

Mechanical Simulation of the Pressure and the Relaxation to Thermal Equilibrium of a Hot and Dense Rare Gas Cluster

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Received: September 5, 2006; In Final Form: September 18, 2006

A cold atomic cluster can be very rapidly heated and compressed by a hypersonic impact at a hard surface. The impact can be simulated by computing a classical trajectory for the motion of the atoms. By suddenly confining the hot and dense cluster within a rigid container, it is possible to monitor the time evolution of the force acting on the faces of the container. It is found that the pressure computed this way very rapidly decays to a time-independent value. After a somewhat longer time, this value reproduces the value for the pressure computed as the sum of the kinetic and internal pressures. This agreement is expected for a system in equilibrium. These observations support the conclusion that there is a fast relaxation to thermal equilibrium in these essentially hard-sphere systems. The deviation from equilibrium is primarily due to the propagation of shock waves within the cluster. The equilibrium pressure can reach up to the megabar range.

I. Introduction

There is an increasing arsenal of laboratory techniques for the study of systems in extreme physicochemical conditions.^{1–44} Earlier, the prime source of information was from shock tube studies,^{32,45–48} including laser-driven microshocks,¹³ but the upper limit of kinetic temperatures that can be conveniently reached by this approach is about 5000 K. Fast, focused, laser heating and plasma chemistry^{49–51} is another approach to driving high-energy processes. More specialized techniques include the chemistry of translationally very hot atoms¹⁸ produced, e.g., via the nuclear recoil technique,^{52,53} sonochemistry,^{8,31,54–56} and detonation fronts.^{39,42,44,57–59} There have also been numerous theoretical studies.^{60–85} The more recently studied technique of cluster impact^{1,9,11,12,21,22,33–37,43,67,72,80,86–93} offers access to a new dynamical regime where collisions within the hot cluster can be made to occur at hypersonic relative velocities. Then, the collision duration is rather short as compared to intermolecular motions, and from early on, there has been much theoretical and experimental interest in inducing chemical reactions within such a medium.^{11,12,16,17,20–22,65,67,75–78,83,86,87,94–102} The interesting chemistry that is suggested by the computational studies, e.g., the polymeric forms of nitrogen,¹⁰³ and by the experiments, as recently reviewed, e.g., in ref 43, is also of interest for the similarities and differences with the new chemistry revealed in static ultra-high-pressure experiments.^{104–108} There are other processes that are indicative of the special conditions¹⁵ that prevail at the impact such as pickup from the surface¹⁰⁹ at low impact velocities or electron^{17,110} or light emission^{98,111} at high energies. In this paper, we examine the “macroscopic” rather than microscopic evidence for the extreme conditions. Our work can also be viewed as part of the going interest in defining thermodynamic functions for finite systems.^{112–117} Specifically, this paper examines a theoretical approach to the definition of pressure in a finite time evolving system such as a hot cluster.

To characterize the mechanical state, we follow the evolution of the system by the methods of molecular dynamics and generate the initial extreme disequilibrium by letting a cold cluster impact a hard surface at a hypersonic velocity. Our primary attention is on the definition of the pressure from the mechanical equations of motion,^{79,118–122} and we compare different computational implementations with adequate agreement between them. It is shown that such an agreement is expected when a system satisfies an equipartition theorem^{119,123–125}

$$\langle q_\alpha \partial H / \partial q_\alpha \rangle = kT \quad (1)$$

for the potential energy where q_α is a coordinate. We have previously shown¹²⁶ that the complementary form of the equipartition theorem, the equipartitioning of the kinetic energy

$$\langle p_\alpha \partial H / \partial p_\alpha \rangle = kT \quad (2)$$

is satisfied rather soon after the cluster impacts the surface. What determines the time interval required for equilibration is that atom–atom collisions communicate the initial impact of the front layer of atoms that hit the surface to the other end of the cluster. That also the potential energy is rapidly equipartitioned allows us to define an equilibrium pressure. We report that pressures up to the terapascal range can be reached in clusters of heavy particles, e.g., clusters of Xe atoms.

To simplify the language and notation, we take it that we are dealing with clusters of rare gas atoms. On this basis, the dynamic simulations use classical mechanics with a potential function describing the atom–atom interaction. This excludes the possibility of electronic excitation due to the compression of the cluster that occurs upon impact. In further work, we would like to allow such processes and, in particular, examine if the high values of the pressure do open up the possibility of driving electronic phase transitions^{113,127–130} in rapidly heated and compressed clusters.¹³¹ The onset of electronic nonadiabaticity as a function of the impact velocity as judged by electron emission is rather steep.^{17,94,110} By using rare gas atoms and

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impact velocities only up to about 10 km s^{-1} , we can be reasonably safe in neglecting this channel.

In this paper, the pressure of the cluster is computed in two quite different ways. One is by confining the cluster to a hard rigid box and evaluating the force on the walls due to collisions of the atoms, as first done by the Bernoullis in the 18th century. This is a completely straightforward procedure and produces a series of spikes, each representing the change in momentum due to a collision of a cluster atom with a hard surface per unit integration time step. Because the collision with the hard surface is instantaneous, there is no time for the interaction with the other atoms to slow or to accelerate the atom as it collides with the wall. Therefore, this determines the force on the faces of the container even though the cluster is quite compressed and it is not an ideal gas. We show that an equivalent procedure is based on the virial of Clausius^{123,124} for the external force acting on the atoms of the cluster. The alternative procedure is based on the equipartition theorem for the potential energy as expressed by eq 1. This route to computing the pressure is that discussed in refs 118 and 119. The two computations will therefore agree only when the potential energy is indeed equipartitioned. The comparison therefore provides a criterion for how fast this equipartitioning occurs. By examining the derivation of the virial theorem for nonequilibrium conditions,¹²² as in the case of a hot cluster, we show below that the pressure computed from the virial equals the sum of the kinetic and internal pressures and requires that the hyperradius ρ , defined for a cluster of identical atoms as

$$\rho_\alpha = \left(\sum_{i=1}^N (r_{i\alpha} - r_{\text{cm}\alpha})^2 / N \right)^{1/2} \langle \epsilon \theta \sigma \epsilon \pi; 9\theta \rangle \alpha = x, y, z \quad (4)$$

to be constant in time. In eq 3, $r_{i\alpha}$ is the position coordinate of atom i in the direction α , and r_{cm} is the position of the center of mass. There are N atoms in the cluster. It is found that although the cluster is confined to a rigid container the hyperradius does not immediately settle down to a constant value, because as we will discuss, there is a shock wave going through the cluster and it takes time for this collective motion to dephase. The oscillations in the instantaneous pressure of the cluster have already been reported in ref 122. The difference is that here the cluster is confined to a rigid container. In ref 122, the cluster evolved unconstrained up to a time t at which point its pressure was computed. Therefore, with time the cluster expanded, and its pressure decreased as its volume increased. Here, at equilibrium, the pressure will be time-independent because the volume is constant. Any nonconstant value of the pressure is therefore a diagnostic for a nonequilibrium process.

The molecular dynamics simulations of impact of atomic clusters have been discussed before, so section II highlights the new features in the dynamics due to the confining of the cluster atoms within a rigid box and presents the computation of the pressure from the force on the faces of the rigid container. In section III, the results for the pressure from section II are compared to the results for the pressure computed as the virial of the force on the cluster, since we can show that the two results should be the same. The use of the virial theorem of Clausius to compute the pressure and why this requires a somewhat longer relaxation time to settle to a constant value are discussed in section IV.

II. Mechanical Definition of Pressure

Computing a trajectory for the collision of an atomic cluster with the surface is described, e.g., in ref 132. The energy loss

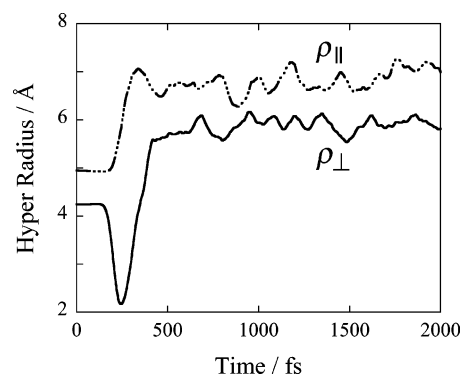


Figure 1. The components of the hyperradius, eq 3, in angstroms, in the direction parallel and normal to the surface vs time in femtoseconds. The cluster expands freely until the atoms hit rigid walls placed at ± 10 and ± 11 Å in the normal and parallel directions with respect to the center of mass. The side of the box in the parallel direction is larger with the result that the two curves in the figure are displaced. Note how fast the collision with the surface is. The hyperradius, eq 3, is the mean (rms) distance of the atoms from the center of mass and is about half of the side of the box.

to the surface at which the impact occurs is not of central interest here, and so we do not include a friction at the surface nor any other mechanism for such dissipation. The essential new feature is that from a certain point in time the cluster is not allowed to expand by confining it to a rigid box (= rectangular parallelepiped). The box is centered at the center of mass of the cluster, and its faces are parallel and perpendicular to the surface at which the impact occurs. Upon impact, the cluster is compressed in the direction normal to the surface but immediately begins to expand parallel to the surface. Therefore, the sides of the box need not be chosen to be equal, although they can be. Nor is it necessary to have the collisions with the rigid walls begin to take place at the same time in the directions parallel and normal to the surface. What is essential from a numerical point of view is that all the atoms of the cluster are within the box. We therefore specify the length of the perpendicular and parallel sides beforehand, and the box is imposed from the very beginning of the trajectory. However, the presence of the box is first felt, for a given direction, at that instant of time (minus one integration time step) when the first atom reaches the wall of the box.

Figure 1 shows the time dependence of the components of the hyperradius in the directions parallel and perpendicular to the surface (eq 3). At the beginning, the motion is unconstrained by the presence of the box. The extreme contraction of the cluster in the normal direction and the rapid expansion parallel to the surface are clearly seen. By symmetry, the components of the hyperradius in the two directions parallel to the surface should be the same, and their small difference is a measure of the fluctuations due to the finite number of atoms, $N = 125$, in the case shown. The box is imposed at lengths with respect to the center of mass: ± 10 Å and ± 11 Å in the normal and parallel directions. Note that the hyperradius, eq 3, is the mean (rms) distance of the atoms from the center of mass and so is smaller than the side of the box. Seemingly upon being confined within a rigid box, the components of the hyperradius should settle down to time-independent values. The quite clear oscillations reflect the eddy that persists for some time due to the shock waves within the cluster and due to the finite size fluctuations of a hot cluster. We return to this point in section IV.

It is the faster outward-moving atoms of the cluster that are the first to reach the rigid walls and be reflected back. The confining walls therefore narrow down the distribution of the

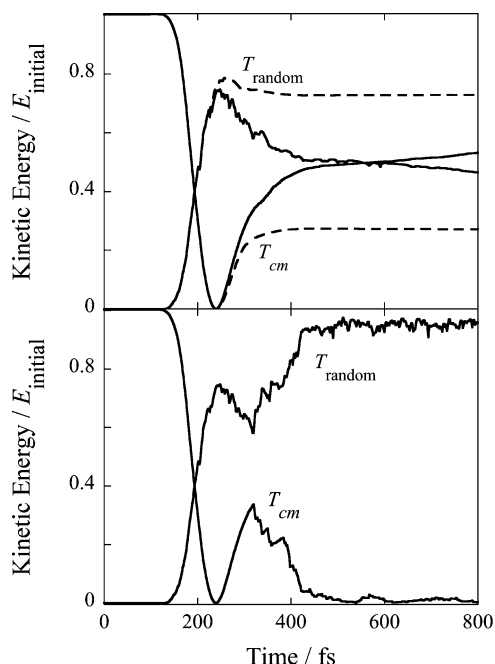


Figure 2. The kinetic energy, measured in terms of the initial energy of impact, vs time, in femtoseconds. Shown is the kinetic energy of the center of mass, cm, and of the random part of the motion of the atoms. Dashed curves: unconstrained motion. Solid curves: Top panel—A cluster confined by rigid walls perpendicular to the surface. The walls deflect back the faster atoms and so enable more energy to return to the center of mass motion and rebound from the surface. Bottom panel—A cluster confined in all three directions by a rigid box.

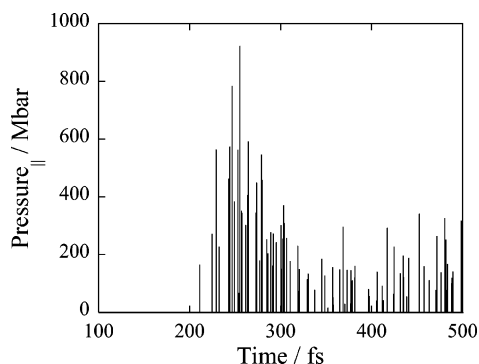


Figure 3. Change in the momentum in the direction parallel to the surface per unit integration time step of atoms that rebound from the rigid walls of the box that confine the surface, vs time. The width of the time step is much smaller than the width of the spike as drawn. Therefore, the average pressure is in the few megabars range or less; see Figure 5.

velocities of the atoms with respect to the center of mass of the cluster. The total kinetic energy of the atoms is the sum of the kinetic energy of the center of mass and the kinetic energy of the velocities of the atoms with respect to the center of mass. Because the velocity of the center of mass is the mean velocity of the atoms, the kinetic energy of the velocities of the atoms with respect to the center of mass is the random part of the kinetic energy. Therefore, as compared to a freely expanding cluster, the confined cluster has a lower random kinetic energy. To emphasize this point, Figure 2 shows the partitioning of the initial kinetic energy of the cluster during the impact for a (top panel) freely expanding cluster and (top panel) for a cluster confined to a box with walls only perpendicular to the surface of impact. Such a box allows the cluster to approach and recede, but it limits its expansion in the direction parallel to the surface. It is evident from the figure that a significantly higher fraction

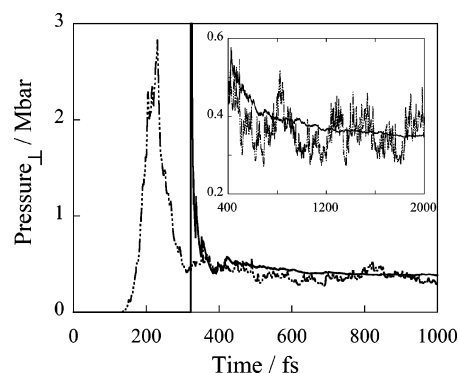


Figure 4. The pressure in megabars vs time in femtoseconds. The pressure plotted is the component in the direction perpendicular to the surface computed from the virial theorem, solid line, as the sum of the kinetic and internal terms, and, dashed curve using the force on the face of the box or, equivalently, as the virial of the external force. Compare to Figure 5. The value for the pressure computed from the force on the face of the box is averaged over a few integration time steps so as to smooth the spikes shown in Figure 3. These spikes are due to the discreteness of the collisions of atoms with the surface. Beyond that, the results are smooth as shown. The insert shows that at longer times the virial of the force is indeed equal to the time-averaged value of the sum of the kinetic and internal terms. This sum has longer time oscillations due to collective motions within the cluster, as seen in Figure 1.

of the initial kinetic energy, energy that for a cold cluster is very largely the energy of the center of mass motion, goes back to directed motion. Even so, a large fraction of the initial kinetic energy of the center-of-mass motion is still converted to random kinetic energy, so the receding confined cluster is quite hot. The bottom panel in Figure 2 shows how a box imposed on all three directions makes the fast atoms that recede from the surface impact turn back due to the wall of the box and thereby slow the motion of the center of mass away from the surface. The effect of the parallel face of the box is first felt at about 300 fs, as also seen in Figure 4.

The mechanical pressure is computed from the change in momentum of the atoms that are reflected from the rigid wall of the box. Each collision with the wall produces a finite force, because in the trajectory computation, the integration time step, δt , is finite, so the change in momentum occurs over a finite time interval δt . Figure 3 is a sample of the force spikes along a trajectory. For each spike, the force is

$$f_{ia}^{\text{ext}} = m(v_{ia} - v_{cm\alpha})/\delta t \quad (4)$$

The impact velocity is $10 \text{ km/s} = 0.1 \text{ \AA/fs}$, so over an integration time step $\delta t = 0.01 \text{ fs}$, the atoms move only about 10^{-3} \AA . For the clusters of 125 atoms that are shown in Figure 2, the spikes are so close in time that any averaging in time will produce a smooth pressure vs time curve as shown in Figure 4. This is what we mean by the statement that the trajectory is “typical”. Mechanical expectation values computed for this trajectory will not be meaningfully different from those for any other trajectory for a cluster at the same internal energy and velocity of impact. This will no longer be the case if there are far fewer atoms in the cluster. Then, finite size fluctuations in the pressure are possible.

In section III, we compare the pressure computed from the force on the faces of the cube and the virial of the external force on the system.

III. Virial of the External Force

For a gas at a higher densities where deviations from ideal gas behavior are possible, the compressibility, $P\tilde{V}/RT$, is usually

expanded as a virial equation of state.¹²³ Here, in the notation of ref 123, \tilde{V} is the volume per mole. An exact, closed form for the virial equation of state is provided by the virial theorem of Clausius.^{123,124,133} In this equation, the $P\tilde{V}$ product is computed by confining a mole of the gas to the volume \tilde{V} and using Green's theorem to equate the virial of the force acting on the atoms within the volume to the force acting on the surface of the confining volume. Independently, the virial of the external force is shown to be the sum of the pressure of an ideal gas at the same temperature plus a correction term, due to the intermolecular forces and often known as the internal pressure. We show in section IV why this latter equality will only be valid when the system settles down. For the hot clusters of interest to us here, this relaxation takes a picosecond or longer. Here, we show the far simpler result; namely, that for the cluster confined to a rigid box, the pressure·volume product as computed by the Bernoullis is numerically equal to the negative of the virial of the external force.

By definition,^{123,124,134} the virial of the external force in the direction α is

$$W_{\alpha}^{\text{ext}} = \sum_i (r_{i\alpha} - r_{c\alpha}) f_{i\alpha}^{\text{ext}} \quad (5)$$

Here, i ($i = 1, \dots, N$) enumerates the atoms in the cluster, and $f_{i\alpha}^{\text{ext}}$ is the external force on atom i ; see eq 4. The position coordinates of the atoms are taken with respect to the center of mass of the cluster. For the special case of a rigid container, the external force operates only when the atom is "at" the surface so that, when the external force on atom i is not zero, $(r_{i\alpha} - r_{c\alpha}) = d_{\alpha}$, where $2d_{\alpha}$ is the linear dimension of the box in the direction α .

The Bernoullis result where $P_{\alpha}V$ is the force that the atoms apply per unit area on the face normal to the direction α times the volume is clearly equal to minus the virial W_{α}^{ext} , that is, the force the face normal to the direction α applies on the atoms times the linear extension of the box in the direction α . This equivalence does not require that the number of atoms is large or an appeal to Green's theorem, since the summation in eq 5, while nominally over all the atoms in the volume of the cluster, is de facto limited to the atoms at the surface.

The Bernoullis result for $P_{\alpha}V$, or equivalently the virial of the external force, is very rapidly varying on the time scale δt of the integration of the mechanical equations of motion as can be seen in Figure 3. However, this expression has the computational advantage that averaging over a few time steps leads to a smooth result as shown in Figure 4. This is unlike the pressure as computed from the virial theorem that, as discussed in section IV, has in addition to the fast, subfemtosecond variation, slower temporal oscillations reflecting collective motions within the cluster.

IV. Virial Theorem

The equipartition theorem of the potential energy, eq 1, readily shows¹¹⁹ that minus the virial of the external force is the sum of the kinetic pressure (= the pressure of an ideal gas at the same temperature, where the temperature is defined via eq 2) and the virial of the intermolecular forces known as the internal pressure. Here, we are concerned with when this equality can fail, and we proceed in a manner similar to the derivation in ref 122. For this purpose, consider the acceleration of the hyperradius

$$\frac{1}{2} mN \frac{d^2 \rho_{\alpha}^2(t)}{dt^2} = \sum_{i=1}^N (r_{i\alpha} - r_{c\alpha}) m \frac{d^2 (r_{i\alpha} - r_{c\alpha})}{dt^2} + \sum_{i=1}^N m \left[\frac{d(r_{i\alpha} - r_{c\alpha})}{dt} \right]^2 \quad (6)$$

Because $\sum_{i=1}^N (r_{i\alpha} - r_{c\alpha}) = 0$, the first sum on the right-hand side is the virial of the total force acting on the atoms, and it can be written as a sum of the internal and external forces

$$\frac{1}{2} mN \frac{d^2 \rho_{\alpha}^2(t)}{dt^2} = \sum_{i=1}^N (r_{i\alpha} - r_{c\alpha}) (f_{i\alpha}^{\text{int}} + f_{i\alpha}^{\text{ext}}) + 2 \sum_{i=1}^N m \left[\frac{d(r_{i\alpha} - r_{c\alpha})}{dt} \right]^2 \sum_{i=1}^N (r_{i\alpha} - r_{c\alpha}) f_{i\alpha}^{\text{int}} + 2 \sum_{i=1}^N m \left[\frac{d(r_{i\alpha} - r_{c\alpha})}{dt} \right]^2 + W_{\alpha}^{\text{ext}} \quad (7)$$

Using Green's theorem to replace the volume integral by an integral over the surface, the virial of the external force equals the instantaneous value of the pressure·volume product^{123,124,133,134}

$$P_{\alpha}V = -W_{\alpha}^{\text{ext}} \quad (8)$$

This result for the pressure·volume product as the external force applied on the container is an immediate generalization of the procedure of the Bernoullis. From eqs 7 and 8 and by invoking the rapid equipartitioning of the kinetic energy to represent the internal kinetic energy by a temperature, we provide a mechanical equation for the instantaneous value of the pressure·volume product

$$P_{\alpha}V = \sum_{i=1}^N (r_{i\alpha} - r_{c\alpha}) f_{i\alpha}^{\text{int}} + 2 \sum_{i=1}^N m \left[\frac{d(r_{i\alpha} - r_{c\alpha})}{dt} \right]^2 - \frac{1}{2} mN \frac{d^2 \rho_{\alpha}^2(t)}{dt^2} = W_{\alpha}^{\text{int}} + NkT - \frac{1}{2} mN \frac{d^2 \rho_{\alpha}^2(t)}{dt^2} \quad (9)$$

This pressure·volume product, computed as $-W_{\alpha}^{\text{ext}}$, is not quite identical to what is sometimes called the instantaneous pressure

$$P_{\alpha}V = W_{\alpha}^{\text{int}} + NkT \quad \text{instantaneous} \quad (10)$$

Both values are shown in Figure 5 for the direction normal to the surface. Figure 4 showed the pressure itself for a direction parallel to the surface. It is seen that the instantaneous pressure, $(W_{\alpha}^{\text{int}} + NkT)/V$, takes longer to settle down to a constant value than for the virial of the external force. Equation 9 proves that the two definitions of the pressure need only agree when the cluster has settled down to a point where the hyperradius has ceased to oscillate in the manner shown graphically in Figure 1. From earlier work, we know that these oscillations are due to damped periodic contractions and expansions that can be described as microshock waves^{79,100,121} within the cluster.

The usual derivations of the expression for the pressure from the virial expansion do not use eq 8 or equivalently eq 9 but assume that the pressure is a time-averaged quantity, averaged over a long enough time interval such that (see Figure 6)

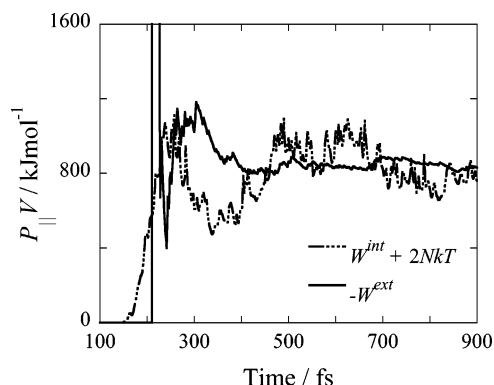


Figure 5. Two computations of the pressure of the cluster. Shown is the pressure-volume product vs time in femtoseconds. The solid line is the pressure computed ala the Bernoullis, that is, in terms of the momentum transfer to the walls of the box, or the numerically the same value given from the virial of the external force on the cluster; see eq 5 and section III. The dashed line is the “instantaneous pressure-volume” computed as the sum of the virial of the internal forces and the random kinetic energy. The reasons for the early time differences between the two curves are discussed in section IV.

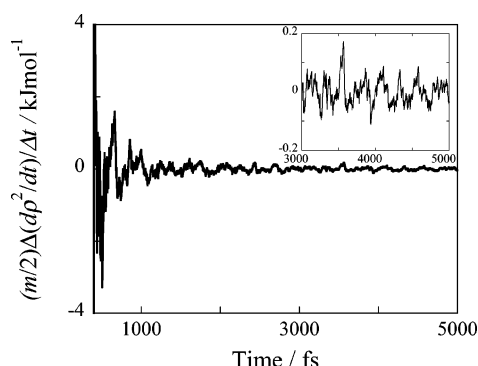


Figure 6. The decay of the averaged hypervelocity to zero. Shown is the left-hand side of eq 11 vs the time. The virial theorem can be used to compute a (time-averaged) pressure only once the averaged hypervelocity goes down to zero; see eq 9.

$$\frac{d^2 \rho_\alpha^2(t)}{dt^2} = \left[\frac{d\rho_\alpha^2(t')}{dt'} - \frac{d\rho_\alpha^2(t)}{dt} \right] / (t' - t) \rightarrow 0 \quad (11)$$

The vanishing is because the hypervelocity $d\rho_\alpha^2(t)/dt$ remains finite while the denominator grows. When eq 11 settles down to about zero, we have from eq 9

$$\overline{P_\alpha V} = \overline{W_\alpha^{\text{int}}} + \overline{NkT} \quad (12)$$

In an earlier work, we defined an instantaneous value of the pressure by imposing on the cluster a force of constraint that ensured that, from the time t , $d^2 \rho_\alpha^2(t)/dt^2 = 0$. Here, we placed the cluster in a box. To use the virial theorem to compute a time-averaged pressure as in eq 12, it is necessary to wait for the acceleration of the hyperradius to go down to zero. As shown in Figure 6, if the initial time for the averaging is about 100 fs or longer after the cluster first hit the box, then the decay is practically completed in less than another 100 fs or so. There are two factors that facilitate the rather fast return to equilibrium. One is the inherent packing disorder of the cluster as it is compressed against the surface.¹²⁶ This is the mechanism whereby a trajectory becomes “typical”, meaning¹³⁵ that it is not distinguishable by its thermodynamic properties from another trajectory. The other is that at the high velocities in the hypersonic range, an order of magnitude or more above room

temperature, the duration of an atom–atom collision is rather shorter than what we are used to. So, the physical clock beats at a faster rate as is also shown by the scaling of the pressure with impact velocity.¹²² The asymptotic trend to zero is dominated by the collective behavior and is exceedingly slow because the hypervelocity depends on time like a stretched exponential.

As Fowler¹³⁴ points out, Green’s theorem can also be applied for any subregion within the system. This theorem is required to connect the pressure to the volume integral that defines the virial, eq 8. A pressure within the cluster can thereby be defined by summing the virial only over the atoms of the subsystem.

V. Concluding Remarks

A cluster of rare gas atoms can be driven very far from equilibrium in a very short time by a hypersonic impact at a hard surface. After a few atom–atom collisions, the distribution of kinetic and potential energies settles to their equilibrium value computed for the temperature that corresponds to the mean value of the random kinetic energy. By confining such a hot and compressed cluster to a rigid container, it is possible to compute the pressure that the cluster applies. Two ways of defining the pressure were discussed. One, in the manner first introduced by the Bernoullis, is by computing the force on the walls of the container by the atoms reversing their velocities upon impact. This gives the same result as computing the pressure-volume product as the virial of the force due to the walls. The other expression is from the virial theorem where there are two terms that contribute, the kinetic and the internal pressures. The latter contribution is the virial of the internal forces. The two ways to compute the pressure converge after the brief interval during which time the turbulence in the cluster to settle down. Pressures up to the megabar range are computed for velocities of impact that are below the threshold for ionization of the cluster atoms.

Acknowledgment. This work was supported by the U. S. Air Force office of Scientific Research. A.G. is a Clore Foundation fellow.

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