesced, between 60 and 200 ps. Subsequent to creation of the particle dimer, equilibrium

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 non-bonded constants[a]
$\epsilon = 0.4937$ kJ/mol
$\sigma = 4.335$ Å

[a] Refs. [24,25].
[b] Refs. [22,23].

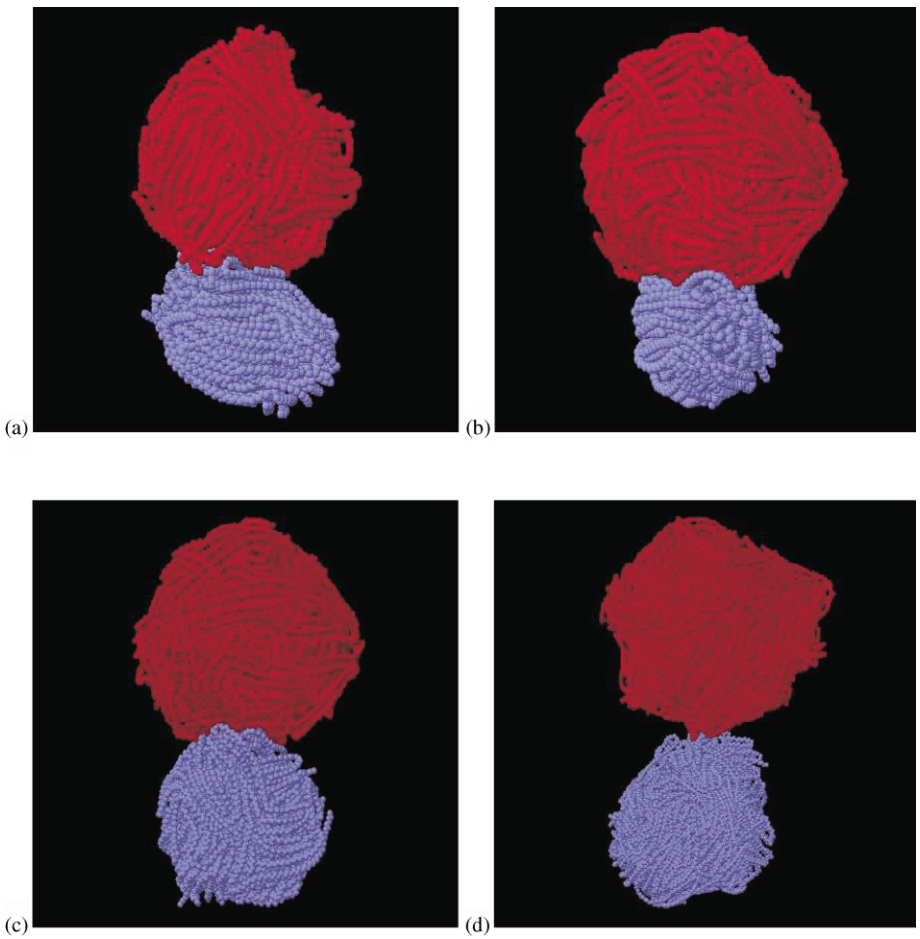

Fig. 1. Structure of polymer particle dimers. Each particle is composed of 100 monomer unit chains: (a) 6000 monomer unit and 3000 monomer unit particle dimer; (b) 12,000 and 3000 monomer unit particle dimer; (c) 12,000 and 6000 monomer unit particle dimer; (d) 24,000 and 12,000 monomer unit particle dimer.

positions for each of the monomer units in the structure was obtained by finding the local potential minimum. The method employed in the present approach was 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) [26]. The resulting particle dimers are shown in Fig. 1.

For the interpretation of results, we require a measure of the interfacial area between the particles and the approximate particle sizes. The interaction regions shown are not circular, as is expected in the somewhat larger experimentally derived particles [11], so it is necessary to obtain an approximate area of interaction. We have defined the interfacial region as those monomer units in a particle, which lie within 10 Å of the other particle, identical to the interaction cutoff. The area is computed by dividing the total number of monomer units in the interfacial area by the known monomer unit density [16], $\rho = 0.033$ Å^{-3} and by the interfacial thickness, 20 Å, obtained from the interaction cutoff. The cross-sections of the interfacial region are shown in Fig. 2. The approximate particle radii are obtained in a similar fashion, by assuming spherical particles and using the relation $R = (3N/\pi\rho)^{1/3}$, where N is the number of monomer units in the particle, and ρ is the monomer unit density. The numerically calculated particle radii agree with the observed particle radii to within approximately 10%, given allowances for the slightly non-spherical nature of the numerically simulated polymer particles.

3. Dimer vibrations

We intend to interpret our results in terms of 'multibody' vibrational analysis of the polymer particles. In essence, the vibrations of the system are classified in terms of motions in which the individual atoms in the polymer particles remain fixed with respect to each other, and there is no internal elasticity of the particles. In the present work, we confine ourselves to the coordinate representing the interparticle distance, which would be a stretching vibration in the multibody vibration case.

In order to interpret our results, we consider the potential

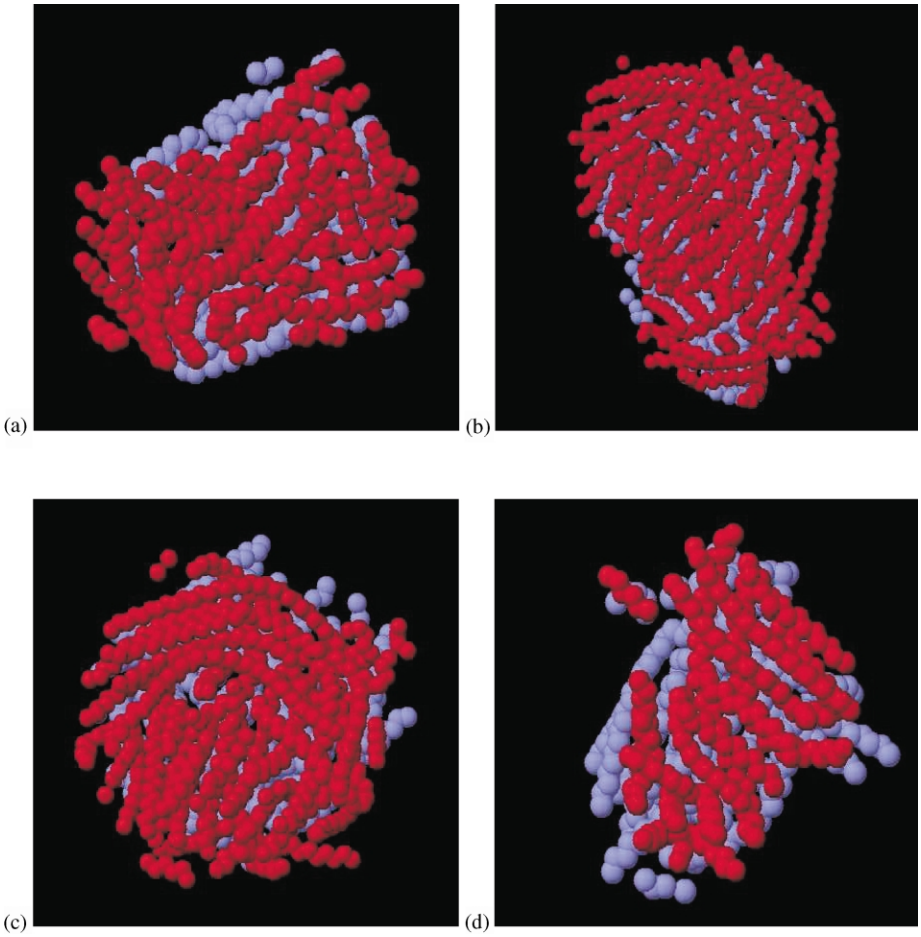

Fig. 2. Interfacial region for polymer particle dimers shown in Fig. 1.

as a Taylor series about a local minimum for interaction between the two bodies [9]

$$V(D) = V_0 + \left(\frac{\partial V}{\partial D}\right)_{D=D_0}(D - D_0) + \frac{1}{2}\left(\frac{\partial^2 V}{\partial D^2}\right)_{D=D_0}(D - D_0)^2 + \cdots \quad (6)$$

where D is the distance between the surfaces of the two particles and D_0 is the location of the local minimum. Setting the zero of energy to V_0, and recognizing the first derivative vanishes at the local minimum, we obtain the usual harmonic approximation

$$V(D) = \frac{1}{2}\left(\frac{\partial^2 V}{\partial D^2}\right)_{D=D_0}(D - D_0)^2 \quad (7)$$

In the usual harmonic oscillator approximation, the vibrational frequency is given by

$$\nu = \frac{1}{2\pi}\mu^{-1/2}\left(\frac{\partial^2 V}{\partial D^2}\right)^{1/2}_{D=D_0} \quad (8)$$

where $\mu = M_1M_2/(M_1 + M_2)$ is the reduced mass of the two particles. The masses are known, and thus the only remaining parameters required are the second derivative of the potential and the location of the local minimum.

Empirically, we know that the force between the particles should be proportional to the area of interaction [16]. Using such an empirical relationship, we write the second partial derivative as

$$\left(\frac{\partial^2 V}{\partial D^2}\right)_{D=D_0} = 4\pi^2\alpha^2 A \quad (9)$$

where α is a proportionality constant to be obtained from a fit to the calculated vibrational frequencies, and A is the area of the interfacial region between the two particles, which has been estimated from the structure of the particles. The resulting scaling law for the vibrational frequencies is

$$\nu = \alpha\mu^{-1/2}A^{1/2} \quad (10)$$

3.1. Time averaged normal coordinate analysis

The detailed description of the time averaged normal coordinate analysis technique can be found elsewhere, and only a brief description is given here. The

Table 2
Idealized geometry for particle dimer systems

N_1	N_2	R_1 (Å)	R_2 (Å)	A (Å^2)[a]
6000	3000	35.1	27.9	1352
12,000	3000	44.3	27.9	2141
12,000	6000	44.3	35.1	1670
24,000	12,000	55.8	44.3	814

[a] Estimated from interfacial area computed from molecular structure in Fig. 2.

minimized configuration is used to generate a trajectory averaged Hessian matrix. The accurate integration of the trajectories is rendered particularly rapidly due to expressions for analytic derivatives which have evolved in our laboratory [3,4]. The Hessian matrix is subsequently diagonalized using sparse matrix techniques to yield the eigenvalues (squared frequencies) and eigenvectors (displacements) of the molecular normal modes. The details of the computations employed have been described and reviewed extensively elsewhere [5–8]. Finally, the eigenvectors are searched to evaluate their character as consisting largely of inter- or intra-particle motions.

There are a number of types of typical vibrational motion which appear to be characteristic of the particle dimer systems (Table 2). These motions include coupled rotations of the particles and 'spectator modes' where the dominant contribution to the motion is restricted to one of the two particles [17]. In the present case, we have focused our attention to so-called dimer vibrations, where the particles have concerted motions, which resemble the vibration of a diatomic molecule. Given a large set of normal modes, we can rapidly search the set for eigenvectors of this type by looking for peaks in

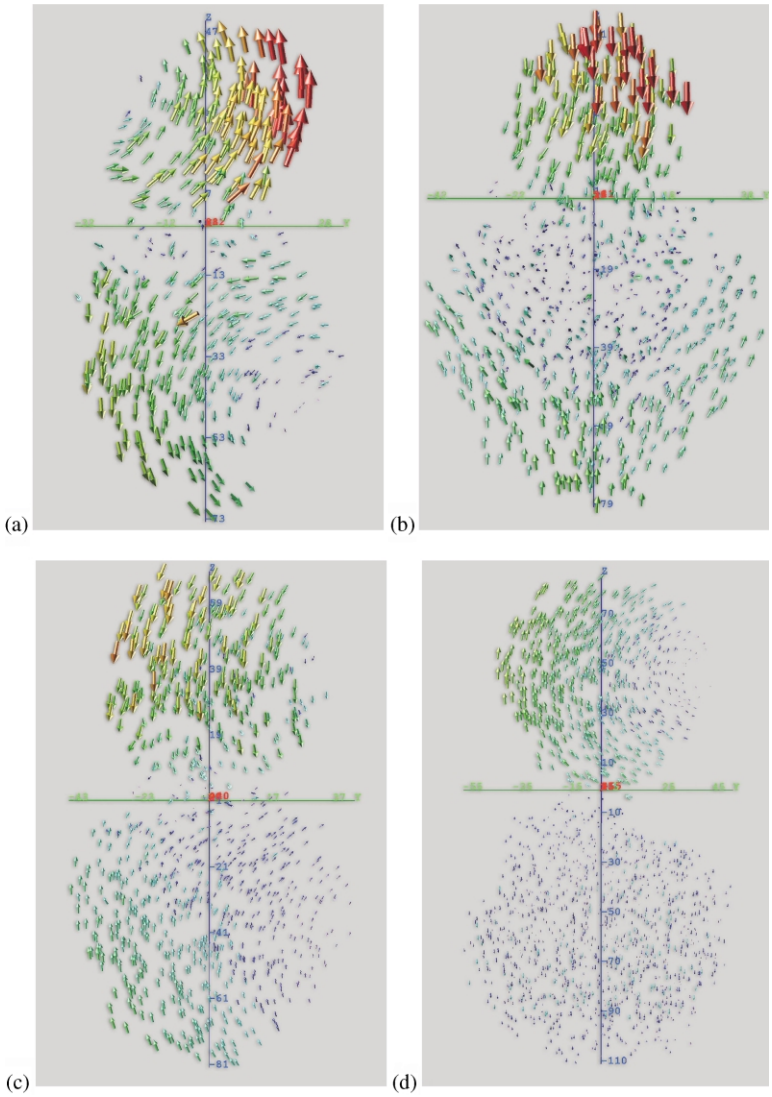

Fig. 3. Normal mode vibrations for polymer particle dimers shown in Fig. 1.

Table 3
Calculated vibrational frequencies

N_1	N_2	ν (cm^{-1})[a]
6000	3000	6.8
12,000	3000	8.7
12,000	6000	5.5
24,000	12,000	3.3

[a] Time averaged normal coordinate model, Section 3.1.

the function

$$P = \sum_{i=1}^{N} (\mathbf{R}\cdot\mathbf{r}_i) \tag{11}$$

where the $\mathbf{r}_i$ are the vibrational displacements of the monomer units in the system, and $\mathbf{R}$ is the vector which connects the centers of mass of the two bodies. When a set of possible vibrational modes has been determined, final assignment was made by a visual inspection of the normal mode displacements. None of the modes observed were pure 'dimer stretching modes', however for each particle dimer pair, there was a normal mode (typically near mode 10) which was observed to be principally composed of a dimer vibration with some additional internal motion representing coupling to internal elasticity. The normal modes are represented in Fig. 3, with the corresponding vibrational frequencies in Table 3. The 'purity' of the vibrational modes (and the other modes which are described elsewhere [17]) appear to be controlled by the interfacial interaction area, with particles having greater overlap exhibiting a larger amount of vibrational mixing between the particles and less single particle motion.

5. Discussion

The molecular dynamics approach to polymer systems has been widely applied in the past, with good result. Here, we have used a short classical trajectory, which is confined about a local minimum to find the Hessian matrix in that vicinity. This so called time averaged normal coordinate method has been shown to be useful in the past for eliminating the occurrence of negative eigenvalues of the Hessian matrix, and finding only positive eigenvalues, which represent real (rather than imaginary) vibrational frequencies [5–8].

One caveat to the vibrational frequencies observed here is that there may be substantial dependence on the nature of the interfacial region. As is observed in Fig. 2, the polymer particles in the present system are largely independent, with no intertwining polymer strands. Any intertwining of the polymer chains of the two particles may lead to higher force

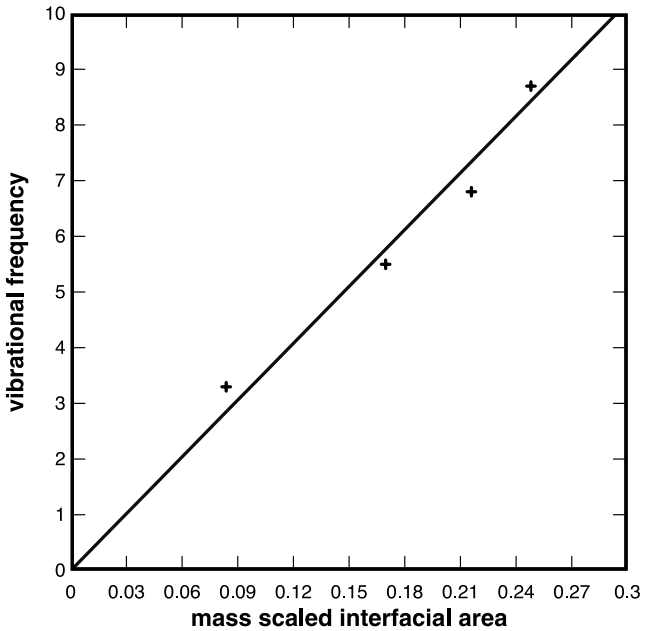

Fig. 4. Scaling law for polymer particle dimer frequencies. Frequencies are in cm^{-1} and mass scaled area is $\sqrt{AI\mu}$ from Table 3.

constants, and correspondingly higher vibrational frequencies.

A straightforward fit of the calculated vibrational frequencies to the scaling law, Eq. (10) enables us to obtain the parameter $\alpha = 34\ cm^{-1}\ Å^{-1}\ g^{-1/2}\ mol^{1/2}$. This scaling rule could be extrapolated to estimate the vibrational frequencies of larger experimental systems when the data for vibrational frequencies in such systems becomes available. In these systems, which would lie on the low end of the scaled masses in Fig. 4, the mass of the particles is known (or can be estimated from the particle density) and the interaction area known as the interaction geometries can be represented well by intersecting spheres [11].

The observation of the normal modes in the present case demonstrates that the treatment of the 'dimer vibration' of the system with a multibody vibration may not be entirely warranted, as there is a substantial amount of internal elasticity of the particle which is coupled to this vibration. Nonetheless, we have extracted approximate dimer vibrational frequencies from the normal mode calculation. A calculation using force constants obtained from continuum models [16] based on planar and spherical interactions obtains vibrational frequencies, which are approximately an order of magnitude too small [27]. However, using the expected scaling law for the forces and vibrations, based on the interfacial area, we can derive an approximate fit to the data. The approximate fit leads us to the conclusion that perhaps a significant portion of the particles is not in motion for these vibrations, leading to a smaller effective mass. This is, in fact, observed in the normal modes in Fig. 3, where the interfacial region appears to be more

static than the bulk of the particles during the course of the vibrational motion, and thereby undergoes an elastic compression due to the polymer particle dimer vibration.

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References

[1] Noid DW, Sumpter BG, Wunderlich B, Pfeffer GA. J Comput Chem 1990;11:236.
[2] Gray SK, Noid DW, Sumpter BG. J Chem Phys 1994;101:4062.
[3] Tuzun RE, Noid DW, Sumpter BG. Macromol Theor Simul 1996;5:771.
[4] Tuzun RE, Noid DW, Sumpter BG. J Comput Chem 1997;18:1804.
[5] Noid DW, Fukui K, Sumpter BG, Yang C, Tuzun RE. Chem Phys Lett 2000;316:285.
[6] Fukui K, Noid DW, Sumpter BG, Yang C, Tuzun RE. J Phys Chem B 2000;104:526.
[7] Fukui K, Sumpter BG, Yang C, Noid DW, Tuzun RE. J Polym Sci: Polym Phys 2000;38:1812.
[8] Fukui K, Sumpter BG, Yang C, Noid DW, Tuzun RE. Comput Theor Polym Sci 2001;11:191.
[9] Goldstein H. Classical mechanics, 2nd ed. Reading, MA: Addison-Wesley; 1980.
[10] Yang C, Noid DW, Sumpter BG, Sorensen DC, Tuzun RE. Macromol Theor Simul 2001;10:756.
[11] Mahurin SM, Mehta A, Barnes MD, Hathorn BC, Sumpter BG, Noid DW, Runge K. Opt Lett 2002;27:610.
[12] Hathorn BC, Sumpter BG, Barnes MD, Noid DW. J Phys Chem B 2001;105:11468.
[13] Hathorn BC, Sumpter BG, Barnes MD, Noid DW. Macromolecules 2002;35:1102.
[14] Hathorn BC, Sumpter BG, Barnes MD, Noid DW. Polymer 2002;43:3115.
[15] Eisler H-J, Hennrich FJ, Werner E, Hertwig A, Stoermer C, Kappes MM. J Phys Chem A 1998;102:3889.
[16] Israelachvili J. Intermolecular and surface forces, 2nd ed. London: Academic Press; 1995.
[17] Hathorn BC, Sumpter BG, Noid DW, Tuzun RE, Yang C. Submitted for publication.
[18] Fukui K, Sumpter BG, Barnes MD, Noid DW. Polym J 1999;31:664.
[19] Hoover WG. Ann Rev Phys Chem 1983;34:103.
[20] Klein ML. Ann Rev Phys Chem 1985;36:525.
[21] Sumpter BG, Noid DW, Wunderlich B. J Chem Phys 1990;93:6875.
[22] Weber TA. J Chem Phys 1978;69:2347.
[23] Weber TA. J Chem Phys 1979;70:4277.
[24] Sorensen RA, Liam WB, Boyd RH. Macromolecules 1988;21:194.
[25] Boyd RH. J Chem Phys 1968;49:2574.
[26] Fletcher R. Practical methods of optimization. New York: Wiley; 1987.
[27] Hathorn BC, Sumpter BG, Noid DW. Unpublished results.