Size and time dependence of the elastic constants of a two-dimensional solid near melting

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By using molecular dynamics simulations, the behavior of the Lamé elastic constants of a two-dimensional (repulsive Lennard-Jones potential) solid near melting has been studied over a wide range of systems and very long evolution times. The shear modulus μ is found to vary logarithmically with system size until some critical value of the evolution time is reached for sufficiently large systems. The shear modulus then vanishes, leaving the thermodynamic properties, T and p, invariant. This result provides experimental evidence that the system melts as its size is increased.

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Over the last 10–15 years, the two-dimensional (2D) solid near (or at) melting has been widely studied from many different, and often controversial, points of view [1]. The main point of discussion has been the determination of the transition's order, whether first [2,3] or second [4,5]. The difference is the way in which the liquid system is reached, whether abruptly from the solid (first order), or continuously (second order) with a "critical slowing down." A continuous transition is associated with long-range correlations which are suppressed in small computer models. Hence the way to investigate the melting transition is by analyzing size-dependence properties of a 2D solid near or at melting. For one thing, surprisingly few studies of size dependence have been performed for the melting of 2D atomic systems, but there have been indications of the existence of strong finite-size effects [6] and Van der Waals' loops [7]. When a weak first-order transition had become almost universally accepted, further studies of the size dependence of various physical quantities cast doubt on this assumption because of the existence of strong finite-size effects, as Toxvaerd [8], and Udink and Van der Elsken [9] have pointed out. For another thing, there has been very little detailed examination of finite-time effects, and, in the transition region, the possibility always exists of relaxation times longer than the longest run, as shown by Novaco and Shea [10], who interpreted this effect as evidence of "critical slowing down" and thus of a continuous transition. These results again give timeliness to the problem, and the debate continues.

In light of these two considerations, the most interesting physical property to study is the elasticity of a 2D solid near melting, through calculations of the Lamé shear modulus μ. Because, in principle, μ should vary logarithmically with system size [8,11], and its instantaneous value fluctuate [12], the calculations have to be performed over a wide range of large systems and for very long intervals of time. Previous results have been obtained for small systems (from 64 to nearly 16 500 particles) and "short" evolution times (10^5 time steps for the larger system) which do not resolve the problem of the order transition in 2D. The aim of the present work, therefore, was to obtain the shear modulus, taking into account the combination of these two factors (size dependence and time evolution) in order to obtain results which may be meaningfully compared with earlier work, especially Ref. [8].

The shear modulus μ was obtained directly by considering the stress tensor in a system with modified boundary conditions and applying a small homogeneous shear strain, as described by Broughton, Gilmer, and Weeks [13]. If small strains s are applied to the system and the resulting stress $P_{xy}(s)$ is measured in a long molecular-dynamics run, it is possible to obtain a linear relation between stress and strain in the form

$$P_{xy}(s)=s\mu+\Theta(s^2)\ , \tag{1}$$

where the pressure tensor is given by

$$P_{xy}(s)=\frac{kT\rho}{N}\sum_{i<j}^{N}\left\langle\frac{1}{kT}U'(r_{ij})\frac{(x_i-x_j)(y_i-y_j)}{r_{ij}}\right\rangle_s\ , \tag{2}$$

in which $\langle\ \rangle_s$ is the normalized ensemble average in the modified system with the given strain s.

First of all, one has to be sure that the strain introduced into a system to measure the elastic constants does not exceed the linear regime, in particular very close to the melting zone where the correlation length may become very long. Moreover, as in principle the region of linearity may be a function of the wavelength of the shear, which presumably increases with system size, one has to determine the extent of this region for each system under study. Indeed, because there appears to be such strong size dependence, it is not unlikely that the linear region may shrink as the system size is increased, especially near the melting transition. Figure 1 shows this behavior: one can see that there is a linear regime for one of the larger systems studied, of $N=7744$ particles, and that this large system linear regime has shrunk with respect to the linear regime found for $N=64$ in Ref. 8 at the same conditions of temperature, density, and number of time steps. The value 0.01 chosen for the strain, for all the systems studied, was well inside the linear regime of strain at temperature $kT/\varepsilon=1$ for both densities studied. Here k is Boltzmann's constant, and ε the energy unit of the repulsive Lennard-Jones potential $U(r_{ij})$. Table I

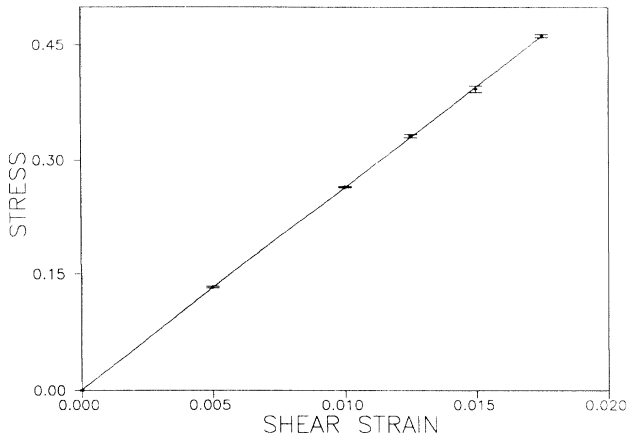

FIG. 1. The stress $p_{xy}r_m^2/\varepsilon$ in a $N=7744$-particle system at the density $\rho r_m^2=1.18$. The points for the strain were obtained for 10^5 time steps.

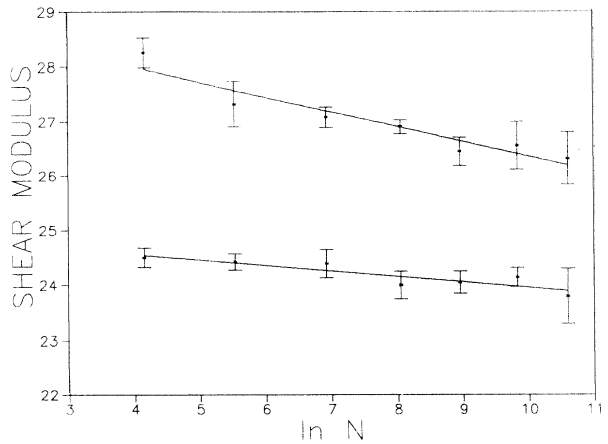

FIG. 2. Shear modulus $\mu r_m^2/\varepsilon$ as a function of ln N. The upper line corresponds to $\rho r_m^2=1.18$, and the lower line to $\rho r_m^2=1.17$. The evolution times of the systems are the N_i's listed in Table I.

lists the systems selected for study. They cover a wide range of particle numbers from $N=64$ up to 40 000, at two densities very close to the melting zone [14], $\rho r_m^2=1.17$ and 1.18, where r_m is the distance at which the Lennard-Jones potential has its minimum (the potential cutoff). These systems cover and go beyond the systems used by Toxvaerd [8], Udink and Van der Elsken [9], and Zollweg, Chester, and Leung [11]. The radius for the neighbor table was $r_{sd}=1.4r_m\cong 1.57\sigma$, and the molecular dynamics time steps unit h was $0.005(m\sigma^2/\varepsilon)^{1/2}$. The total number of time steps is denoted by N_t, and $N_i<N_t$ is an intermediate number of time steps. Figure 2 shows the shear modulus μ as a function of ln N for the two densities. The uncertainties are the root-mean-square (rms) deviations from the means and are obtained from independent subsets. The time evolution of the systems is given by the values N_i in Table I. The seven points of each straight line show a clearly logarithmic size dependence when the systems have evolved these N_i time steps, which is much more time than any previous simulation [1]. This result is in concordance with the Toxvaerd [8,15] and Zollweg, Chester, and Leung [11] suggestions, but not with the results of Hoover, Combs, and Massobrio [16] which predict a shear dependence proportional to the inverse of the size of the system. However, if the systems are left to evolve longer, the smaller systems do not suffer any change in their shear modulus, while for the larger systems the value of μ drops abruptly, as Fig. 3 clearly shows. It is very interesting to note that for the density closer to the melting zone, the $N=7744$ system is not capable of maintaining the μ value constant, while for the upper density it does. For the larger systems, neither density can avoid the fall of the shear modulus. This fact is seen better if the time evolution of the shear modulus is studied. Figure 4 shows three different time evolutions of the first system whose μ value drops ($N=7744$ at $\rho r_m^2=1.17$). As one can see, the three behaviors are qualitatively the same. First the systems start by fluctuating around the mean, but after 25×10^4, 12.5×10^4, and 10×10^4 h, according to each case, μ falls abruptly and begins to fluctuate around values close to zero. The first system whose μ value falls at $\rho r_m^2=1.18$ is $N=18\,496$, but after a very long evolution time (460 000 h) during which the shear modulus stays almost constant, as can be seen in Fig. 5 (curve 1). Comparing the same system at $\rho r_m^2=1.17$ (curve 4), the sharp decline to zero occurs sooner (after 160 000 h) as a consequence of the proximity to the melting zone. The results for the very large system

TABLE I. Size of the systems and their evolution times at the two densities considered.

N	$N_i(10^3$ h) ($\rho r_m^2=1.17$)	N_t (10^3 h) ($\rho r_m^2=1.17$)	N_i (10^3 h) ($\rho r_m^2=1.18$)	N_t (10^3 h) ($\rho r_m^2=1.18$)
64	1000	2000	1000	2000
256	700	1000	800	1000
1024	700	1000	800	1000
3136	700	1000	800	1000
7744	250	700	700	900
18 496	160	360	460	680
40 000	100	475	170	490

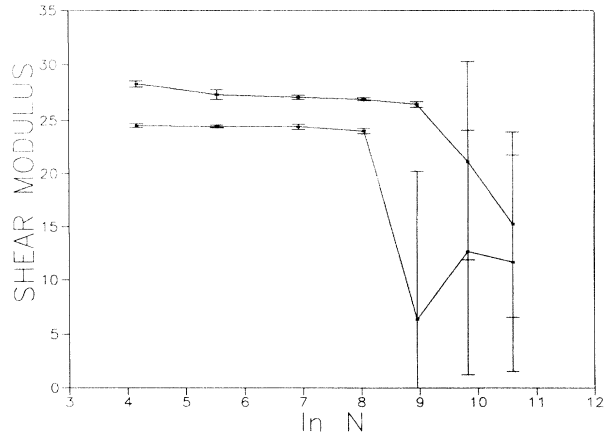

FIG. 3. The same as Fig. 2, but for the total evolution time N_t.

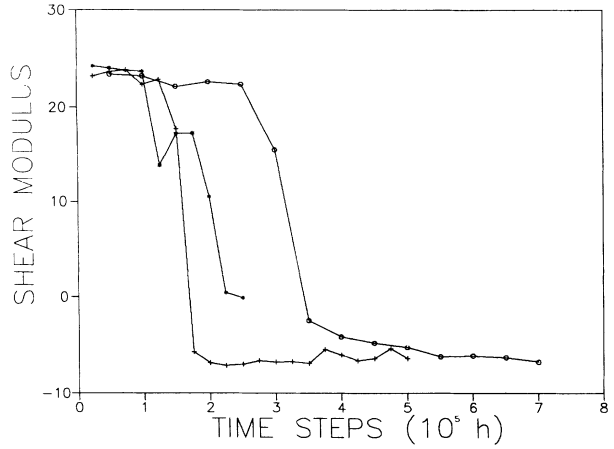

FIG. 4. Three different temporal evolutions of the shear modulus for $N=7744$ at $\rho r_m^2 = 1.17_m^2 = 1.17$.

of $N=40\,000$ present similar behavior, but the resistance against the value of μ falling is considerably less. In this case, for $\rho r_m^2 = 1.18$ (curve 2) the decline is in two stages: after 170 000 h the shear modulus drops to about the value 10, which is maintained for about the following 150 000 h, with the subsequent drop to smaller values presenting large fluctuations. For $\rho r_m^2 = 1.17$ (curve 3) the behavior is quite clear cut: the decay occurs sooner (after 10^5 h) and tends to zero faster than before, representative of the general behavior that one may expect for systems larger than $N=40\,000$ particles.

To continue with the study of elasticity in the solid, once the shear modulus has been calculated, it is a straightforward matter to calculate the other elastic constant λ through the isothermal compressibility [13], i.e.,

$$\mu+\lambda=\rho\left[\frac{\partial p}{\partial \rho}\right]_T , \tag{3}$$

where the value of the compressibility can be easily ob-

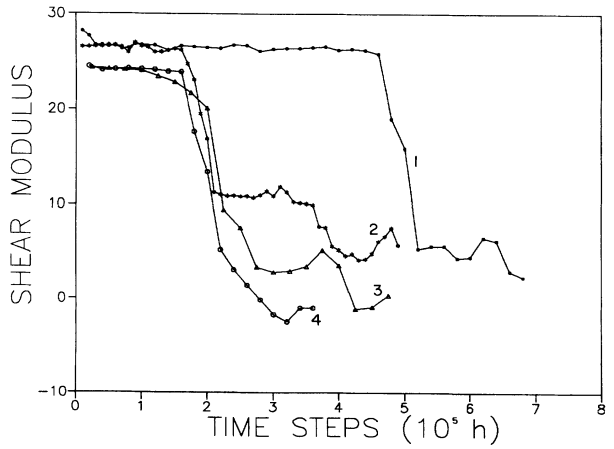

FIG. 5. Temporal evolution of the shear modulus for the two largest systems at the two densities: 1 ($N=18\,496$, $\rho r_m^2 = 1.18$), 2 ($N=40\,000$, $\rho r_m^2 = 1.18$), 3 ($N=40\,000$, $\rho r_m^2 = 1.17$), and 4 ($N=18\,496$, $\rho r_m^2 = 1.17$).

TABLE II. Compressibility factor obtained from the pressure results at the two densities considered. The standard deviation is σ. The calculations were performed for the total number of time steps N_t given in Table I.

N	$p\pm\sigma$ ($\rho r_m^2 = 1.17$)	$p\pm\sigma$ ($\rho r_m^2 = 1.18$)	$\left[\frac{\partial p}{\partial \rho}\right]_T$
64	13.02±0.01	13.60±0.01	58.0
256	13.154±0.005	13.735±0.006	58.1
1024	13.19±0.01	13.771±0.003	57.7
3136	13.23±0.03	13.780±0.004	55.0
7744	13.27±0.03	13.80±0.02	53.0
18 496	13.24±0.03	13.80±0.01	56.0
40 000	13.25±0.02	13.80±0.01	55.0

tained by computing the pressure p at two closely spaced densities. Table II lists the pressures at the two densities of the study and the values derived for the compressibility for the total evolution time N_t of the systems, and shows that the fall in μ does not affect the calculated values of thermodynamic properties such as temperature (not listed in the table) and pressure. The pressure shows a very weak increase with increasing size, as Toxvaerd [14] noted for his smaller systems, until reaching a constant value for the larger systems. The compressibility factor, however, tends to fluctuate around a mean value that is almost independent of N. (For smaller systems, Zollweg, Chester, and Leung [11] found a weak decrease of compressibility with size for an r^{-12} potential and $\rho r_m^2 = 1.28$.) As a consequence, the size dependence of λ is logarithmic and determined by μ as in Eq. (3).

An appropriate combination of the Lamé elastic moduli μ and λ forms the well-known expression for the triangular lattice [13]:

$$K=\frac{3}{\sqrt{8}}\frac{\beta}{\rho}\frac{\mu}{1+\frac{\mu}{\mu+\lambda}} . \tag{4}$$

In the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory [17], K shows a universal temperature dependence as melting is approach, first declining to the value 16π and then dropping to zero at melting. The statistical errors in the determination of K are considered to be of the order of 10–20% near melting [1]. Figure 6 shows this logarithmic dependence of K when, as in Fig. 2, N_i time steps (Table I) are considered, but this behavior is broken from $N=7744$ at $\rho r_m^2 = 1.17$ and from $N=18\,496$ at $\rho r_m^2 = 1.18$ when the whole evolution time N_t is used. The interesting thing here is that the drop in K is neither sharply to zero, nor at a value of $K\cong 16\pi$, nor for such very large systems as the KTHNY theory predicts. On the contrary, the fall starts when K reaches a value of 68–73, it is less sharp, and the systems are much smaller than expected.

The results of Toxvaerd [8,15] for very small systems of $N=64$, 256, and 1024, predict, by extrapolating their logarithmic dependence of K, a value of $K\cong 55$ for $N=40\,000$ at $\rho r_m^2 = 1.17$, but this estimate is uncertain (Hoover [16] gives $N=10^{11}$). Extrapolating the calcula-

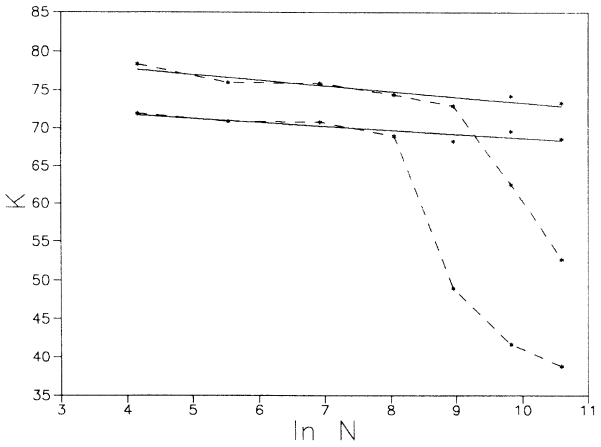

FIG. 6. The same as Fig. 2 but for K. The fit to a straight line is for the N_i time steps listed in Table I, and the dashed line corresponds to the total number of time steps N_t.

tions of the present work, the theoretical estimate of $K \cong 55$ should be reached for $N \cong 7 \times 10^{11}$ particles. This large discrepancy is due to the fact that the slope of K here is smaller and closer to that of Zollweg, Chester, and Leung [11] than to that of Toxvaerd [8]. Nevertheless, these theoretical predictions are not very meaningful because the very important point here is that the solid system near melting gives up its resistance to shear much earlier than the KTHNY theory predicted [17]. Physically, this means that the system is in a nonequilibrium state caused by the long-wavelength phonons allowed in the $N=7744$ system. The system can, however, still resist shear at a higher density $\rho r_m^2 = 1.18$, but when the system at this density is enlarged to $N = 18\,496$ particles this density also gives up resisting shear, and so on. What one should expect is just that when the shear modulus (and consequently K) drops to about zero, all other thermodynamic properties are left unaffected. These predictions by Toxvaerd, repeated more recently by Zollweg, Chester, and Leung [11], are verified in the present work. The fact that the system cannot resist shear makes it look like a pseudosolid with local order, and interesting in this context is the mechanics by which it yields to shear. Is it by a layerwise parallel shift, or by creating disclinations, etc.? Swope and Andersen [18] recently reported evidence of a non-first-order phase transition in 2D systems. Doubtless, the debate is still alive.

Finally, we give two technical details about the calculations. Toxvaerd's results for the shear modulus in Ref. [8] where imprecise not only because of the small size of the systems and the short evolution times used, but also because he used the traditional molecular dynamics method which simulates the microcanonical ensemble. This means that the temperature of the system fluctuates during the simulation, leading to large uncertainties in the calculations of μ. The results presented here were obtained with a very accurate molecular dynamics isothermal-isochoric algorithm which fixes the temperature of the systems perfectly to the desired value perfectly, and makes the uncertainty in the pressure considerably smaller, giving a shear modulus with more precision. This method, originally performed by Nosé [19] and Hoover [20], has been tested previously near the phase transition [21], and recently improved [22].

Simulating such large systems over such long times was possible due to a computer technique called the CNT method [23], which combines the cell method with the traditional neighbor table method (with N^2 time dependence) to give an N time dependence, with the consequent huge saving of CPU time and the additional advantage that it does not essentially require the use of the new generation computers, such as the CM, etc. Instead, these calculations were performed on a modest CONVEX 210.

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