Argon cluster evaporation dynamics

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Expansion of argon clusters in a vacuum is simulated via molecular dynamics computations. The resulting evaporation dynamics is investigated with observations of temperature and \( pV \) energy loss curves. Observed cooling curves (\( T \) vs \( n \)) and collapse curves (\( pV/n \) vs \( n \)) are found to depend on final cluster size but not the initial cluster ensemble. The evaporation mechanism consists of an initial rapid cooling-and-collapse stage of a preliquid dense-gas-like cluster, followed by “equilibrium” evaporation, and then another cooling stage of the resulting relatively incompressible liquidlike subcluster. Elements of this dynamics evaporation mechanism are tested by examination of finite \( n \) phase diagrams constructed using Metropolis Monte Carlo simulations of the fixed \( T \) and \( p \) ensemble. © 1995 American Institute of Physics.

I. INTRODUCTION

It is well known, and well understood for macroscopic systems via thermodynamics, that both adiabatic expansion and evaporation of a fluid cause cooling. Recent efforts have sought a more detailed understanding of these cooling phenomena at a microscopic level, particularly in the case of microscopic cluster systems. For example, Klots has developed a simple model of evaporation kinetic energy release for water clusters based on treating the cluster as a collection of Debye oscillators and hindered rotors and accounting for water clusters based on treating the cluster as a collection of Debye oscillators and hindered rotors and accounting for evaporative increase in surface tension. Stace has modeled evaporative rotational cooling (and heating) using phase space theory applied to three-dimensional cluster-and-atom separation dynamics. Other studies simulate cluster evaporation via molecular dynamics computations and a variety of initial activated cluster states.

A simple qualitative microscopic explanation of cooling due to adiabatic expansion or evaporation is straightforward. (Here we actually consider spontaneous adiabatic expansion where there is no external wall on which the expanding fluid can do work, see Ref. 8.) Both processes conserve the total energy of the fluid (or liquid plus gas, in the case of evaporation), and both involve an increase in interatomic separations resulting in a net increase in potential energy. Adiabatic expansion and evaporation are entropy-controlled processes, favoring looser configurations where the dominant attractive potential tail is diminished. Since the kinetic energy must decrease to conserve energy, the fluid is observed (via decreasing temperature) to cool. In addition, expansion and evaporation are driven by thermal energy, so their rate decreases with cooling. We deduce from simple dynamical considerations that cooling progresses at a diminishing rate until a stable fluid is achieved or until the fluid vanishes.

In this article, the simple atomic picture is elaborated specifically in the case of small cluster expansion into a vacuum. With small clusters there is the possibility of finite size effects not ordinarily described by thermodynamics—the “graniness” of the atomic scale is important in small cluster dynamics. In addition small clusters are amenable to a close examination of the underlying dynamics. Below, we present a detailed dynamics mechanism of isolated cluster evaporation which emerges from observations of small cluster evaporation simulations.

An illustration of finite size effects is found in the \( p=0 \) neighborhood of \( Tp \) phase diagrams. At \( p=0 \) a bulk liquid (or solid) can evaporate at any temperature. This is because the bulk material has essentially infinite energy, if it is measured in atomic units. There is always sufficient energy to overcome the barrier to single atom evaporation no matter what the temperature. In contrast, because of its finite energy, a microscopic cluster of atoms has a non-negligible energy threshold below which evaporation cannot take place. The implication for a bulk liquid in a vacuum is that it evaporates only until it reaches microscopic proportions. In general, a bulk liquid evaporates to an equilibrium state consisting of an assortment of microscopic clusters. However, this assortment of clusters actually constitutes the macroscopic equilibrium gas. Thus, from a macroscopic standpoint, the evaporation of a bulk liquid in a vacuum proceeds to completion for any initial temperature. Correspondingly, the liquid–gas coexistence curve in a \( Tp \) phase diagram cuts the \( T \) axis at \( T=0 \). We show below that the \( Tp \) plane of a small collection of argon atoms exhibits a coexistence band (see Sec. III) analogous to the coexistence curve of the thermodynamic-limit bulk fluid. However, due to the non-negligible evaporation energy threshold, the finite \( n \) coexistence band cuts the \( T \) axis between 45 and 65 K. There is, effectively, a temperature threshold below which small liquidlike (and solidlike) argon clusters can exist at zero pressure.

In this study we simulate the expansion of clusters of \( n \) argon atoms into a vacuum in Sec. II, and we examine argon phase diagrams for small \( n \) (21, 30, and 40) in Sec. III. The evaporation cooling and collapse seen in Sec. II is characterized as “universal.” Specifically, thermal and mechanical energies (defined below) follow certain pathways independent of the initial activated-cluster ensemble temperature and pressure. Only the final cluster size distribution depends on these initial ensemble properties. Examination of the universal pathways of thermal and mechanical energy losses, and other observations, leads to construction of a detailed dy-

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namical mechanism where the observed sequence of evaporation events is divided into three stages. The last two stages are in accord with the observations of equilibrium evaporation in Sec. III.

In a companion article the cooling (T vs n) and collapse (pV/n vs n) data presented here are reproduced using a statistical model, described briefly in Sec. IV, which effectively replaces trajectory propagation by an E J ensemble Metropolis Monte Carlo process.

II. CLUSTER EXPANSION IN A VACUUM

In the absence of constraining forces a cluster can fragment if it has sufficient energy to overcome fragmentation thresholds. Fragmentation is viewed as evaporation if one fragment (or subcluster) is much larger than the others. Successive evaporation is possible if product subclusters exceed their fragmentation (or evaporation) thresholds. The underlying molecular dynamics of activated-cluster sequential evaporation is readily studied. The only question is how to choose the initial activated-cluster ensemble. For example, we could consider an ideal “experiment” wherein a small group of atoms is “transported” (Star Trek style) into a vacuum from a bulk characterized by specific temperature and pressure. In such an experiment one controls the degree of compression of the cluster and its kinetic energy via the bulk temperature and pressure. This permits an investigation of the effects of such initial cluster characteristics on subsequent evaporative dynamics.

Other molecular dynamics studies of cluster evaporation employ a variety of different initial ensembles. For example, Markovic and Pettersson produce activated Ar₇Ne₇ via simulated collisions with a hard surface. In Goldberg et al. active cluster ions are generated by simulated ionization. Real experiments typically employ photodissociation of an inert molecule, or ionization to generate an activated cluster ensemble. This study of argon cluster evaporation employs a simple initial ensemble similar to the T p ensemble described above. But, because of a universality described in this section, our results do not depend on the choice of initial ensemble. They are, however, limited to the case of neutral argon evaporation. Application to real experimental situations requires modified forces to account for an inserted chromophore or electron holes. Associated studies are deferred to future articles.

In this work we start with small clusters of argon atoms (typically with n ≤ 50) at fixed temperature, T, within a spherical cavity of variable volume subject to a fixed external pressure, p. The cavity wall is removed instantaneously leaving the cluster free to expand. The selection of cluster states from this “initial ensemble” is simulated using a Metropolis Monte Carlo algorithm adapted for the T p ensemble where the fixed volume is that of a spherical cavity. The cluster initial conditions generated by this Monte Carlo procedure are then propagated numerically via Hamilton’s equations for approximately 200 ps, a long time on the scale of argon cluster dynamics yet small enough to allow the propagation of sufficiently many trajectories to get converged ensemble averages. Some 1 ns runs were carried out for comparison. The extended time scale presented nothing qualitatively different from that described below.

The many-body argon potential is modeled as a sum of two-body 6-12 Lennard-Jones potentials (ε₅₆ = 119.4 K, σ₅₆ = 6.425 bohr). Hamilton’s equations are solved using the fourth order Runge–Kutta algorithm with step size, Δt = 0.015 ps. Trajectories computed with these parameters typically conserve angular momentum very accurately on time scales of interest, but energy tends to drift downwards. However, the latter effect translates into temperature and pV/n errors which are much smaller than Monte Carlo errors in even the most accurately determined average values presented below. In addition, the chaos inherent in the dynamics is expected to render numerical trajectory ensembles roughly indistinguishable from corresponding true trajectory ensembles; i.e., whereas individual trajectories may not be accurate, we expect ensemble dynamics to be well represented. The need for rapid trajectory computation influenced our adoption of simple potential energy function and trajectory integrator.

Evaporation events in the course of a trajectory are identified in terms of a graph-theoretic scheme used to define the “cluster.” Specifically, we assign a “bond” to pairs of atoms within a certain maximum distance, r_bond = 25 bohr. A cluster is defined as a collection of atoms which determine a connected set of bonds. Evaporation occurs when a cluster breaks into a set of smaller subclusters. Typically, breakup occurs with the loss of 1 or 2 atoms by the largest subcluster. We view the largest subcluster as the evaporating cluster and focus our attention on its properties. The cluster definition employed here is essentially the same as that described in Ref. 2.

Temperature T and mechanical energy pV are observed, as a function of cluster size n, through sequences of evaporation processes resulting in relatively stable “final” clusters. The times between evaporation events are also recorded. Cluster T and pV are defined by

$$\frac{kT}{2} = \langle (3n - 8)/[E - V(r) - J^2]^{-1}(r) J^2/2 \rangle^{-1}$$

and

$$pV = n kT - \frac{1}{3} \sum_{j < j' \in \{1, \ldots, n\}} r_{jj'} v(r_{jj'})$$

where r_{jj'} is the distance between the jth and j'th atoms, r represents the complete cluster configuration (i.e., the full set of atomic position vectors), and \( v(r_{jj'}) = \Sigma_{j=1}^{N} m_j (r_{jj'} - r_{ij}) \) is the inertia matrix with respect to center of mass ( superscript T denotes transpose, i.e., \( r_{ij}^T \) is a dyad). Use is made in Eq. (2) of the assumed pairwise character of the potential, \( V(r) = \Sigma_{j < j' \in \{1, \ldots, n\}} v(r_{jj'}) \), i.e., \( V(r) \) is a sum of two body energies, \( v(r_{jj'}) \). J and E are the cluster energy and angular momentum which are conserved between evaporation events. They are not conserved at evaporation events due to the loss of atom(s). The brackets \( \langle \cdot \rangle \) denote time average over the lifetime of the n atom cluster.

Equation (1) is specific to the fixed E J ensemble associated with a cluster of n atoms. It is derived by differenti-
ating the $EJ$ partition function with respect to energy. This ensemble is appropriate as it corresponds to the long time limit of trajectory time averages. The expression for temperature used here equates $(kT/2)^{-1}$ to the mean reciprocal vibrational kinetic energy per effective number of vibrational degrees of freedom, $3n - 8$. Since there are actually $3n - 6$ vibrational degrees of freedom, the connection between this temperature and the more physically motivated mean kinetic energy per degree of freedom breaks down when $n$ is small. Otherwise ($n > 7$) these different definitions of temperature produce qualitatively similar results.

Equation (2) is adapted from an expression derived for the canonical ensemble. The original expression differs only in that its bracket denotes canonical ensemble average. Along with $T$, this expression provides an unambiguous characterization of the state of the cluster (distinct from that provided by $T$, except in the ideal gas limit). The pressure and volume of a cluster expanding into a vacuum are, strictly, zero and infinity, respectively; therefore, by themselves $p$ and $V$ do not well characterize the state of the cluster. Since $pV$, which does conveniently characterize the cluster state, is an extensive quantity it is generally reported below in the form of the intensive $pV/n$. Note that although both terms in Eq. (2) scale with $n$ the intensive quantity still has an $n$ dependence through the scaled virial term (second term) when $n$ is small.

It is instructive to consider the microscopic interpretation of $pV/n$ which is deduced from Eq. (2). The limit of well separated atoms corresponds to the ideal gas case where $pV/n$ equals thermal energy, $kT$. Compressing such atoms decreases $pV/n$ via attractive potential tail contributions to the virial term. Here the value of $pV/n$ is governed by the decrease in the cluster volume rather than the increase in the pressure (diminished by attractive internal forces). Such a cluster resembles a nonideal dense gas. At sufficiently high compression, further compression increases the repulsive contribution to the virial (associated with small $r_{ij}^{1/k}$) more than it decreases the attractive contribution. Such a cluster clearly resembles a relatively incompressible liquid wherein $pV/n$ and $p$ are positively correlated.

$pV/n$ is viewed as a measure of cluster “looseness” with two cases to be distinguished. In the case of a “dense-gaslike” cluster, larger $pV/n$ corresponds to looser clusters. The trend is reversed in the denser “liquidlike” clusters. With this in mind we expect a minimum $pV/n$ value (with respect to compression) to correspond to the transition between the two cluster types. This is shown in Sec. III, and in this section via dynamics simulations.

In the discussion below we treat $T$ and $pV/n$ as effective “phase space” variables with temperature characterizing the average atomic momentum, and $pV/n$ characterizing the cluster configuration as described above. In this analogy with classical mechanics the “mechanical energy,” $pV$, and the “thermal energy,” $nkT$, are roughly identified with potential and kinetic energy, respectively.

**A. Evaporative cooling, $T$ versus $n$**

A set of data was produced by the means described above. In Fig. 1 we show average $T$ vs $n$ for initial ensembles with $n_i = 30$, $p_i = 60$ atm and $T_i = 115$, 120, and 125 K. The averaging in question is with respect to the initial ensemble. Note that since $T$ and $pV$ ($pV$ is not shown in this figure) are recorded for each trajectory as sequences of time averages (over the range of $n$ values), it is necessary to weight each time average by its associated cluster lifetime in order to get an unbiased average with respect to initial ensemble. This is justified by appealing to Liouville’s theorem which tells us that the invariant phase space measure associated with a trajectory segment is in proportion to its length in time.

The $p_i$ and $T_i$ values of Fig. 1 were chosen primarily because they generated interesting results. Larger $T_i$ and/or smaller $p_i$ values produce loose, relatively energetic initial clusters which evaporate (actually fragment) rapidly. In this case there is little opportunity for intracluster forces and associated dynamics to have much impact on the course of the evaporation sequence and its outcome. Smaller $T_i$ and/or larger $p_i$ values produce clusters which are more tightly bound. They evaporate slowly and are difficult to study because long trajectories present greater computational demands. Very small $T_i$ and/or very large $p_i$ produces clusters which essentially do not evaporate.

**FIG. 1.** Average temperature cooling curves; average temperature vs cluster size during evaporation sequence associated with initial ensembles with $p_i = 60$ atm and initial temperatures, $T_i = 115$ (asterisks), 120 (triangles) and 125 K (squares). Note that initial temperature, $T_i$, and average $T$ (up to the first evaporation event) both appear as $n = 30$ points. $T_i$ > $T$ is indicative of cooling due to adiabatic expansion. Data with $n < 6$ are not shown. Errors are small compared with variation of $T$ along the curves. The 115, 120, and 125 K ensembles are represented by 31 597, 3 094, and 3 016 trajectories, respectively.
with the data provided, cooling due to adiabatic expansion from that due to evaporation. This is not a problem, though, since it is not necessary to separate the two processes—the entire evaporation sequence is a single adiabatic expansion into a vacuum with evaporation events signaling special milestones. However, in our discussion of this and other data we term all cooling “evaporative,” since evaporation is the most obvious characteristic of cluster expansion in a vacuum. Clusters typically expand in a vacuum only in the sense that evaporated atoms occupy a greater effective volume. In fact, the subcluster remaining after evaporation is usually relatively collapsed on a volume per atom basis.

Figure 1 exhibits evaporative cooling in two apparent stages, rapid initial cooling followed by a long sequence of slowly cooling evaporation steps. We first consider the last few evaporation steps where there seems to be a slight evaporative heating (at least in the case of 125 K). At this point, we note that the figure only incorporates data associated with final clusters with \( n_f \geq 7 \) atoms. Inclusion of all trajectories produces similar curves but with a greatly enhanced upturn in temperature for small \( n \) values. We have traced this “anomaly” to the effective number of vibrational degrees of freedom used in Eq. (1) \((3n - 8)\); scaling the data to “correct” this number produces relatively flat cooling curves in the small \( n \) regime. This observation lead us to question the use of the formal micro-canonical temperature formula, Eq. (1), used in this work. Nevertheless, because the formula works well for \( n > 7 \) and these larger \( n \) values are the focus of the results presented below, we retain the formula in its current form.

Each temperature datum presented in Fig. 1 is an average over all cluster states of a given size represented in the evaporating cluster ensemble. In particular, there are cluster states associated with every stage of the evaporation process. Some of these clusters have essentially stopped evaporating, while others are much more energetic and continue evaporating. We first consider the last few evaporation steps where there seems to be a slight evaporative heating. At this point, we note that the figure only incorporates data associated with final clusters with \( n_f \geq 7 \) atoms. Inclusion of all trajectories produces similar curves but with a greatly enhanced upturn in temperature for small \( n \) values. We have traced this “anomaly” to the effective number of vibrational degrees of freedom. Inclusion of all trajectories produces similar curves but with a greatly enhanced upturn in temperature for small \( n \) values. We have traced this “anomaly” to the effective number of vibrational degrees of freedom used in Eq. (1) \((3n - 8)\); scaling the data to “correct” this number produces relatively flat cooling curves in the small \( n \) regime. This observation lead us to question the use of the formal micro-canonical temperature formula, Eq. (1), used in this work. Nevertheless, because the formula works well for \( n > 7 \) and these larger \( n \) values are the focus of the results presented below, we retain the formula in its current form.

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Figure 2 shows \( n_f \) specific cooling curves wherein averaging is performed only over sets of similar clusters evolved from the initial ensemble—similar in that they give rise to the same final cluster size. The \( n_f \) specific cooling curves seen here are typical. They are all characterized by three distinct stages of evaporation. In the first stage (i.e., at \( n \) close to \( n_f \geq 7 \)), there is rapid initial cooling. The second stage consists of slow cooling near an effective temperature plateau always in the neighborhood of \( T = 65 \) K. In the final “quenching” stage there is rapid cooling, stopping at a relatively stable final cluster. It is important to note, however, that while the cooling seen in the final stage is rapid when viewed in terms of evaporation steps, it is not rapid when viewed in real time. This distinction results because evaporation time scale increases dramatically for the last few steps, see Fig. 3.

Qualitative features of the evaporative cooling seen in Fig. 2 are of much interest, and a physical understanding of these features is a principal goal of this article. Perhaps the most striking features is the agreement of \( n_f \) specific cooling curves irrespective of initial ensemble temperature. Differences evident in Fig. 1 are removed when data is binned according to \( n_f \). It follows that the differences in Fig. 1 are due almost entirely to the different final cluster size distributions (shown in the second column of Fig. 4) associated with the three initial ensembles. Note that Fig. 1 can be constructed by summing corresponding curves in Fig. 2 with weights taken from the final cluster size distributions of Fig.
We conclude that, at least for the \((T_i, p_i)\) cases considered so far, the cooling curve depends principally on \(n_f\), and the initial ensemble is manifest primarily in the distribution of \(n_f\), i.e., how far the evaporation process proceeds on average. The cooling curves of Fig. 2 are therefore suggestive of “universal” cluster-state pathways which are \(n_f\) specific.

The apparent universality of \(n_f\) specific cooling curves is further investigated in Fig. 2 by including cooling curve data associated with individual trajectories (one for each of the chosen \(n_f\) values) taken at random from the \((T_i, p_i)=(115 \text{ K}, 60 \text{ atm})\) initial ensemble. The temperature distributions along the evaporation sequence have variance ranging from 10 to 6 K as \(n\) ranges from 30 to 9. These variances are manifest as fluctuations seen in individual trajectory cooling data. However, the averages which we have thus far focused on clearly emerge as a central pathway which the individual cooling curves straddle, and this behavior is in no way exceptional—virtually all randomly chosen trajectories exhibit similar behavior. The temperature distribution variance results from fluctuations in individual trajectory cooling curves, not from systematic variation of cooling curve pathway from one trajectory to another. It is therefore not surprising that different ensemble averages of such cooling curves produce the same “universal” result.

The independence of \(n_f\) specific cooling curves on initial ensemble is investigated with \(p_i=10\) atm initial ensembles. To produce final cluster size distributions comparable to those for \(p_i=60\) atm, smaller \(T_i\) were required (see Fig. 4). Figure 5 shows \(p_i=10\) atm cooling curves for \(T_i=70\), 80, and 84 K. The \((115 \text{ K}, 60 \text{ atm})\) data of Fig. 2 are also shown for comparison.

At \(p_i=10\) atm the initial rapid cooling stage is not as pronounced as for the \(p_i=60\) atm data. However, the temperature plateau at \(\sim 65\) K and the final quenching stage appear just as before. Moreover, the initial systematic differences between the 10 atm and 60 atm cooling curves is essentially eliminated after the first evaporation event. The \((T_i, p_i)=(50 \text{ K}, 1.2 \text{ atm})\) ensemble was also treated. In this case, the low initial pressure generated initial clusters of less than 30 atoms \((16–20)\)—there is rapid initial fragmentation. Nevertheless, cooling curves (not shown) of the resultant evaporating subclusters follow universal pathways in the third stage and exhibit slow cooling about \(60\) K in the second stage (with large fluctuations due to poor convergence of the available data). In particular, the brief initial stage of sequential evaporation of a 50 K subcluster exhibits heating in order to attain the plateau thermal energy.

Clearly, the strongly diminished initial rapid cooling stage is expected for the lower \(T_i\) values used in Fig. 5. The initial stage seen in Fig. 2 seems to be a period of excess energy dissipation until the desired evaporation temperature of near 65 K is attained. It is also the stage where the three averaged cooling curves differed the most. When \(T_i\) is close to 65 K little energy dissipation is necessary and, in fact, if \(T_i\) is less than 65 K, heating is required. It is important to note that the heating observed in the latter case is due to collapse of the initially rather loose clusters in the associated initial ensemble and the corresponding conversion of mechanical energy into thermal energy. Had the initial clusters not been so loose (i.e., if the initial pressure were not so low), little or no evaporation would be seen.

The universality of the cooling curves, seen in the second and third stages of evaporation, ensures that our choice of initial ensemble does not affect the interpretation of the cooling curve data. It is reasonable to surmise that the Star Trek style “transporter” experiment described at the beginning of this section would have produced the same cooling...
curves. It would be interesting to see if a yet broader range of initial ensembles and forces, such as those associated with experiments, produces the same universal behavior. We are currently considering such future studies.

B. Final cluster size distribution and evaporative collapse, \( n_f \) and \( pV/n \) versus \( n \)

One of the most compelling observations arising from experimental studies of rare gas clusters is that of “magic number” cluster sizes apparent in mass spectra taken subsequent to supersonic jet expansion. Since we expect free evaporation processes (and the equivalent reverse processes) to play a role in the production of stable neutral clusters in the supersonic jet, it is reasonable to suppose that the simulations of the current article might provide some insight into the dynamical mechanism of magic number cluster formation. We are thus led to examine the final cluster size distributions resulting from the free expansions treated in this study. Note that the “final clusters” are the only clusters stable on a sufficiently long time scale to be observed by most experiments.

Inspection of final cluster size distributions in Fig. 4 and similar data (not shown) associated with different initial ensembles shows no preferential formation of magic number clusters. Our results do provide one clue, however. The observed correlation of initial cluster ensemble and final cluster distribution suggest that activated cluster preparation may be important in the generation of magic numbers. Of course there is also the possibility that magic numbers are only associated with ionized clusters, as these are the only clusters observed in experiments. The issue is not further addressed here.

In addition to temperature we computed the mechanical energy per atom, \( pV/n \), during the course of cluster evaporation. Figure 6 shows \( n_f \) specific collapse curves (average \( pV/n \) vs \( n \) binned according to final cluster size) with \( (T_i, p_i) = (115 \text{ K}, 60 \text{ atm}) \), and individual trajectories taken from the same ensemble. Collapse curves for the \( T_i = 120 \) and \( 125 \text{ K} \) ensembles (each with \( p_i = 60 \text{ atm} \)) are also shown. Like the cooling curves, collapse curves exhibit a plateau in \( pV/n \) during the second stage of evaporation. However, unlike the cooling curve data, the plateau in \( pV/n \) persists into the last stage. Also, as in the case of cooling curves, collapse curves exhibit an apparent universality; i.e., the \( n_f \) specific collapse curves are relatively independent of initial ensemble. This universality is not as evident in the individual trajectory data, however. Individual trajectories exhibit large fluctuations with less tendency to track the “universal” pathways than corresponding individual trajectory cooling curves. The \( pV/n \) distribution variance ranges from 15 to 5 K over the range of \( n \) from 30 to 9. Since the average \( pV/n \) values are smaller than the corresponding average temperatures, the \( pV/n \) distributions are broader on a relative scale.

An important difference between \( pV/n \) and \( T \) data are the \( n_f \) dependence of the \( pV/n \) plateau value which ranges from \( \sim 16 \text{ K} \) (Ref. 17) for \( n_f = 9 \) to \( \sim 8 \text{ K} \) for \( n_f = 16 \); whereas the \( n_f \) dependence of the temperature plateau is weak and not clearly indicated by the data. Also, beyond the initial stage of evaporation the temperature is not well correlated to the final cluster size. In contrast, the mechanical energy per atom is always negatively correlated with final cluster size. Larger \( pV/n \) leads to smaller clusters which retain the signature of greater mechanical energy. This last point is made clear in Fig. 7 which overlays \( n_f \) specific cooling and collapse curves (in the top and bottom panels, respectively) associated with the \( (T_i, p_i) = (115 \text{ K}, 60 \text{ atm}) \) ensemble.

It is interesting to explore the factors which determine the final cluster size more closely. Figure 4 shows that increasing \( T_i \) or decreasing \( p_i \) decreases the typical final clus-
The obvious conclusion that the initially hottest and/or loosest clusters evaporate most readily, leads us to investigate the dynamical mechanism by which the initial excess energy (thermal or mechanical) is translated into additional evaporation. We can already address this question by comparing the different \( n_f \) specific cooling curves shown in Fig. 7. The figure clearly shows, as one might expect, that clusters with the highest \( T \) and \( pV/n \), after the initial adiabatic expansion of the \( n=30 \) atom cluster, are those which lead to the smallest final cluster size. These are the hottest and/or loosest clusters of the initial ensemble. Note that we assume positive correlation between \( pV/n \) and cluster looseness amongst initial configurations, i.e., dense-gas like configurations [see the discussion of Eq. (2)]. Conversely, the coldest and/or tightest clusters lead to the largest final clusters.

As one might expect from a Fick’s law standpoint, the hottest clusters cool the fastest in the initial rapid cooling stage. However, they cool so fast that they end up coldest in the second cooling stage. In contrast the loosest clusters remain loosest throughout the entire evaporation process. Only the mechanical energy is always correlated with the extent of evaporation. This and the fact that collapse curves exhibit a more gradual transition to plateau behavior than cooling curves leads us to hypothesize that excess thermal energy extends evaporation by first being stored, as mechanical energy, during the initial rapid cooling stage. It is the mechanical energy alone which drives the evaporation process after the first stage. In this picture evaporation proceeds, after the first stage, via concerted atom ejection and remaining—subcluster collapse—no excess kinetic energy is required. This hypothesis is further investigated in terms of \( pV/n \) vs \( T \) and \( pV \) vs \( T \) curves shown in Fig. 8. In the first stage the “evaporation pathways” of the top panel follow a roughly constant slope with points bunching up as the plateau stage is entered. The second stage corresponds to a kink in the \( pV/n \) vs \( T \) pathways (especially for the smaller \( n_f \) values) with fixed plateau value \( pV/n \) and \( T \). It is here that correlation of \( T \) and final cluster size is lost. In the last stage, these pathways bend into an almost horizontal band. It is interesting that while this band spans a range of \( pV/n \) values correlated with \( n_f \), the corresponding \( pV \) values shown in the bottom panel are very nearly the same. \( pV \) values appear to converge to near 120 K. It is also interesting that all of the pathways end up with a final temperature of about 50 K. In the last stage temperature is almost completely uncorrelated with cluster size.

The plateau \( pV/n \) and \( T \) appear in the top panel of Fig. 8 as kinks in the evaporation pathways associated with the bunching up of data points. These kinks separate the first and last stages of evaporation which both appear with roughly constant slope. We propose that the kinks be viewed as the uniquely defined (as a \( pV/n \) vs \( T \) point) equilibrium state of a liquidlike cluster evaporating at zero pressure. The \( n_f \) dependence of the kink locations is a finite size effect—each \( n \) value effectively has its own distinct \( pV/n \) vs \( T \) thermodynamic state space. With this proposal, the first stage of each evaporation pathway is viewed as evaporation on the dense-gas-like side of condensation, while the third stage corresponds to the liquidlike side of the evaporation induced condensation process.

In the above picture, dense-gas-like clusters approach condensation in the first stage of evaporation by loosing atoms with more than their share of both mechanical and thermal energy. The second stage of evaporation is an “equilibrium” condensation stage with \( pV/n \) and \( T \) conservation (see Sec. III). Eventually the evaporating cluster becomes decidedly liquidlike and the second stage gives way to the last stage wherein the relatively incompressible liquidlike clusters loose only thermal energy upon evaporation, on a rapidly increasing time scale. There is even a slight increase in \( pV/n \) during the liquidlike cooling stage, consistent with the behavior of an incompressible liquid wherein cluster tightening due to evaporation corresponds to an increasing \( pV/n \). Tightening of a liquidlike cluster increases the repulsive component of the virial more than the attractive contribution is decreased, see Eq. (2). In contrast, as we have seen, tightening a dense-gas-like cluster decreases mechanical energy because the attractive contribution to the virial dominates its response. This distinction between liquidlike and dense-gas-like clusters is substantiated in Sec. II B with equilibrium Monte Carlo computations.

The convergence of all collapse curves to constant \( pV \) seen in the bottom panel of Fig. 8 provides an important clue regarding the \( n_f \) dependence of the plateau \( pV/n \) values. The latter plateaus are clearly approximately reciprocal to \( n_f \). In particular the associated constant \( pV \) value of \( \sim 120 \) K is consistent with a model wherein the low temperature limit \( pV \) corresponds to the dissociation energy, \( E_{\text{dis}} \), of an \( n \) atom cluster. \( E_{\text{dis}} \) is weakly dependent on \( n \) because the minimum energy required to remove a single atom from the cluster is always (given our definition of cluster) associated with configurations for which the evaporating atom interacts primarily with only one of the remaining cluster atoms. Therefore,
$E_{\text{dis}}$ is close to 119 K, the well depth of the Ar–Ar Lennard-Jones potential used in these computations.

The $(T,p,V/n)$ location of the condensationlike transition, observed here as the second stage in our simulation of evaporation dynamics, agrees with a phase-transition-like phenomenon examined in Sec. III via $(T,p)$ ensemble Monte Carlo computations. Phase-transition-like phenomena have been observed in other molecular dynamics studies of a wide range of atomic and molecular clusters. It is typically the solidlike liquidlike transition that is most easily characterized.27

III. CLUSTER “PHASE DIAGRAMS”

A. $T$ $p$ phase diagram

In macroscopic systems the liquid–gas phase transition is most conveniently studied using phase diagrams which assign phase labels to distinct regions in thermodynamic state space. For example, evaporation of a macroscopic liquid to completion is manifest in a $T$ $p$ phase diagram by the liquid–gas coexistence curve intersecting the origin. In contrast, a finite sized cluster generally cannot evaporate to completion. In this section, we consider the phase diagrams of finite size clusters in order to make the finite size effects explicit. At the same time we are able to identify the stages of evaporation seen in Sec. II with equilibrium cluster states.

The same $T$ $p$ equilibrium ensemble used to generate initial conditions in Sec. II was chosen for this study. We consider an ensemble of $n_i$ argon atoms in a variable-sized spherical cavity with fixed external pressure, $p$, and temperature, $T$. Ensemble averages are computed using the Metropolis Monte Carlo algorithm of Sec. II. Approximate coexistence curves appear as sharp changes in thermodynamic observables such as $\langle E \rangle$ and $\log(V)$ considered as functions of $T$ and $p$. Here the brackets indicate $T$ $p$ ensemble average. Examples of such coexistence curves, seen as dense narrow bands of contours, are shown in Figs. 9 and 10 for $n_i=21$, 30, and 40. Figure 9 contrasts the $n_i=30$ phase diagram with corresponding data for bulk argon. The bulk argon is simulated using a variation on the second order virial series equation of state. Specifically, the repulsive part of the second virial term is replaced by an infinite geometric series resulting in a van der Waals equation of state. Knowing the thermodynamic state of the system $p$, $T$, $V$, and $n_i$ (note that we effectively consider $n_i$ representative atoms from a bulk), one can then calculate the energy $E$ from its corresponding second order virial series.28 (No geometric resummation is needed for $E$.) Finite-size cluster $T$ $p$ ensemble average energies are computed using

$$\langle E \rangle = \frac{3}{2} n_i kT + \left( \sum_{j \neq j'} v(r_{jj'}) \right).$$

The $n_i=30$ equilibrium ensembles used as initial conditions in Sec. II are located in the phase diagrams. The top panel of Fig. 9 shows that the $p_i=60$ atm initial ensembles correspond to supercritical fluids. We expect these initial conditions to have an excess of both thermal and mechanical energy. In addition one expects finite-size-effect fluctuations of observables sampled from such ensembles. For example, liquidlike states should exhibit small density fluctuations, while states nearer the coexistence band should have large fluctuations in all observables.29 Fluctuations expected for the $p_i=60$ atm supercritical initial ensembles are consistent with the dynamics observations of Sec. II. The $p_i=10$ atm initial ensembles used in Sec. II are close to the coexistence band with the $T_i=70$ K well into the liquidlike region. If $T_i$ is increased beyond 84 K into the gaslike part of the phase diagram, evaporation (actually fragmentation) is fast and leads to a predominance of very small final clusters. Alterna-

FIG. 9. $T$ $p$ phase diagrams; contours of $\langle E \rangle$ for 30 atoms (top panel) and bulk argon (bottom panel). The bulk argon data corresponds to the bulk energy per atom scaled by $n_i=30$ for comparison with the top panel.

FIG. 10. $T$ $p$ phase diagrams for $n_i=21$ (top row), 30 (middle row), and 40 (bottom row); contours of $\langle E \rangle$ (left column) and $\log(V)$ (right column). The rectangular kinks in the contours are artifacts of the limited $(T,p)$ space resolution.
tively, decreasing $T_i$ below 70 K produces very little evaporation on a reasonable time scale. Note the dramatic shift in the final cluster size distribution (see Fig. 4) in going from $T_i=80$ K to 70 K. Not only does the distribution shift to larger final clusters, but it also narrows as might be expected from a liquidlike ensemble with small fluctuations. The $T_i=80$ and 84 K ensembles have broader final cluster size distributions seen in Fig. 4. These are consistent with coexistent region ensembles which have large fluctuations. It is interesting that the large fluctuations in these ensembles do not affect the apparent universality of the cooling and collapse curves of Sec. II.

Remarkably, the cooling-curve plateau temperature seen in Sec. II emerges here as the $p=0$ condensation temperature for 30 atoms. The $n_i=30$ liquid–gas coexistence band, shown in Figs. 9 and 10, clearly intersects the $T$ axis at 60–65 K. Of course, the Monte Carlo computation is not carried out at $p=0$, since at zero pressure the $(T,p)$ ensemble is unbounded and Monte Carlo ensemble averages are not clearly defined. The identification of the plateau temperature with a zero-pressure liquid–gas coexistence equilibrium state is based on extrapolation of the available data as it appears in the figure. In fact, close examination of the $n_i=30$ phase diagrams reveals that the coexistence band splits into two bands at small pressure. There is a corresponding secondary intersection with the $T$ axis in the neighborhood of 55 K. Thus, there appear to be two condensationlike transitions at zero pressure for $n_i=30$. Higher resolution data at low pressures (not shown here) actually show only the lower temperature band intersecting the $T$ axis, in the 50–55 K range.

The following picture emerges when observations of $n_i=30$ phase diagrams are compared with the results of Sec. II: (i) The low-resolution zero-pressure coexistence temperature of $\sim 65$ K, seen in Figs. 9(b) and 10, matches the second-stage plateau temperature which is identified in Sec. II with finite-size equilibrium condensation. (ii) The high-resolution zero-pressure coexistence temperature of $\sim 50$ K coincides with the lowest temperature attained in the third stage of evaporation seen in Sec. II. This latter temperature corresponds to clusters with energies approaching their dissociation threshold and evaporation time scales rapidly approaching infinity.

Figure 10 and other computations not presented here show that zero-pressure coexistence temperatures are positively correlated to $n_i$. This trend persists in the range of $n_i=14–100$. These observations are counterintuitive as we know that the zero pressure coexistence temperature must eventually tend to zero as $n_i\rightarrow\infty$. Apparently an approach to macroscopic behavior does not set in until $n_i$ is much larger. We do not address this question further here—it could lead to an interesting future study. Instead we focus on more detailed aspects of the observed condensationlike transitions, and note here that surprises are quite common when one attempts to extrapolate finite size system behavior to $n=\infty$.30

**B. Compression curves, $\langle n \rangle$ versus $pV/\langle n \rangle$**

In Sec. II evaporating clusters are characterized by mechanical energy in addition to temperature. We wish to compare $pV/n$ for the dynamically evaporating clusters with ensemble average $pV/n$ values associated with the zero-pressure liquid–gas coexistence states observed in this section. However, the volume which appears in Fig. 10 means determining the total mechanical energy of liquid–gas mixtures, not the liquidlike subcluster. To get ensemble average mechanical energy of the liquidlike subcluster we proceed by analyzing the $n_i$ atom configurations of the Monte Carlo process in the graph-theoretic fashion described in Sec. II. Subcluster $pV$ is determined using Eq. (2) with $T$ $p$ ensemble average instead of time average. In principle, subcluster size $n$ varies from 0 to $n_i$ in the coexistence region. Small liquidlike subclusters are observed in the gaslike side of the coexistence region, while near $n_i$-atom subclusters correspond to the liquidlike side. Because the evaporation transition state defined by $r_{bond}=25$ bohr is loose, there are generally residual subclusters well into gaslike portion of the phase diagram, even at the lowest pressures. We expect these subclusters to represent dense-gas-like drops in equilibrium with a low density gas (approaching zero density as $p\rightarrow 0$), rather than liquidlike drops; alternatively, they represent high density fluctuations in an otherwise low density gas. Note, however, that the residual subclusters may be artifacts of a long Monte Carlo relaxation time due to near unboundedness of the equilibrium configuration space at low pressures. Nevertheless, whether the residual subclusters are equilibrium gaslike drops or Monte Carlo metastable states, they are easily identified by small $\langle n \rangle$ and qualitatively distinct characteristics in comparison with liquidlike properties.

Figure 11 plots ensemble averaged subcluster size, $\langle n \rangle$, and subcluster energy vs corresponding subcluster $pV/\langle n \rangle$ for a range of $T$ and small $p$ in the case of $n_i=30$. Points with the same temperature are joined to make “compression” curves which illustrate the condensation of liquidlike clusters. In the following discussion we describe such curves.
in the sense of decompression; i.e., we imagine traversing the curves from large to small $p$.

At all but the highest temperatures ($< 73$ K) compression curves exhibit horizontal lines at $\langle n \rangle = 30$ in the bottom panel of Fig. 11. (The $80$ K curve also has a few points near $\langle n \rangle = 30$, but these are considered to be outside the neighborhood of zero pressure.) Energy, in the top panel, is approximately horizontal at the same pressures. The subcluster states represented on these lines are liquidlike. Characteristic of an incompressible liquid, $pV/\langle n \rangle$ decreases as $p$ decreases along the horizontal lines. At all but the lowest temperatures ($> 46$ K), rapidly decreasing $\langle n \rangle$, and increasing $\langle E \rangle$ and $pV/\langle n \rangle$ are observed with further decompression. The middle range of temperatures show both types of behavior. The turn in the compression curves signals a finite-size liquid to gas phase transition; i.e., the change in response of the energy to gas phase transition; i.e., the change in response of the energy in the process, but at a much greater rate after the transition. The attractive contribution to the energy is dominant at all pressures represented here. Negative energies are consistent with an strong attractive component in Eq. (3). However, since the liquidlike cluster configuration responds only weakly to decompression, its energy changes very little. In contrast decompression of the dense-gas-like subcluster results in significant expansion and a corresponding loss of van der Waals attraction.

The equilibrium vaporization process in the $T_p$ ensemble is signaled by $\langle n \rangle$ suddenly dropping away from $n_i$. Corresponding $pV/\langle n \rangle$ values are identified with this process. To get these values in the zero pressure limit, we note that equilibrium evaporation pressure decreases with decreasing temperature, but only to a point. There are lower temperatures for which equilibrium evaporation does not occur; i.e., $\langle n \rangle$ remains at 30. The zero-pressure equilibrium evaporation temperature is identified as the lowest temperature for which a transition does occur. In Fig. 11 this temperature is seen to be about 46 K. If we do not insist on zero pressure then the equilibrium evaporation temperature and $pV/\langle n \rangle$ have a pressure dependence. For example, for the range of pressures represented in Fig. 11, the equilibrium temperatures range from 46 to 73 K (the 80 K compression curve shown does not have a distinct transition to a liquidlike phase). This range roughly corresponds to the zero-pressure coexistence band seen in Figs. 9 and 10. Associated equilibrium evaporation $pV/\langle n \rangle$ is in the range of 6–12 K, in accord with plateau values seen in Sec. II.

We extract equilibrium evaporation $pV/\langle n \rangle$ values, as described above, for a range of temperatures (and associated range of pressures). It is instructive to plot these equilibrium evaporation mechanical energies vs corresponding temperatures. Such a plot is given in Fig. 12 for $n_i = 17, 24$, and 40. The $n_i$ dependence of the pathways is a finite-size effect with a trend consistent with that seen for $n_i$ specific pathways determined in Sec. II. Specifically, smaller $n_i$ shifts the equilibrium evaporation pathways to larger $pV/\langle n \rangle$. Figure 12 also shows three $n_i = 30$ dynamics evaporation pathways (the average, and $n_j = 9$ and 15 specific pathways). They map out a band in the thermodynamic state space which overlaps the equilibrium pathways band.

Whereas the dynamical evaporation data of Sec. II and the phase diagrams of Sec. III A single out $T_{50} = 65$ K as a principal evaporation temperature, Fig. 12 identifies a range of evaporation temperatures. As described in Sec. II B, $T = 60–65$ K is where temperature plateaus and evaporation pathways kink. However, dynamical evaporation also occurs at higher and lower temperatures (the first and third stages), and Fig. 12 connects dynamical evaporation events with corresponding equilibrium evaporation states for all three stages of evaporation. Examination of the data used to construct Fig. 12 reveals that as temperature is increased above 65 K the associated equilibrium evaporation pressure begins to rise swiftly from about 2 atm. Equilibrium evaporation at higher temperature does not occur in the neighborhood of zero pressure. In Fig. 12, higher pressure equilibrium corresponds roughly to zero pressure evaporation of the preliquid dense-gas-like clusters in the first stage of the evaporation dynamics. Equilibrium evaporation in the zero-pressure neighborhood corresponds to stage two and three dynamical evaporation. Note, in particular, that both equilibrium and dynamical evaporation have a low temperature bound of near 50 K seen in Fig. 12.

C. $p E$ and $T E$ phase diagrams

The $n_i = 30$ data used to construct the top panel of Fig. 9 is presented here again in the form of $p E$ and $T E$ phase diagrams. In Fig. 13, we plot isotherms and isobars as functions of $p$ and $\langle E \rangle$ and $T$ and $\langle E \rangle$, respectively. The resulting phase diagrams are similar to the $p V$ diagram traditionally used to describe liquid–gas equilibrium. Both $\langle E \rangle$ and $\langle V \rangle$ of coexistence states are sharply varying since
The elucidated evaporation mechanism consists of three stages. First, there is rapid cooling and collapse stage of a "preliquid" or dense-gas-like cluster. The second stage consists of equilibriumlike evaporation at constant pressure and temperature. The associated cooling curve plateaus at near $T_0 = 65$ K for most final cluster sizes. $p/n$ plateau values exhibit an $n_f$ dependence which is well described by $E_d/n_f$, where $E_d = 119$ K is the dissociation threshold of an $n_f$ atom cluster. The third stage of evaporation consists of rapid (in terms of evaporation steps, not real time) cooling of the resulting relatively incompressible "liquidlike" subcluster. The evaporation time scale increases dramatically in this last stage.

(3) Metropolis Monte Carlo simulations of the fixed $T$ and $p$ ensemble are used to determine a variety of finite cluster phase diagrams. Computed $T_p$ phase diagrams exhibit a well defined condensationlike process in the form of a coexistence band which intersects zero pressure in the neighborhood of $T_0 = 65$ K for $n_i = 30$. The associated lower temperature bound on coexistence at $T = 50$ K is in accord with the lowest temperatures achieved in the dynamics simulations.

V. SUMMARY

The mechanism of argon cluster evaporation has been investigated using trajectory ensemble and Monte Carlo techniques. The principal conclusions of this investigation are as follows:

(1) Dynamical cooling curves ($T$ vs $n$) and collapse curves ($p/V/n$ vs $n$) specific to fixed final cluster size exhibited an apparently "universality." Specifically, they are independent of initial ensemble characteristics. The latter characteristics were manifest only in the final cluster size distribution.

(2) The elucidated evaporation mechanism consists of three stages. First, there is rapid cooling and collapse stage of a "preliquid" or dense-gas-like cluster. The second stage consists of equilibriumlike evaporation at constant $T$ and $p/V/n$. The associated cooling curve plateaus at near $T_0 = 65$ K for most final cluster sizes. $p/V/n$ plateau values exhibit an $n_f$ dependence which is well described by $E_d/n_f$, where $E_d = 119$ K is the dissociation threshold of an $n_f$ atom cluster. The third stage of evaporation consists of rapid (in terms of evaporation steps, not real time) cooling of the resulting relatively incompressible "liquidlike" subcluster. The evaporation time scale increases dramatically in this last stage.

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8 The distinction between adiabatic and spontaneous (adiabatic) expansion is made, in J. H. Noggle, Physical Chemistry, 2nd ed. (Scott Foresman, Glenview, 1989), p. 105.
9 Note that the adiabatic cooling we study requires nonideality. The well-known cooling of an ideal gas undergoing adiabatic expansion depends on the presence of a wall on which the gas does work and therefore loses kinetic energy. Also, an ideal gas model of cooling in a supersonic jet expansion accounts only for a “geometric” cooling due to selection of one velocity direction. See, for example, R. Kubo, Statistical Mechanics (North–Holland, Amsterdam, 1965), p. 66.
10 Recall the Mayer cluster expansion method for determining the properties of a nonideal gas by treating it as a collection of clusters. Whereas monomers generally predominate, clusters of arbitrary size make some contribution to overall gas properties.
15 D. W. Heermann, Computer Simulation Methods (Springer, Berlin, 1986), Sec. 4.3.3 presents the $T\rho$ ensemble Metropolis algorithm in the case of a rectangular cavity.
16 Although it is well known that the Lennard-Jones potential does not accurately describe the two body argon interaction, it has served well in describing argon cluster dynamics. See, for example, T. L. Beck, J. Jellinek, and R. S. Berry, J. Chem. Phys. 87, 545 (1987). Also note that these authors claim that a Verlet (essentially time symmetric second order numerical integration) algorithm with step size of 0.01 ps produces back integrable trajectories on the longest relaxation time scale relevant to the dynamical variables of interest in their study.
17 We use thermal atomic units wherein the Boltzmann constant is unity and energy has units of Kelvin.
19 The evaporation transition state defined by the choice of $r_{\text{field}}=25$ bohr is loose (see Ref. 11). Such a choice is important to this study since our interpretation of the data depend on the neglect of transition state recrossing which is rare in the case of a loose transition state.
21 Application of the ergodic theorem to relate time average between evaporation events to $E\mu$ ensemble average is based on assumed ergodicity of the argon cluster dynamics (see Ref. 18) and a separation of intracluster relaxation and evaporation time scales (see Sec. IV and Ref. 11).
22 Equation (2) is a variant of the equation of state found on p. 182, in C. E. Hecht, Statistical Thermodynamics and Kinetic Theory (Freeman, New York, 1990).
24 Clusters with sufficiently large initial pressure will actually explode due to their large repulsive potential energy. This effect requires pressure well in excess of $10^5$ atm however.
25 See, for example, S. Sugano, Microcluster Physics (Springer, Berlin, 1991), Chap. 6, and references therein.
26 Just as rate of diffusion scales with concentration gradient, heat conduction is proportional to temperature gradient. See, L. E. Reichl, A Modern Course in Statistical Physics (University of Texas, Austin, 1980), Chap. 13.
29 States in the coexistence region correspond to a mixture of two phases. Since first order phase transitions are associated with discontinuous thermodynamic state functions, the breadth of a coexistence ensemble state function distribution must span a discontinuity and is correspondingly typically large.
30 See, for example, F. M. Beniere, A. Boutin, and J.-M. Simon, J. Phys. Chem. 97, 10 472 (1993).