Thermal Disorder, Fluctuations, Growth and Fragmentation of Finite One-Dimensional Atomic Chains

James M. Phillips[1] **and J. G. Dash**[2]

Ordering in one-dimensional atomic chains is studied using computer simulation. We find that dense ordered chains may exist if the system is cold enough and not macroscopically long. Growth of finite length chains from the vapor and by vapor exchange between chains begins rapidly, then slows down exponentially in time. As temperature rises density fluctuations increase, causing the chains to fragment. Independent of fragmentation, disordering begins at the ends, a condition similar to the precursor of edge and surface melting in two and three dimensions. The chemical potential of finite ordered chains is a function of length and temperature, due to the competition between attraction and internal thermal excitation. Equilibrium of chains coexisting with one-dimensional vapor produces a distribution of sizes, peaked at a temperature dependent chain length. Several results may be relevant to experimental studies of adsorption on carbon nanotubes.

1. INTRODUCTION

Certain current experimental studies suggest the possibility of quasi-one-dimensional solid states in films adsorbed on carbon nanotubes.[1−9] Such phenomena may appear to conflict with well known proofs of the impossibility of one-dimensional condensed phases. However, condensed states of finite length are not excluded, and the present study explores their growth and equilibrium lengths.

[1]Department of Physics, University of Missouri, Kansas City, MO 64110, USA; e-mail: phillipsj@umkc.edu
[2]Department of Physics, University of Washington, Seattle, WA 98195-1560, USA.

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The basic proof is given in Section 149 of Landau and Lifshitz' *Statistical Physics*.[10] The argument, as simplified by Mattis,[11] posits heuristically that separate one-dimensional phases cannot exist, for if there were a condensed phase of N atoms, it could be broken at $(N-1)$ places, thereby contributing a term of order $\log N$ to the free energy. Since the energy e of a rupture is of order unity, a break in a long chain contributes a negative term in the free energy at finite temperature. This drives an increasing number of breaks, so that segments of macroscopic length cannot exist.

Van Hove,[12] for multi-neighbor interactions, and Takahashi,[13] for the nearest-neighbor interactions, showed that the density is a continuous monotonic single-valued function of the pressure in the thermodynamic limit, hence there can be no separate phases. Mattis[11] summarizes the results, "at most, condensed clusters can exist provided they are not macroscopically long." Several additional conditions enable a system to escape the restriction. These include certain interaction potentials such as long range forces, or in the case of momentum condensation, external fields.[14] An obvious condition which escapes the simple Landau restriction is that a finite chain can remain condensed at low temperature $T < T_0$, where

$$kT_0 = \frac{e}{\ln N}. \tag{1}$$

Equation (1) pertains to arrays without internal excitations. It is therefore interesting to examine how internal modes may affect the stability of finite arrays.

Some related aspects of our present work, specifically one-dimensional ensembles of hard rods, continue to excite significant interest. Various models of the one-dimensional system and their dynamics have recently been studied by density functional theory and analytic methods.[15−29] These investigations use pair interactions as an excluded volume (hard rods or hard spheres). Zhang[19] has given a density functional method finding a form of "crystallization" in a system of one-dimensional hard rods with a periodic interaction. Truskett *et al.*[21] have published their work on density fluctuations in a many body system and gave an example of the one-dimensional hard rod problem. Piasecki and Peliti[22] derived the harmonic properties of hard-sphere crystals in a one-dimensional model. Kaup and Paine[23] reports a closed form solution of the one-dimensional Born-Green-Yvon equation for a hard-rod fluid. Our work is distinctive in that it studies finite one-dimensional atomic systems with dispersion forces. Punnathanam and Corti[24] studied the nucleation theorem in one-dimensional arrays. Marconi and Tarazona[25] studied the dynamic

density functional theory for fluids and gave one-dimensional examples. Other examples of recent work on one-dimensional statistical mechanics are offered by Hodak and Girifalco[27−29] applying quasi-one-dimensional arrays of C_{60} encapsulated in carbon nanotubes.

2. METHOD FOR A FINITE SYSTEM BOUND PERIODICALLY

We test the theories by Monte Carlo computer simulation of finite atomic chains. First, we use a canonical ensemble (NVT) with periodic boundary conditions to measure the bulk modulus of the chain. The interaction potential is a Lennard–Jones (LJ) interaction, with 12, 6 exponents[30] and reduced variables are used throughout.[31] The reduced variables are distance $x* = R/\sigma$ and temperature $t^* = kT/\varepsilon$, where σ and ε are the LJ parameters. The calculations are for dimensionless internal energy U/NkT, pressure PL/NkT, heat capacity C_L/Nk, and bulk modulus BL/NkT. The internal energy is an ensemble average of the pair interactions plus the ideal gas contributions and the pressure is the same for the average of the virial. The heat capacity is the average of the energy fluctuations and the bulk modulus is the average of the pressure fluctuations. To cross-check our simulations, we did quasiharmonic lattice dynamics with periodic boundary conditions on 100 particle systems at several temperatures. We found good agreement between the calculated compressibilities with those computed by the simulations.

We studied finite chains containing 50, 100, and 1000 molecules, and searched for systems where the pressure is nearly zero and the compressibility is positive. These conditions give the average density of the stable configuration for that temperature. For these condensed clusters, we computed the probability of fluctuations in density[21,32] from the average density using

$$P(n)dn = (2\pi\sigma_0)^{-1/2}e^{-(n-n_{\text{av}})^2/2\sigma_0^2}dn \qquad (2)$$

and the density dispersion is

$$(n-n_{\text{av}})^2 = n_{\text{av}}^2(kT/BL).$$

We tested for density fluctuations in a finite chain by measuring the bulk modulus in the simulation. In this set of simulations, we denied the system free ends by the use of periodic boundary conditions. The results of Eq. (2) for a 100-atom chain in a range of reduced temperatures are given in Table I and plotted in Fig. 1. The probability of a density fluctuation large enough to form a break in the 100-atom chain is quite low for

Table I. Density fluctuations during the simulations of 100 atom chains, at reduced temperatures $t^* = 0.10$ to 0.16

t^*	$\overline{(\Delta n^*)^2}$	$\int_0^{\rho_c} P(n^*)dn^*$
0.10	0.0496	0.0526
0.11	0.0427	0.1685
0.12	0.1009	0.1685
0.13	0.0975	0.1611
0.14	0.1172	0.1894
0.15	0.4525	0.3669
0.16	1.612	0.4681

The compressibilities are the results found by the corresponding simulations. For the purposes of comparison, the lower limit was taken to a fluctuation with density less than one half the average density.
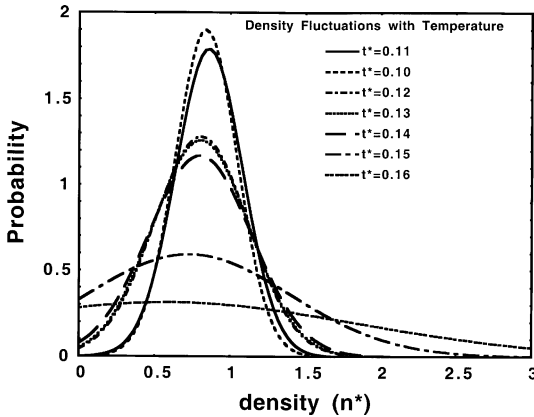

Fig. 1.   Plots of Eq. (2) for the probability of density fluctuations with density for a range of temperatures.

reduced temperatures below $t^* = 0.12$. However, if the chain is macroscopically long there is substantial probability that sufficiently large fluctuations will occur, in agreement with van Hove.[12] In these calculations the identification of a break is somewhat arbitrary, for the density fluctuations are transitory. If the system were not confined large density defects could allow the fragments to drift far apart, but in the restricted space of the small container the segments eventually rejoin.

3. STRUCTURAL RESULTS FOR THE PERIODICALLY BOUND SYSTEM

To illustrate the results of many simulation runs, Fig. 2 shows the configuration of the system with 1000-atoms at $t^* = 0.10$. For visual clarity, we plot vertically the shift of the atoms' lateral displacements from a uniform distribution, with the index of the atom as the abscissa. This gives us a snapshot view of the exaggerated longitudinal thermal displacement of the atom versus its number index. There are no breaks at $t^* = 0.10$, but increasing the temperature to $t^* = 0.12$ (Fig. 3), we begin to see breaks in the chain. One occurs just beyond atom $n = 200$ and another near $n = 950$. We note that between $n = 600$ and 700, a stretch of the chain appears to have an incipient break. Note, that at the break in the chain the two ends have pulled apart leaving a space for two atoms. Because of the periodic boundary conditions, the atom at the left end is the nearest neighbor of the atom at the right end.

To better see how fragmentation varies with temperature, we show several snapshots of a smaller system, 100-atoms, in Fig 4. In this shorter chain, we had to increase the temperature to $t^* = 0.13$ before observing a break. The number of segments of the chain increases with the temperature. At $t^* = 0.14$, the chain fragments into three clusters (see Fig. 5) and at $t^* = 0.16$ there are 12 clusters (see Fig. 6).

The internal excitations of the finite chains cause fragmentation at significantly lower temperature than the "Landau temperature" T_0 in Eq. (1). For the 1000-atom chain, we find breaks beginning at about 60% of T_0, while for 100-atoms we observe a break at 80% of T_0.
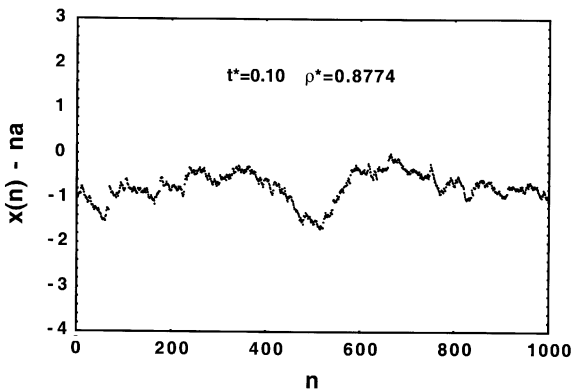

Fig. 2. A snapshot of the atomic displacements from a uniform distribution, under periodic boundary conditions, for chain length $N = 1000$ and reduced temperature $t^* = 0.10$. There are no breaks in this chain.
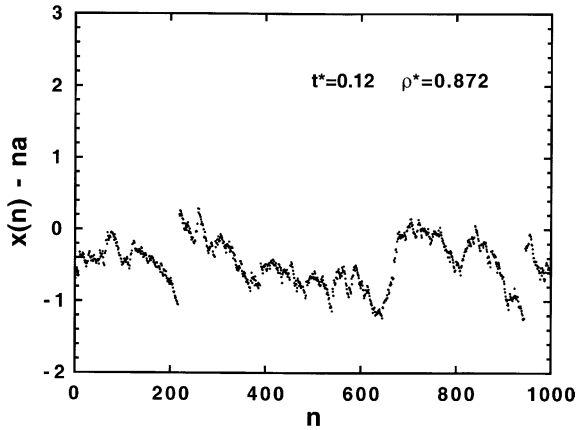
Fig. 3. A snapshot of the atomic displacements from a uniform distribution, under periodic boundary conditions, for chain length $N = 1000$ and reduced temperature $t^* = 0.12$. There are two breaks in this chain.
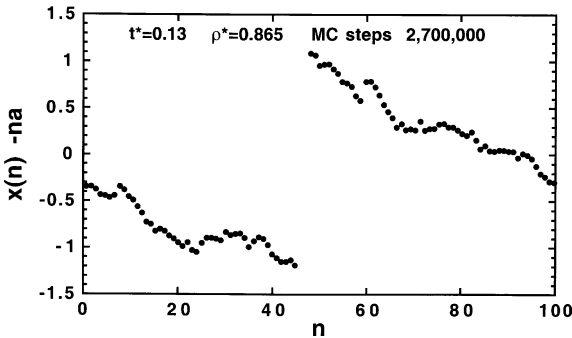

Fig. 4. A snapshot of the atomic displacements from a uniform distribution, under periodic boundary conditions, for chain length $N = 100$ and reduced temperature $t^* = 0.13$. There is one break in this chain.

4. STRUCTURAL RESULTS AS THE SYSTEM IS WARMED

Now our basic question becomes, *Are there any precursor conditions before breakup*? To address this issue, we studied 50- and 100-atom systems in a Monte Carlo relaxation simulation. An ensemble was equilibrated at very low temperature $t^* = 0.02$. The density was then decreased to $\rho^* = 0.2$, so that the sample was now four-fifths empty. With this highly quenched configuration as a starting point, the temperature was increased in intervals of $\Delta t^* = 0.01$ for tens of millions of Monte Carlo steps (MCS) at each temperature. Monitoring the pair correlation function $G(r^*)$ at each
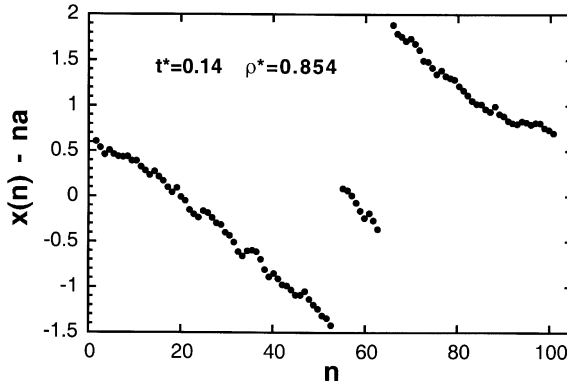
Fig. 5. A snapshot of the atomic displacements from a uniform distribution, under periodic boundary conditions, for chain length $N = 100$ and reduced temperature $t^* = 0.14$. There are two breaks in this chain.
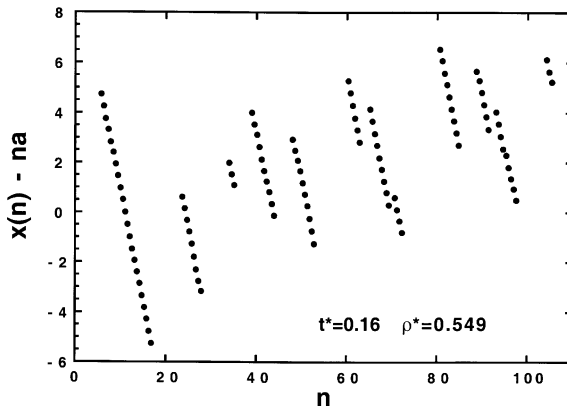

Fig. 6. A snapshot of the atomic displacements from a uniform distribution, under periodic boundary conditions, for chain length $N = 100$ and reduced temperature $t^* = 0.16$. There are 12 breaks in this chain.

temperature from $t^* = 0.02$ to 0.08, we found the highly ordered chain to be continuous even to the endpoints (see Fig. 7), but with a monotonic decrease in the amplitude of $G(r^*)$ as the end is approached. This decrease is due to the combined effects of finite length and finite temperature. At $0\,K$ $G(r^*)$, would be a series of sharp spikes at the periodic atomic positions, but the amplitude would decrease steadily with increasing separation as r^* approached the chain length. An additional decline in correlation occurs at finite temperature, caused by thermal vibrations. The thermal destruction of spatial order in a one-dimensional atomic
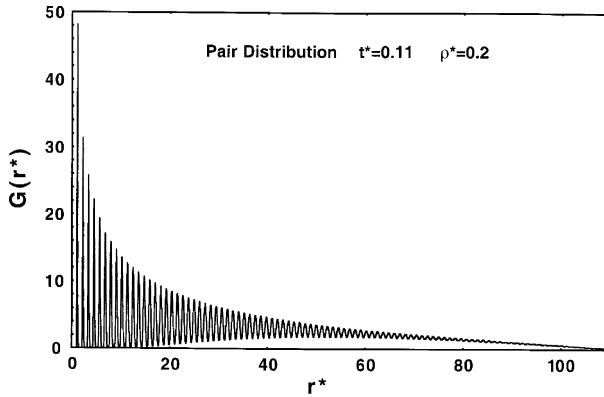
Fig. 7. The pair correlation function $G(r^*)$ for 100 atoms at $t^* = 0.11$. The chain has free ends. The chain is dense and ordered over its entire length without breaks. For the details of the endpoints, see the expanded views in Figs. 8 and 9.

chain was pointed out by Peierls,[33] on the basis of a simple model of an infinite array of identical atoms joined by the nearest-neighbor harmonic forces. Peierls predicted that the mean squared atomic displacement increases linearly with temperature T and distance. Peierls' model was subsequently detailed and adapted to two dimensions.[34,35] For the one-dimensional chain,

$$\langle (x_n - nd)^2 \rangle = \langle \delta_n^2 \rangle = nd^2 kT/2mc^2, \tag{3}$$

where d is the interparticle spacing and c is the speed of sound. Our simulation shows such a monotonic loss of positional order with particle number n, consistent with the trend of Eq. (3). For a quantitative comparison we evaluated c for a chain of argon atoms with 6–12 LJ interactions by a quadratic fit to the atomic potential well, and assumed c to be frequency independent. We evaluated Eq. (3) to $\langle \delta_n^2 \rangle = 0.034\ nd^2 t^*$. Accordingly, the atoms near the end of a 100-atom chain are predicted to have large deviations at moderate temperature. For example, at $t^* = 0.08$, the atom at $n = 90$ has a fractional rms displacement $[\langle \delta_n^2 \rangle / d^2]^{1/2} = 0.5$. This is comparable to our simulation *near the end, but not including the last few atoms of the chain*. A different mechanism increases the disorder of the endmost atoms, as discussed in Section 5.

5. HOW THE SYSTEM DISORDERS AT A FREE END

At the end of the chain a different mechanism appears when the temperature becomes sufficiently high; the atoms become completely

delocalized in the last few atoms at the end. In Fig. 8 we enlarge the end region and inspect it at three temperatures. At $t^* = 0.08$ the chain is dense and has finite positional order all the way to the end, but at $t^* = 0.09$ the last few atoms are completely delocalized. A one-dimensional dilute gas is evident in the empty space beyond the chain, produced by evaporation from the end. The changes, which are distinct from the Peierls mechanism, are caused by the weaker binding at the ends. This "end melting" effect is similar to the start of the premelting phenomenon at interfaces of two- and three- dimensional matter.[36]

Simulations with 50 particles show similar behavior (Fig. 9), but the end disordering begins at a slightly higher temperature, $t^* = 0.11$. We attribute the difference to the size dependence of the spectrum of vibrational excitations. Further discussion of this point is given later in the paper.

6. GROWTH AND FRAGMENTATION OF CLUSTERS

We explored the time and temperature dependence of chain growth in a sequence of long computer runs over a range of temperatures. Each run began with 100-atoms arranged as a well separated regular array in a fixed volume at a low temperature, $t^* = 0.02$. The atoms rapidly condensed and then more slowly grew into increasingly large clusters; the number C of clusters decreased in a short time, and then growth progressively slowed. The detailed evolution at reduced temperature $t^* = 0.02$ can be seen in
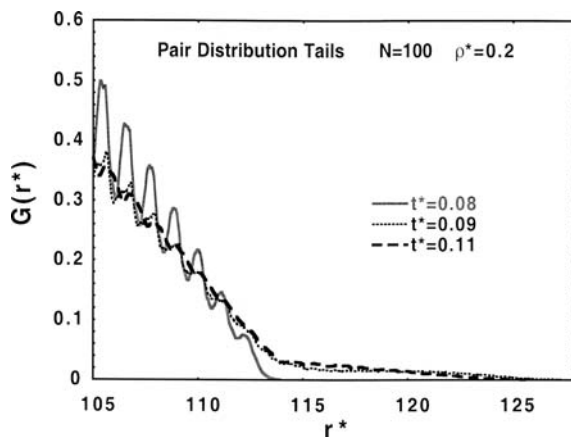

Fig. 8. A magnified view of the pair correlation function $G(r^*)$ for $N = 100$, in the end region at $t^* = 0.08$. The vapor density is too low to show any atoms in the limited vapor space.
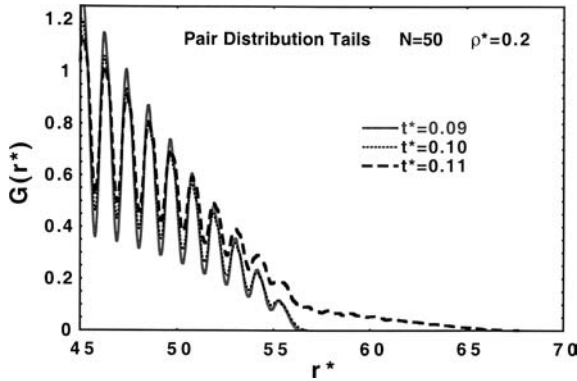
Fig. 9. A magnified view of the pair correlation function G(r^*) for $N = 50$ in the end region at $t^* = 0.11$ shows that some atoms have detached from the chain, to form a low density vapor.

Table II. Progressive growth and coarsening of 100 atoms at
low temperature $t^* = 0.02$

MCS	No. Clusters	U/NkT
1	100	-9.177
1000	52	-23.866
5×10^3	49	-24.395
1×10^4	45	-24.862
2×10^4	41	-25.831
4×10^4	36	-27.553
8×10^4	32	-29.838
1×10^5	29	-30.477
2×10^5	24	-32.568
6×10^5	18	-35.743
2×10^6	16	-39.265
4×10^6	13	-41.058
8×10^6	13	-42.381
2×10^7	10	-43.865
4×10^7	7	-45.119
6×10^7	6	-46.151

With increasing time MCS, the atoms progressively cluster and the
average binding energy increases.

Table II and Fig. 10. We see that the decrease of C with time (MCS) is approximately exponential over a range of four decades in time.

Cluster evolution was also studied at successively higher temperatures. As in the run at $t^* = 0.02$, at each temperature the number of clusters
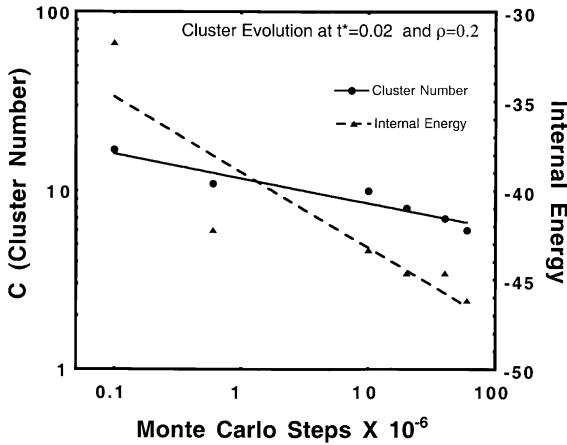
Fig. 10. Formation and growth of clusters in an ensemble of 100 atoms at low temperature $t^* = 0.02$. The number of clusters C as a function of time steps.
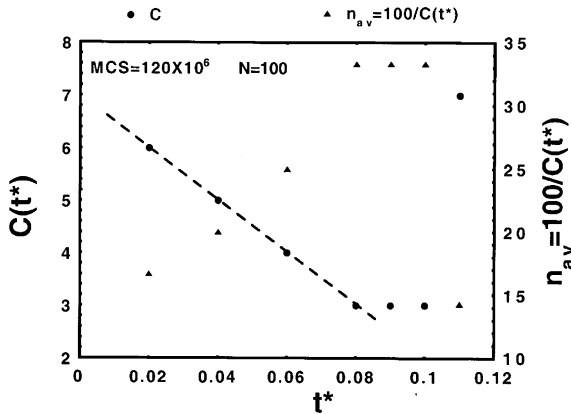

Fig. 11. The limiting cluster size $C(t^*)$ after growth has slowed to an imperceptible rate, as a function of temperature.

fell rapidly at first, then progressively slowed. We continued each run until there was no longer any perceptible change in the internal energy, which was typically reached at tens of million MCS. The number of clusters remaining at the termination at each temperature, designated $C(t^*)$, is shown in Fig. 11. We see that $C(t^*)$ decreases to a minimum as the temperature is stepped from $t^* = 0.02$ to $t^* = 0.10$, but $C(t^*)$ then increases at higher temperature. This increase is attributed to the strengthening importance of fluctuations, which cause breakup and evaporation.

We compare our results with studies of the growth and coarsening of a variety of one-, two- and three-dimensional systems.[37−42] An extensive review of mainly three-dimensional experimental and theoretical work by Gunton *et al.*[37] describes typical behavior as a power law in time, an evolution typically driven by a combination of interfacial energy and surface curvature. Curvature plays no role in one-dimensional matter, but there is a size effect due to the decreased binding at the ends. In the one-dimensional studies[36−42] the models are actually two-dimensional but with one-dimensional diffusive growth. In two of the most detailed studies[40,41] the long time behavior is exponential, toward a maximum grain size consistent with constraints. Our system's trend is exponential, but with a temperature dependent end point. The basic cause is the thermal excitations, which are either ignored or are less important than strains, defects and wetting phenomena in the previous work. In Section 7 we explore the role of excitations in more detail.

7. AN EQUILIBRIUM DISTRIBUTION

As suggested above, the simulations involve a competition between growth and dissolution. Figure 11 shows that the competition tends toward an equilibrium statistical distribution. However, the exponentially slowing growth rate makes it impractical to obtain the true equilibrium distribution by extending the computer runs. An alternative employs the free energy function of a finite chain. The rationale is that an equilibrium distribution will have a range of chain lengths, with corresponding chemical potentials, which will range about a central value. The chemical potential of the most probable length will be at a minimum.

To derive an expression for the chemical potential of a finite chain we begin with the general expression for a one-dimensional harmonic solid,[34,35] which is adapted from the statistical mechanics of a bulk crystal.[10] The finite length enters in two ways. First, the cohesive energy lacks contributions from the end atoms and, depending on the specific growth law, a portion of the interaction energy of the neighboring atoms. The second is a more subtle effect, for it depends on the size dependence of the excitation spectrum, which in a simple chain, are vibrational modes, The spectrum ranges in energy down to the lowest mode, which has a wavelength equal to twice the chain length. The effect of this length dependence is to make longer chains less favorable, especially at high temperatures. The effect can be quantified with an analytic expression for the chemical potential.

For simplicity we use a Debye approximation, which assumes a frequency independent sound speed. The spectrum of a chain of n atoms extends from a maximum frequency ω to the lowest frequency ω/n. With

specific parameters for argon with LJ interactions, we find that the major terms in n and t^*

$$\mu(n, T) = -0.47\varepsilon - 3.2\varepsilon \; n^{-5} - 2.93\varepsilon t^{*2}[1 - 1/(1-n)^2]. \qquad (5)$$

With Eq. (5), we obtain the most probable length n_{eq} as a function of temperature as the value at which μ is a minimum:

$$(n_{eq} - 1)^3/n_{eq}^6 = 0.37 \; (t^*)^2. \qquad (6)$$

Equation (6) predicts that n_{eq} diverges only $t^* = 0$, consistent with the fundamental prohibition of condensed macroscopic one-dimensional phases at finite temperature.[10-13] But Eq. (6) shows that finite chains can exist at finite temperature, and that n_{eq} steadily decreases as t^* rises. Table III lists some sample sets of n_{eq} and t^* computed from Eq. (6). The equilibrium temperatures are much lower than the Landau temperature kT_0/e for any given size. The difference is due to the great importance of thermal excitations in reducing the stability of long chains, whereas thermal excitations are not included in the Landau argument.

8. CONCLUSIONS

We have studied two types of finite linear systems by Monte Carlo simulation. For the first, we used periodic boundary conditions to investigate how a stochastic model of a finite linear system begins to break into segments. We generated canonical ensemble averages for the thermal and structural properties as well as snap shots of the configurations. Our model demonstrates that relatively small segments of the chains are quite stable and ordered at low temperatures. At reduced temperatures $t^* = 0.10$ and below, chains of 1000-atoms are free of spontaneous breaks, and clusters of 100-atoms at $t^* = 0.12$ are also free of breaks. As temperature

Table III. Equilibrium lengths of one-dimensional atomic chains

n_{eq}	t^*
100	0.00165
50	0.0047
20	0.0171
10	0.0446
5	0.106
4	0.134

rises above these values, the number of breaks increases. The lack of a condensed phase in the thermodynamic limit is consistent with theory, but finite length chains survive to appreciable temperatures.

In the second type of simulation we studied finite segments with free ends. In these systems at temperatures too low for breakup the ends disorder while the main body of the cluster remains dense and continuous. At these temperatures the chain has an appreciable vapor pressure, hence one sees that the chain coexists with a one-dimensional gas. The end disorder occurs at temperatures dependent upon the number of atoms in the cluster. In the one hundred atom clusters this occurs between $t^* = 0.08$ and 0.09. In 50-atom clusters the endpoint disordering temperature is between $t^* = 0.10$ and 0.11. This variation results from the length dependence of the lower bound of the spectrum of vibrational modes. The simulations show an evolution toward larger clusters at low to moderate temperature, but at higher T fragmentation occurs, due to the increasing strength of fluctuations.

We obtain the true equilibrium state analytically, from an explicit formula for chemical potential. In a large population of atoms in thermal equilibrium, there will be a distribution of clusters of different lengths, ranging about a most probable length at which the chemical potential is a minimum. The thermal distribution recalls the aggregation of one-dimensional rods of biological molecules,[43,44] and the thermodynamic principles are similar.

This study suggests the variety of behavior that may be seen in experiments on adsorbed systems that are effectively one-dimensional.

ACKNOWLEDGMENTS

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