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Fragmentation of Suddenly Heated Liquids

James Allen Blink

(Doctor of Philosophy)

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FRAGMENTATION OF SUDDENLY HEATED LIQUIDS

By

JAMES ALLEN BLINK
M.S. (Georgia Institute of Technology) 1971

DISSERTATION

Submitted in partial satisfaction of the requirements for the degree of

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Abstract

Fragmentation of free liquids in Inertial Confinement Fusion reactors could determine the upper bound on reactor pulse rate. The x-ray ablated materials must cool and recondense to allow driver beam propagation. The increased surface area caused by fragmentation will enhance the cooling and condensation rates.

Relaxation from the suddenly heated state will move a liquid into the negative pressure region under the liquid-vapor P-V dome. The lithium equation of state was used to demonstrate that neutron-induced vaporization uses only a minor fraction of the added heat, much less than would be required to drive the expansion. A 77% expansion of the lithium is required before the rapid vaporization process of spinodal decomposition could begin, and nucleation and growth are too slow to contribute to the expansion.

An energy minimization procedure determined the fragment size that produces the least amount of non-fragment-center-of-mass energy, i.e., the sum of the surface and dilational kinetic energies. Considerable fragmentation is predicted in the high energy density HYLIFE reactor, with minimum fragmentation in the low energy density Pulse*Star, EAGLE, and HIBALL reactors.

A two-dimensional molecular dynamics (MD) code was developed to test the model at a microscopic scale for the Lennard-Jones (LJ) fluid. The two LJ constants, σ and ϵ , were chosen to represent lithium. The LJ properties were generated from equation of state data

and MD calculations. A 2-D calculation most closely models a jet, permits easy graphical inspection of the results, and allows consideration of larger radius systems. (Surface tension is a strong function of the system radius at this scale.) MD calculations were run using five levels of heating and four system sizes. The numerical experiments were consistent with the model: fragment size (in atoms) $\sim (\text{system size})^{2/3}$ and $(\text{initial pressure})^{-20/3}$. The larger fragment sizes were within an order of magnitude of the predictions. Additional analysis of two Italian three dimensional MD experiments also agreed with the model.

Dedication

To my wife, Freida Del Papa Blink, without whose love and encouragement this dissertation would not have been completed.

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Fragmentation of Suddenly Heated Liquids

by James A. Blink

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Chapter 1: Introduction

In several inertial confinement fusion (ICF) reactor concepts, the fusion neutrons are suddenly deposited into liquid metals having free surfaces within the vacuum chamber. The neutron energy deposition is so fast that the liquid has little opportunity to expand during the deposition time: hence, the deposition is effectively at constant volume, or isochoric. In this study, energy deposition is considered "isochoric" if the deposition time is less than the sound wave transit time of the liquid region. The suddenly increased temperature and energy content of the liquid produces a sudden increase in pressure. Since the free surfaces are exposed to effectively zero pressure, tensile relief waves propagate inward from these free surfaces. Tension eventually causes liquids to cavitate, and this cavitation leads to fragmentation in liquids with available expansion volume. The fragments have velocities due to acceleration by the pressure difference across the tensile wave.

Fragmentation of liquid metals inside ICF reactor vessels has two impacts on reactor design. First, the fragments eventually collide with the structure, causing a pressure load which can be estimated from average fragment velocities predicted by continuum mechanics computer codes. (However, fragment velocity distributions could cause an additional erosion problem from the higher-than-average-velocity fragments). Second, the fragment size determines the liquid surface area available to interact thermally with superheated gas or plasma produced by the absorption of the short-ranged fusion x rays and debris. Since the cooling and condensation times depend on the

cooling surface area, it is possible that the maximum chamber pulse rate will be set by the degree of fragmentation.

The Electric Power Research Institute (EPRI) and the ICF reactor design community have identified fragmentation as the top priority ICF reactor design experiment.¹ Although an EPRI funded report² surveying potential experiments concluded that several energy addition techniques are feasible for isochoric heating experiments, the high experiment costs will cause delays. Further, each technique has flaws, including competing physical effects, difficult diagnostics, or insufficient energy for full-scale simulations. This study develops the models needed for experiment design and validates them at the microscopic level using molecular dynamics computer simulations. The results of this study should increase the credibility of ICF reactor designs, prepare the way for laboratory (macroscopic) simulations of liquid fragmentation, and aid in the design of an ICF Engineering Test Reactor in which full scale testing of the models will occur.

Liquid fragmentation was approached from two viewpoints before this study began. In the first, the expansion of the fluid into the non-equilibrium region under the liquid-vapor two-phase dome was considered to be resolved by rapid phase separation back to the saturation lines. Further, the phase change was considered the source of the energy driving the expansion and consequent vaporization. The second viewpoint was purely hydrodynamic. Although the expansion was also assumed to proceed into the tensile region (negative pressure) under the liquid-vapor two-phase dome, no immediate phase separation was considered. Instead, the liquid was expected to fracture, with vapor later filling the new voids. This is analogous to fracture of a

solid. The purpose of this thesis is to expand these two viewpoints, to use numerical experiments to justify a choice between approaches, and to recommend a method of calculating liquid fragmentation in ICF reactors.

In Chapter Two, several ICF reactor designs are described, and the degree of isochoric heating is estimated for each design. In Chapter Three, the literature on liquid fragmentation in atomizer nozzles is reviewed and found to be unsuitable for prediction of response to isochoric heating. In Chapter Four, rapid vaporization is considered as a driving mechanism for fragmentation. The phase diagram for lithium is presented, and thermodynamic paths followed during and after the sudden heating are estimated. Then, the alternative phase separation mechanisms of spinodal decomposition and of nucleation and growth are considered. Because the hydrodynamic expansion of the liquid is faster than the vapor bubble growth time, nucleation and growth can not drive the fragmentation. For lithium, the isentropic spinodal line can not be reached until the fluid expands by about 77%, and by that time, the (hydrodynamic) fragmentation process should be well advanced. Also, the energy used in phase change (assuming the vapor is in thermal equilibrium with the heated liquid) is much less than the expansion energy, and thus cannot be expected to be the driving mechanism for the expansion.

In Chapter Five, force balance and energy minimization models (hydrodynamic models) of liquid fragmentation are developed and applied to the various ICF reactor designs. Because these models do not consider the dynamic process of fragmentation, numerical experiments were undertaken to study the fragmentation dynamics and to

test the predictions of the energy minimization model. These experiments used the technique of molecular dynamics to follow the evolution of up to several thousand liquid atoms following sudden heating. For simplicity, and to better model the quasi-two-dimensional expansion of an ICF reactor jet column, the numerical experiments were performed in two dimensions using the Lennard-Jones (LJ) 6-12 interatomic potential. The phase diagram for this potential is shown in Chapter Four; the two LJ constants are set to match lithium properties in the same section. The energy minimization model is applied to the LJ fluid in Chapter Five. The numerical experiment techniques are developed in Chapter Six and applied in Chapter Seven. Chapter Seven also includes the significant result of this thesis: a comparison between the energy minimization model predictions and the molecular dynamics experiments, with comments on the scalability of the model to reactor situations.

In Chapter Eight, the thesis is briefly summarized and further numerical simulations and laboratory experiments are recommended. Finally, Appendix A is a draft journal article reporting on the results of the thesis. As such, it serves as an executive summary, and it should probably be read before proceeding to the remainder of the thesis.

Chapter 2: Importance of Liquid Fragmentation to Inertial Fusion Reactor Design

All inertial confinement fusion (ICF) reactor designs are cyclic due to the pulsed nature of an inertial fusion energy source. Before a fusion pulse can be initiated by a laser or ion beam, the chamber pressure must be low enough to permit beam propagation: 10 Pa ($\sim 10^{-1}$ torr) for lasers and 10^{-2} Pa ($\sim 10^{-4}$ torr) for heavy ion beams. In this chapter, the cyclic sequence of events is illustrated for one example reactor, several other reactors are described, and the degree of isochoric heating is calculated for each design.

The minimum chamber pressure required for beam propagation is well above the vapor pressures of lithium and $\text{Li}_{17}\text{Pb}_{83}$ (a 17 atomic percent lithium, 83 atomic percent lead eutectic alloy), the two lithium bearing liquids that can breed enough tritium to replace the tritium burned in the plasma.* At a working temperature of 500°C,

* Tritium is burned in the plasma by the D-T reaction,

Tritium is bred in the reactor lithium by two reactions,

The ^6Li reaction is most probable for thermalized neutrons, and ^6Li is 7.4% of natural lithium. The ^7Li reaction requires fast neutrons (E 2.4 MeV), and ^7Li is 92.6% of natural lithium.

lithium and $\text{Li}_{17}\text{Pb}_{83}$ have vapor pressures of 0.4 Pa (3×10^{-3} torr) and 2×10^{-3} Pa (1.5×10^{-5} torr), respectively. It is highly advantageous to utilize one of these liquids between the pulsed fusion plasma and the reactor structure since $\sim 1/3$ of the fusion energy pulse is in the form of ions and x-rays which are absorbed in a very thin layer. Absorption of these energy pulses directly in the structure produces ablation and unacceptable fatigue loads unless the structure is very large (10 m radius). Conversely, absorption of the short-range fusion energy pulses in liquid protects the structure. Furthermore, if the liquid layer thickness is 0.5 m, sufficient neutron shielding is provided to allow a 5 m radius structure to survive for the 30 year plant life, a distinct advantage over other fusion reactor designs which require replacement of reactor structures every several years using remote maintenance equipment. Absorption of the ions and x-rays in liquid vaporizes and ionizes the thin absorbing layer which then causes vaporization of still more liquid by rapid thermal radiation heat transfer. The resulting gas density is much higher than the beam propagation limit, and it must be reduced by vacuum pumping or cooling and recondensation before the next driver pulse. If the bulk liquid fragments, the increased surface area reduces the cooling and condensation times.

The HYLIFE concept³ (High Yield Lithium cooled Inertial Fusion Energy converter) is used as an example throughout this report. HYLIFE was chosen because of its extremely high deposited neutron energy density; if the HYLIFE liquid doesn't fragment adequately, most ICF reactor liquids also would not. The HYLIFE geometry is shown in Fig. 2.1. A 50% packing fraction array of 175 lithium jets falls

freely through the 5 m radius chamber at radii between 0.5 and 2.0 m. The fusion yield of 1800 MJ is pulsed at 1.5 Hz. The sequence of events in one pulse cycle of HYLIFE is shown in Fig. 2.2.

The high yield in HYLIFE coupled with the small liquid metal radius leads to extremely high energy density. The requirement to inject completely new jets every 2/3 seconds implies a very high flow rate, $\sim 72 \text{ m}^3/\text{s}$ ($1.1 \times 10^6 \text{ gpm}$). To reduce the flow rate, the University of Wisconsin proposed in their HIBALL design⁹ (Fig 2.3) that the liquid jets be loosely confined in woven SiC socks such that the liquid transit time through the chamber is increased to the optimum determined by the thermal cycle ($\sim 10 \text{ s}$). Since the socks must contain the isochoric heating, the pulsed energy density in the liquid was reduced by increasing the liquid radius to between 5 and 7 m and by decreasing the yield to 400 MJ. The reactor power was maintained by correspondingly increasing the pulse rate to 5 Hz. (Subsequent Wisconsin calculations have limited the pulse rate to 3.3 Hz due to the cooling and condensation times¹⁰.) The eutectic $\text{Li}_{17}\text{Pb}_{83}$ liquid was used to reduce liquid metal fire hazards, but the increased fluid density (from 485 to 9320 kg/m^3) increased the pumping power and made satisfaction of seismic safety criteria for piping very difficult.

The Los Alamos National Laboratory has proposed a Modified Wetted Wall design (MWW)¹¹ (Fig. 2.4) in which a 1 to 8-cm-thick lithium film flows on a 2 m radius wall. The reactor has 150 MJ fusion pulses at 10 Hz. The Bechtel Group has proposed the EAGLE reactor concept¹² (Fig. 2.5) in which light ion beams propagate to the injected fusion fuel pellet through a high-Z gas. The short-ranged ions and x-rays are absorbed in the gas which is in turn cooled by a spray of

Fig. 2.2. Times of interest for the 1.5 Hz HYLIFE reactor. The gas motion, liquid motion, and cooling times were estimated from calculations in References 4 through 8.

- 15 ms Deuterium-tritium fuel pellet enters the reaction chamber
- 30 ns Pellet is 5 μm from the chamber center and the laser beams enter the chamber
- 15 ns Laser beam contacts the fuel pellet
- 0 Implosion complete, fusion begins
- 10 ps Fusion burn complete
- 2 ns X-rays begin to ablate lithium
- 1 μs Neutron absorption complete
- 20 μs X-ray and thermally ablated lithium reaches maximum compression
- 40 μs Jet fragmentation due to neutron absorption begins
- 60 μs Re-expanding lithium gas reaches the fragmenting jets
- 300 μs Expanding lithium gas clears the fragmenting jets
- 400 μs Lithium gas impacts wall
- 35 ms Lithium liquid impacts wall
- 250 ms Chamber pressure reduced to 10 Pa (10^{-1} torr)
- 630 ms New lithium jets established
- 652 ms Next fusion fuel pellet enters the chamber
- 666+ ms Next laser beam enters the chamber
- 666+ ms Next fusion begins

Fig. 2.3. The Wisconsin HIBALL reactor concept. The woven SiC tubes contain $\text{Li}_{17}\text{Pb}_{83}$ that absorbs the fusion energy, breeds the tritium, and shields the reactor structure. The SiC reduces the liquid flow rate to the value required by the thermal cycle.

Fig. 2.4. The LANL Modified Wetted Wall reactor concept. The liquid lithium film absorbs the short-ranged ions and x-rays, but it does not protect the inner structural wall from neutron damage. The majority of the neutron energy is absorbed behind the wall in the lithium blanket.

Fig. 2.5. The Bechtel EAGLE reactor concept. The chamber gas absorbs the short-ranged ions and x-rays, and the lithium spray cools the gas. The majority of the neutron energy is absorbed behind the wall in the blanket modules.

0.5-mm-diameter lithium droplets at radii of 3 m to the 4-m-radius wall. The fusion yield of 300 MJ is pulsed at 3 Hz. LLNL has proposed the Pulse*Star¹³ reactor concept (Fig. 2.6) in which a spray of $^{11}_{17}\text{Pb}_{83}$ absorbs the fusion neutrons. The spray is confined between a 4 m radius screen and a 5.5 m radius belljar. The wetted screen absorbs the ions and x-rays and the spray absorbs the neutrons. The belljar separates the spray-vacuum region from the outer $^{11}_{17}\text{Pb}_{83}$ pool. Use of a pool eliminates seismic design difficulty associated with high density liquid pipe loops. The fusion yield is 600 MJ at 5 Hz.

In some of these reactor concepts, the liquid metal residence time is less than the interpulse time; in others, it is many times longer. The liquid metal geometries include free spheres, free cylindrical jets, cylindrical jets confined by porous tubes (with some liquid film on the exterior surface), and liquid film on the inside surface of a sphere. Two different liquid metals have been suggested, and the fusion yields vary greatly. Thus, any analytic or empirical theory of isochoric heating-induced fragmentation must span a large parameter space.

Neutron transport computer codes have been used to calculate the time and space dependent neutron energy deposition levels in several of these reactors. Figure 2.7 shows the temporal neutron energy deposition profile for the HYLIFE reactor. The deposition time in any particular region is ~0.1 to 1 μs since the profile was spatially integrated over the entire blanket. Similar results are expected for the other reactor geometries. The time for relief of the induced pressure is the liquid thickness (or diameter) divided by the sound

Fig. 2.6. The LLNL Pulse*Star reactor concept. The wetted screen absorbs the x-rays and ions. The spray absorbs the neutrons from ~ 50 pulses during its transit through the reactor.

Fig. 2.7. Combined neutron and gamma energy deposition in the HYLIFE lithium jet array as a function of time.

Fig. 2.8. Neutron and gamma energy deposition profile in the HYLIFE lithium jet array.

speed. As shown in Table 2.1, the sound speeds, c , of lithium and $\text{Li}_{17}\text{Pb}_{83}$ are 4.5 and 1.8 km/s, respectively. The heating is "isochoric" if

$$\frac{2R}{c} = 2\tau > \tau_{\text{dep}} = 0.1 \text{ } \mu\text{sec} . \quad (2.1)$$

That is, for isochoric heating, the minimum radius of the liquid is

$$R_{\text{min}} = \begin{cases} 0.25 \text{ mm for Li} \\ 0.1 \text{ mm for Li}_{17}\text{Pb}_{83} \end{cases} . \quad (2.2)$$

Table 2.1. Fluid properties at 500°C.

Property	Symbol	Units	Fluid	
			Li	$\text{Li}_{17}\text{Pb}_{83}$
Sound speed	c	m/s	4500	1800
Mass density	ρ_m	kg/m^3	485	9320
Grüneisen parameter	Γ	-	1.0	2.0
Surface tension	γ	J/m^2	0.35	0.435
Vapor pressure	P_g	Pa	0.4	0.002

Figure 2.8 shows the spatial neutron energy deposition profile in the HYLIFE reactor. The neutron energy deposition drops to 35% of the peak value across the inner 20-cm-diameter jets, and is a factor of ~ 15 lower in the outer jets. The leading edge value of ~ 800 kJ/kg can be used to calculate the pressure rise from the Grüneisen equation of state,

$$\Delta P = \rho_m \Gamma e , \quad (2.3)$$

where ρ_m is the mass density (485 and 9320 kg/m³ for lithium and Li₁₇Pb₈₃), Γ is the Grüneisen parameter (1.0 and 2.0 for lithium and Li₁₇Pb₈₃), and e is the specific energy deposited in J/kg. For HYLIFE, the peak neutron induced pressure is then ~ 400 MPa or 4 kbar. The neutron energy deposition per unit volume scales roughly with $(\phi_V Y/R_b^2)$ where Y is fusion yield, R_b is the blanket radius, and ϕ_V is the volume fraction of absorbing material. To scale from lithium to Li₁₇Pb₈₃, the volumetric deposition is increased by another factor of ~ 6. This scaling and the published neutron transport results for the other reactor geometries were used to calculate the induced pressures and relief times for each geometry (Table 2.2). The jump-off velocity, v , of the expanding liquid can be calculated by considering the pressure drop across a moving rarefaction wave. Ahead of the wave, the fluid is at rest. In the frame of reference of the wave, it has a velocity of $(-c)$. Behind the wave, the fluid has a velocity of $(v-c)$ in this frame. The momentum conservation equation is

$$\begin{aligned} \Delta P + (-\rho_m c)(v-c) &= 0 + (-\rho_m c)(-c) \\ \Delta P &= \rho_m c v \end{aligned} \quad (2.4)$$

since the mass flux is $(-\rho_m c)$. For HYLIFE, the 400 MPa pressure results in a 180 m/s jump-off velocity. Table 2.2 also shows the jump-off velocities for the other reactor concepts.

Table 2.2. Isochoric heating in several ICF reactors.

	HYLIFE Inner Jet	Outer Jet	HIBALL Inner Jet†	Modified Wetted Wall	EAGLE	Pulse*Star
Yield (MJ)	1800	1800	400	150	300	600
Pulse Rate (Hz)	1.5	1.5	5	10	3	5
Fluid	Li	Li	Li ₁₇ Pb ₈₃	Li	Li	Li ₁₇ Pb ₈₃
Thickness (cm)	20	20	3	1-8	0.05	1
Relief Time (μs)	44	44	17	2-18	0.1	6
Specific Energy (J/g)	800	50	0.5	3.5	5.7	1
Pressure (MPa)	400	25	9	1.8	1.9	19
Jump-off Velocity (m/s)	180	11	0.5	0.8	0.9	1.1

† ignoring SiC sock

Chapter 3: Liquid Fragmentation in Atomizer Nozzles

At the beginning of this study, some effort was invested to determine if violent fragmentation of liquids has been studied in other applications. One significant body of literature studies the breakup of liquid jets into fine droplets as in diesel engine fuel injectors. In this chapter, the literature is briefly summarized and evaluated to determine its applicability to breakup of liquids in inertial confinement fusion reactors.

In diesel engine fuel injectors, breakup of the fuel jet into small fragments is desirable to promote ignition and uniform combustion. There is extensive literature on this subject; for example, references 14 through 16 and the references cited therein. Typical jets are injected with a driving pressure of ~ 20 MPa into a chamber pressure of ~ 3 MPa. As the jet velocity is increased, four distinct breakup modes are observed¹⁵. At low velocity, surface tension breaks the jet into a series of spheres with diameters somewhat larger than the jet diameter (the Rayleigh breakup regime). At higher velocity, the inertial effect of the surrounding gas accelerates this breakup into drops, still with diameters of the same order as the jet diameter (first wind-induced breakup regime). At still higher velocities, the surrounding gas creates short-wavelength three-dimensional waves on the jet surface which causes breakup downstream of the nozzle into a spray of fine droplets (second wind-induced breakup regime.) Finally, at very high velocities, the jet breaks up at the nozzle exit into a diverging spray of very small droplets (the atomization regime). Typical atomization droplet sizes

from mm size nozzles are tens of microns¹⁴.

The various theories of atomization¹⁶ invoke several possible mechanisms including aerodynamic interactions, liquid turbulence, velocity profile rearrangement, supply pressure oscillations and cavitation. Experiments^{15,16} have shown that only cavitation within the nozzle is capable of producing atomization in the absence of the other phenomena. However, the possibility that a combination of two or more of the other mechanisms could cause atomization was not eliminated by the experiments.

It does not appear that the atomization literature can be used to predict isochoric heating-induced breakup. The theory is uncertain, and the literature is largely empirical. In addition, the boundary conditions are different, and the correspondence of inlet nozzle conditions to isochoric heating conditions is not easily determined.

Chapter 4: Rapid Vaporization as a Fragmentation Mechanism

At the beginning of this study, two potential causes of liquid fragmentation in inertial fusion reactors were proposed. One, initially proposed by Lewis Glenn of LLNL, suggested that the isochorically heated liquid would expand homogeneously due to the tensile relief wave propagating inward from the free surface. The tension would fracture the liquid into fragments and void. The voids would gradually fill with vapor, either from the vapor originally surrounding the liquid in the reactor or from the free surfaces of the newly created fragments.

The second mechanism, initially proposed by Vijay Kulkarny of TRW, suggested that the homogeneously expanding liquid would quickly reach a state under the liquid-vapor two phase dome where rapid phase change could occur, probably by the process of spinodal decomposition. Then, the growing vapor regions would accelerate the remaining liquid which would be in the fragments.

This chapter explores the latter (rapid phase change) mechanism. Lithium in the HY LIFE reactor is used as an example. The known lithium equation of state is used to construct a phase diagram. The thermodynamic paths followed during isochoric heating and subsequent homogeneous expansion into the metastable region under the two phase liquid-vapor dome are determined. The two possible phase change mechanisms to restore equilibrium, spinodal decomposition and nucleation and growth, are reviewed. Finally, rapid phase change is evaluated as a cause of fragmentation. The conclusion is that both phase change mechanisms will be too slow to cause the fragmentation.

In view of this conclusion, hydrodynamic modeling and molecular dynamics simulations were initiated; these are described in Chapters Five, Six, and Seven. The simulations used a simplified fluid (6-12 Lennard-Jonesium) in two dimensions. The known phase diagram for this fluid is also summarized in this chapter, and analytic equations are fit to the Lennard Jones equation of state data.

4.1. Lithium Phase Diagram

In 1977, Young reported an equation-of-state for lithium.¹⁷ The equation of state was used in Glenn's AFTON code¹⁸ calculations⁴⁻⁸ of the HY LIFE inertial fusion reactor hydrodynamics. This section summarizes Young's development of the equation of state. The soft sphere model of Hoover, et. al.¹⁹ is used. This model is based on Monte Carlo calculations for particles interacting with repulsive pair potentials of the form

$$\phi(r) = \psi (\lambda_T/r)^{\xi}, \quad 4 \leq \xi \leq 12 \quad (4.1)$$

where λ_T is the interatomic spacing at which the potential is ψ .

The Helmholtz free energy for Young's equation of state is

$$A = N_m kT \left[-\ln \left(\frac{V e^{\psi}}{N \lambda_d^3} \right) + C_n \rho_y^{\xi/3} \left(\frac{\psi}{kT} \right) + \frac{(\xi+4)}{2} Q_e \rho_y^{\xi/9} \left(\frac{\psi}{kT} \right)^{1/3} - \rho_y^{\eta} \left(\frac{\psi}{kT} \right) \right] + E_{coh} \quad (4.2)$$

In the brackets, the first term represents the ideal gas free energy, the second term is the static lattice potential energy, the third term is the thermal lattice potential energy correction, and the fourth term is the attractive potential energy. In the first term, λ_d is the de Broglie wavelength, $h/(2\pi m kT)^{1/2}$. In the second term, C_n is the face centered cubic "Madelung constant", and ρ_y is the normalized density, $(N_m/V)(\lambda_T^3/\sqrt{2})$. In the third term, Q_e is a multiplier to account for electronic effects on the heat capacity. Since the form of the attractive part of the effective potential in metals is complex and poorly known, a mean-field term is used as an approximation in the fourth term. The final term outside the

brackets, E_{coh} , is the cohesive energy, i.e., the energy required to convert zero Kelvin lithium to completely separated atoms.

The pressure, energy, and entropy may be found from

$$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} \quad (4.3)$$

$$E = A - T\left(\frac{\partial A}{\partial T}\right)_{N,T} \quad (4.4)$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,T} \quad (4.5)$$

The results of the differentiations are

$$P = \frac{N_m kT}{V} \left[1 + \frac{1}{3} \xi C_n \rho_y^{\xi/3} \left(\frac{\psi}{kT}\right) + \frac{\xi(\xi+4)}{18} Q_e \rho_y^{\xi/9} \left(\frac{\psi}{kT}\right)^{1/3} - \eta \rho_y^{\eta} \left(\frac{\psi}{kT}\right) \right] \quad (4.6)$$

$$E = N_m kT \left[\frac{3}{2} + C_n \rho_y^{\xi/3} \left(\frac{\psi}{kT}\right) + \frac{(\xi+4)}{6} Q_e \rho_y^{\xi/9} \left(\frac{\psi}{kT}\right)^{1/3} - \rho_y^{\eta} \left(\frac{\psi}{kT}\right) \right] + E_{\text{coh}} \quad (4.7)$$

$$S = (E-A)/T \quad (4.8)$$

Eqs. 4.6 and 4.7 are equivalent to Young's Eqs. 4 and 5.

The parameters ψ , λ_r , ξ , η , and Q_e are adjustable and are chosen by fitting available enthalpy, volume, and sound speed isobars. Also, ξ is chosen such that $(\xi+2)/6 \approx \Gamma_0$, the Grüneisen parameter at normal solid volume, as predicted by quasi-harmonic lattice theory. Similarly, η should be ~ 1.0 to agree with van der Waals equation of state and its good fits to molecular fluid data. Finally, $Q_e \sim 1$ except where electronic corrections are clearly warranted.

Young's best fit values for Li are

$$\xi = 4, \quad \eta = 0.7, \quad Q_e = 1.30,$$

$$\psi = 1.99436 \times 10^{-17} \frac{\text{J}}{\text{atom}} \text{ and}$$

$$\lambda_T^3 / \sqrt{2} = 1.29408 \times 10^{-31} \text{ m}^3/\text{atom}.$$

Comparisons of the equation of state and experimental data are shown in Fig. 4.1 for enthalpy, thermal expansion, and sound speed; the agreement is reasonable. The equation of state also produces critical point values of $T_c = 3741 \text{ K}$, $P_c = 114 \text{ MPa}$, $V_c = 5.86 V_0$, and $Z_c = P_c V_c / N_m k T_c = 0.28$. The predicted Grüneisen constant at V_0 is 1.0 (comparable to a measurement of 0.9).

The independent variables are $V(\text{m}^3/\text{kg})$ and $T(\text{K})$. Useful Li data are summarized in Table 4.1. After inserting the constants, Eqs. 4.2, 4.3, and 4.4 become

$$A\left(\frac{\text{J}}{\text{kg}}\right) = 1198.16 T [\ln (107.573 VT^{3/2}) + 4.60365 V^{-4/3} T^{-1} + 3.71071 V^{-4/9} T^{-1/3} - 495.542 V^{0.7} T^{-1}] + 2.303 \times 10^7 \quad (4.9)$$

$$P(\text{Pa}) = 1198.16 TV^{-1} [1 + 6.13820 V^{-4/3} T^{-1} + 1.23690 V^{-4/9} T^{-1/3} - 346.8/9 V^{-0.7} T^{-1}] \quad (4.10)$$

$$E\left(\frac{\text{J}}{\text{kg}}\right) = 1198.16 T [1.5 + 4.60365 V^{-4/3} T^{-1} + 1.23690 V^{-4/9} T^{-1/3} - 495.542 V^{-0.7} T^{-1}] + 2.303 \times 10^7 \quad (4.11)$$

When Eq. 4.10 is plotted as a set of isotherms in the P-V plane, a graph similar to Fig. 4.2 results. In the two phase region, the isotherms form Van der Waals loops. These are considered to be analytic continuations of the isotherms into the two phase region; equilibrium isotherms are horizontal in the two phase region. For the critical isotherm, the loop vanishes at the point where both the first

Fig. 4.1. Soft-sphere fit (smooth curves) to experimental lithium thermodynamic data (points). (From Ref. 17.)

Table 4.1. Lithium data.

Li atomic weight = 0.006939 kg/mole

$$N_m = 6.0225 \times 10^{23} / 0.006939 = 8.679 \times 10^{25} \text{ atoms/kg}$$

$$k = \text{Boltzmann constant} = 1.38066 \times 10^{-23} \text{ J/atom K}$$

$$\lambda_d = \text{de Broglie wavelength}$$

$$= 6.62618 \times 10^{-23} (2\pi kT/N)^{-1/2} T^{-1/2} \text{ (meters)}$$

$$E_{coh} = \text{Cohesive energy} = 23.03 \times 10^6 \text{ J/kg}$$

$$C_n = \text{Face centered cubic Madelung constant} = 12.669$$

$$V_o = \text{Volume at room temperature} = 0.001876 \text{ m}^3/\text{kg}$$

$$T_m = \text{Melt temperature} = 453.7 \text{ K}$$

$$V_m = \text{Volume at melt} = 0.001931 \text{ m}^3/\text{kg}$$

$$H_m = \text{Enthalpy at melt} = 1.034 \times 10^6 \text{ J/kg (H = 0 at room temperature)}$$

$$\xi = \text{Repulsive potential exponent} = 4$$

$$\eta = \text{Attractive free energy term exponent} = 0.7$$

$$Q_c = \text{Electronic correction multiplier} = 1.30$$

$$\psi = \text{Repulsive potential at } (r=\lambda) = 1.99436 \times 10^{-17} \text{ J/atom}$$

$$\lambda_r^{3/\sqrt{2}} = \text{Density normalization multiplier}$$

$$= 1.29408 \times 10^{-31} \text{ m}^3/\text{atom}$$

$$T_c = \text{Critical temperature} = 3471 \text{ K}$$

$$P_c = \text{Critical pressure} = 114 \text{ MPa}$$

$$V_c = \text{Critical volume} = 5.86 V_o$$

$$Z_c = P_c V_c / N_m k T_c = 0.28$$

$$\Gamma_o = \text{Grüneisen constant at } V_o = 1.0$$

Fig. 4.2. Equilibrium and nonequilibrium isotherms on a schematic P-V diagram. Shaded regions approach equilibrium by nucleation and growth. The central unshaded region separates to the isothermal spinodal points by spinodal decomposition. The specific volume scale is highly nonlinear; see Fig. 4.4 for a portion of the lithium P-V diagram with a linear abscissa.

Shaded regions approach equilibrium by nucleation and growth.

Central unshaded region separates to the spinodal points by spinodal decomposition

and second derivatives, $(\partial P/\partial V)_T$ and $(\partial^2 P/\partial V^2)_T$, are zero.

Isotherms above the critical temperature have $(\partial P/\partial V)_T = 0$ everywhere. If a liquid is converted to a gas along a path lying above the critical point, no phase separation is observable; instead, the fluid changes gradually from a liquid to a gas without evolution of bubbles. On each isotherm below the critical temperature, there are two specific volumes at which $(\partial P/\partial V)_T$ vanishes; these points are known as the isothermal spinodes. There are analogous isentropic spinodes where $(\partial P/\partial V)_S$ vanishes. The locus of all the spinodes defines the spinodal lines. For states between the two spinodal lines, a homogeneous fluid would be mechanically unstable, with $(\partial P/\partial V)_T = 0$. Hence, if a material is suddenly transformed to a state between the spinodal lines, it is unstable, and it will decompose in a very short period (probably subnanosecond) to a mixture of the two adjacent spinodes. (See Section 4.4 for a more detailed discussion of spinodal decomposition.) Phase separation would then continue by the slower process of growth until the two coexisting equilibrium states of liquid and vapor are reached. Similarly, if a material is suddenly transformed to a metastable state between one spinodal line and its associated coexistence curve, phase separation would eventually occur by the sequential processes of nucleation and growth (see Section 4.5).

The saturated liquid and vapor lines (also known as the coexistence curve or the liquid-vapor two-phase-dome) are constructed by computing the two phase area under each isotherm for a range of pressures. For each computation, the pressure axis is renormalized such that the

Fig. 4.3. Illustration of Maxwell's equal area rule for determining the coexistence curve. For each temperature, the positive and negative areas are equal for only one pressure, the equilibrium pressure.

selected pressure is labeled as zero. For each isotherm, there is only one pressure where the positive and negative contributions to the area total to zero; this is the equilibrium pressure (Fig. 4.3). The two intersections of the isotherm and this equilibrium pressure lie on the saturated liquid and vapor lines. This property of the coexistence curve is known as Maxwell's equal area rule. For the two phases to be in thermal and mechanical equilibrium, they must be at the same temperature and pressure (to prevent energy and momentum exchange, respectively). They must also be in chemical equilibrium to prevent mass exchange.

$$\int dG = 0 = \int V dp - \int S dT + \int \mu_i dn_i \quad (4.12)$$

For phase equilibrium, each n_i is constant, and the last term is zero. Constant temperature is implied by the lack of energy flow. Thus,

$$\int dG = 0 = \int V dp \quad (4.13)$$

If the area is computed relative to the specific volume at which the equilibrium pressure crosses the isotherm, Eq. 4.4 holds for the shaded areas in Fig. 4.3.

Figure 4.4 shows a portion of the lithium P-V plane. The isotherms are from 2750°C to 3500°C in 50°C increments. The open square is the critical point. The dashed lines are the spinodal lines and the open circles lie on the coexistence curve. The coexistence curve peaks at the critical point.

A MATHSY²⁰ macro was written to plot the equations for pressure, internal energy, and entropy. A copy of the macro is available²¹.

Fig. 4.4. P-V diagram for lithium. The isotherms are at 50°C intervals. The dashed lines are the isothermal spinodals. The left isentropic spinodal passes through (0.012, -100), (0.02, -50), and (0.03, -20) and probably does not reach the positive pressure region. Response to isochoric heating will probably be more isentropic than isothermal since there is insufficient time for heat transfer.

4.2. Two-Dimensional Lennard-Jonesium Phase Diagram

Two-dimensional molecular dynamics simulations will be used in Chapter Seven to test the (hydrodynamic) particle size models. Two-dimensional simulations are used because they best simulate the quasi-two-dimensional expansion of a cylindrical jet, because they are easily diagnosed graphically, and because they allow consideration of larger radius systems with limited computer resources. The properties of two dimensional Lennard Jones (LJ) material are well known, as is discussed in this section. This section also includes a comparison of the LJ equation of state data from several authors, construction of analytic fits to the data, and determination of the two "free" LJ constants for lithium.

A general equation for the LJ potential between two particles with interparticle separation variable, r , is

$$\phi(r) = \left(\frac{\epsilon}{r-\sigma}\right) - \left(\frac{\epsilon}{\sigma}\right)^{6/(\xi-6)} \left[\left(\frac{\sigma}{r}\right)^{\xi} - \left(\frac{\sigma}{r}\right)^6\right] \quad (4.14)$$

Most studies use ξ in the 9 to 15 range; $\xi = 12$ is used here.

Then,

$$\frac{\phi(r)}{\epsilon} = 4 \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] \quad (4.15)$$

Since force is $(-\partial\phi/\partial r)$,

$$|F(r)| / \left(\frac{\epsilon}{\sigma}\right) = 24\left(\frac{\sigma}{r}\right)^7 [2\left(\frac{\sigma}{r}\right)^6 - 1] \quad (4.16)$$

These functions are shown in Fig. 4.5. The potential is zero at $r = \sigma$ and $(-\infty)$ at the bond rest length.

Barker²² has established a phase diagram for two-dimensional

Fig. 4.5. The Lennard-Jones 6-12 interatomic potential and associated force function truncated at $r = 2.5\sigma$.

Lennard-Jonesium by using perturbation theory for the fluid phases and a self-consistent cell model for the solid phase. The phase boundaries are shown as solid lines in Figs. 4.6 and 4.7. Monte Carlo calculations by Abraham²³ have confirmed Barker's phase boundaries; Abraham's Monte Carlo results are shown as dashed lines in Fig 4.7. The dimensionless axes used in these figures ($\rho\sigma^2$, kT/ϵ , and $\rho\sigma^2/\epsilon$) allow use of the same phase diagram for any combination of σ and ϵ . These constants can be set to match macroscopic properties of the chosen material.

Barker used the two-dimensional Monte Carlo data to generate Padé-type approximants of the form,

$$\frac{P}{\rho kT} = [1 + \sum_1^5 f_1 \rho^1] / [1 + \sum_1^4 g_1 \rho^1] \quad (4.17)$$

As before, reduced variables are used, $P = P\sigma^2/\epsilon$, $\rho = \rho\sigma^2$, and $T = kT/\epsilon$, with Boltzmann's constant (k) set to 1.0. Barker calculated the values of the coefficients (f_1 through g_4) for temperatures of 0.45, 0.55, 0.70, and 1.0 (Table 4.2). The table also indicates the calculated pressures for a density of 0.6.

Barker's Monte Carlo pressure data²² are compared to the Monte Carlo data of Henderson²⁴, Phillips²⁵, and Tsien²⁶, and the molecular dynamics data of Fehder²⁷ and Toxvaerd²⁸ in Fig. 4.8. The data are plotted as compressibility factor ($P/\rho kT$) contours on a ρ - T diagram. Because Henderson's²⁴ data are the most extensive, they are used as the basis for the contours. Where the other references indicate a shift in a contour, it is shown by dotted lines. The contours allow comparison of the references and

Fig. 4.6. Phase diagram for two-dimensional Lennard-Jonesium (density-temperature plane).

Fig. 4.7. Phase diagram for two-dimensional Lennard-Jonesium (temperature-pressure plane). The solid lines are from perturbation theory²² and the dashed lines are from Monte-Carlo calculations²³.

Table 4.2. Coefficients in Barker's pressure equation and his resulting pressures at $\rho = 0.6$. The one Monte Carlo result at this density is also shown.

	<u>Temperature</u>			
	0.45	0.55	0.70	1.0
f_1	-10.5045	-3.5966	-2.7141	-3.2086
f_2	20.7126	13.6709	16.2753	11.7969
f_3	-13.0723	-9.7282	-37.2291	-18.4305
f_4	2.5803	0.5640	36.7272	17.0168
f_5	0.0	0.0	0.0	0.0
g_1	-2.8466	1.2134	0.0464	-2.1356
g_2	10.9930	15.8445	12.0780	7.0799
g_3	-11.1515	9.6091	-14.2334	-5.9005
g_4	0.0	-40.0	0.0	0.0
P(eq)	-0.108	0.132	0.356	0.936
P(MC)	-0.100			
P/ ρkT (eq)	-0.399	0.401	0.847	1.56
P/ ρkT (MC)	-0.370			

Fig. 4.8. Compressibility factor contours for 2-D Lennard-Jonesium. The solid lines are from Henderson's data. Dotted lines are alternative contours from the indicated references.

- Henderson
- Barker (B)
- Toxvaerd (V)
- △ Fehder (F)
- ▲ Phillips (P)
- ▼ Tsien

$$\rho_c \sigma^2 \sim 0.33$$

visualization of the data. However, analytic expressions for the pressure as a function of temperature and density were derived from the data, rather than the contours.

Points of overlap or inconsistency among the references are summarized in Table 4.3. At high temperatures, the data are very consistent. At low temperature (~ 0.45) and high density (~ 0.75), Barker's²² compressibility factor is lower than Henderson's²⁴. The situation is reversed at a higher temperature (0.55) and lower density (0.5). In general, Phillips' data²⁵ agree with Barker's rather than Henderson's when all three have common points. Phillips' compressibility factor is lower than Barker's at ($T = 0.45$; $\rho = 0.74$), lower than Henderson's at ($T = 0.8$; $\rho = 0.7$) and higher than Henderson's over a range of conditions ($T = 0.6$; $\rho = 0.7$ and 0.75), ($T = 0.7$; $\rho = 0.75$) and ($T = 0.8$; $\rho = 0.5$ and 0.6). Fehder's data²⁷ at ($\rho = 0.5$; $T = 0.84$ and 0.88) are higher than Henderson's comparable data. Some of Tsien's data²⁶ are higher than expected from the contours generated from the other data ($T = 0.55, 0.7$ and 0.95 ; $\rho = 0.74$), ($T = 0.7$; $\rho = 0.67$) and ($T = 0.95$; $\rho = 0.54$). However, other Tsien data ($T = 0.7$; $\rho = 0.54$) and ($T = 0.55$; $\rho = 0.67$) are lower than expected. At two points of overlap ($T = 0.65$; $\rho = 0.7$ and 0.75), Toxvaerd's data²⁸ are five to ten percent less than Phillips' values, but Phillips' data are five to ten percent higher than Henderson's in a nearby region. Toxvaerd's point at ($T = 0.655$; $\rho = 0.6$) is only $\sim 80\%$ of the value interpolated from Henderson's data.

Barker's Monte Carlo data differ significantly from his equation at low temperatures. Tsien's data point at ($T = 0.55$; $\rho = 0.67$) is

Table 4.3 Overlapping points and inconsistencies in the compressibility factor ($P/\rho kT$) data. Sources: H (Henderson²⁴), B (Barker²²), P (Phillips²⁵), V (Toxvaerd²⁸), F (Fehder²⁷), and T (Tsien²⁶).

T	ρ	H	B(MC)	Source B(eq)	P	V	F
0.45	0.6	----	-0.37	-0.40			
0.45	0.7	----	-0.14	-0.12			
0.444	0.7	-0.39					
0.45	0.738	----	----	----	0.03		
0.45	0.739	----	0.15	0.11			
0.45	0.75	----	0.19	0.22	0.18		
0.444	0.75	0.28					
0.5	0.5	0.14**					
0.5	0.7	0.24	----	----	0.13		
0.5	0.75	0.93	----	----	0.85		
0.525	0.4	0.18**					
0.525	0.5	0.19**					
0.55	0.5	0.106*	0.34	0.34			
0.55	0.67	----	----	----			0.23†
0.55	0.7	----	0.60	0.60	0.62		
0.6	0.7	0.07	----	----	0.97		
0.6	0.75	1.69	----	----	1.75		
0.625	0.5	0.39†					
0.625	0.6	0.71					
0.655	0.6	----	----	----		0.59	
0.7	0.6	0.76					
0.65	0.7	----	----	----	1.23		
0.654	0.7	----	----	----		1.16	
0.65	0.75	----	----	----	2.07		
0.651	0.75	----	----	----		1.91	
0.7	0.7	1.41	1.45	1.51	1.47		
0.7	0.75	2.18	2.29	2.21	2.32		
0.8	0.5	0.73	----	----	0.80		
0.838	0.4993	----	----	----			0.98
0.8	0.6	0.96	----	----	1.06		
0.8	0.7	1.97	----	----	1.84		
0.88	0.4993	----	----	----			1.08
0.9	0.5	1.00					
1.0	0.55	----	1.27	1.31			
1.0	0.7	2.31	2.39	2.42			
1.0	0.75	3.13	3.19	3.18			

* not between bracketing temperature or density values (0.206 was used in Fig. 4.8)

** negative value expected

† not between bracketing density values

not between the values at bracketing densities. Similarly, Henderson's data point at ($T = 0.55$; $\rho = 0.5$) does not lie between the values at bracketing temperatures. Finally, Henderson's compressibility factors at ($T = 0.5$; $\rho = 0.5$) and ($T = 0.525$; $\rho = 0.4$ and 0.5) are not negative even though they probably lie within the two phase liquid-vapor region.

The data points from the references are listed in Table 4.4 for the density range 0.45 - 0.76 and the temperature range 0.4 - 1.3. Because Henderson's data are the most extensive, they were used to construct analytic equations for the pressure in terms of the density and temperature for the T - ρ region investigated in the molecular dynamics experiments (described in Chapters Six and Seven). Pressure isotherms are shown in Fig. 4.9 and pressure isochores are shown in Fig. 4.10. These figures also show Barker's equation in the same region. The specific heat at constant volume, c_v , is shown in Fig. 4.11 for three densities. The equations for the specific heat and the pressure isotherms and isochores are shown in Table 4.5. As before, reduced units ($\rho\sigma^2$, kT/ϵ , $P\sigma^2/\epsilon$, $E/N\epsilon$) are used in Table 4.5. The equations for $(\partial P/\partial \rho)_T$ vs. T (isochores) from Henderson's data were generated by fitting a cubic equation in temperature to the $(\partial P/\partial \rho)_T$ data points individually evaluated from cubic fits of the pressure isotherms. This cumbersome procedure was used since data were needed at only a few densities but many temperatures.

The well depth, ϵ , can be estimated from the heat of vaporization. In three dimensions, about 12 bonds must be broken to free one atom, and each bond is shared by two atoms. Hence, the heat

Table 4.4. Compressibility factor data. Source codes are M (Parker's Monte Carlo), E (Barker's equation), H (Henderson), T (Tsien), P (Phillips), V (Toxvaerd), and F (Fehder).

ρ	<u>Temperature</u>							
	0.444	0.45	0.5	0.523	0.525	0.527	0.55	0.6
0.5	-----	-0.59E	0.14H	-----	0.19H	-----	0.34E 0.34M 0.11H	0.34H
0.538	-----	-0.52E	-----	-----	-----	-----	0.35E 0.08T	
0.6	-----	-0.40E -0.37M	-0.02H	-----	-0.02H	-----	0.40E 0.22H	0.39H
0.627	-----	-0.34E	-----	-----	-----	-----	0.43E 0.30T	
0.65	-----	-0.28E	-----	-----	0.12V	-----	0.47E	
0.67	-----	-0.23E	-----	-----	-----	-----	0.51E 0.23T	
0.675	-----	-0.21E	-----	-----	0.25V	-----	0.52E	
0.696	-----	-0.14E	0.07P	-----	-----	-----	0.58E	
0.7	-0.39H	-0.12E -0.14M	0.24H 0.13P	-----	-----	0.46V	0.60E 0.60M 0.62P	0.87H 0.97P
0.738	-----	0.10E 0.03P	-----	-----	-----	-----	0.81E	
0.739	-----	0.11E 0.15M	-----	-----	-----	-----	0.82E	
0.741	-----	0.12E	-----	-----	-----	-----	0.84E 1.28T	
0.75	0.28H	0.22E 0.19M 0.18P	0.93H 0.85P	1.22V	-----	-----	0.93E 1.26P	1.69H 1.75P

Table 4.4 (Continued). Compressibility factor z , a. Source codes are M (Barker's Monte Carlo), E (Barker's equation), H (Henderson), T (Tsien), P (Phillips), V (Toxvaerd), and F (Fehder).

ρ	<u>Temperature</u>							
	0.625	0.646	0.65	0.621	0.634	0.655	0.7	0.75
0.5	0.39H	-----	-----	-----	-----	-----	0.60E 0.60H	
0.538	0.42T	-----	-----	-----	-----	-----	0.66E 0.79T	
0.6	0.71H	-----	-----	-----	-----	0.59V	0.85E 0.76H	
0.65	-----	0.83V	-----	-----	-----	-----	1.10E	
0.67	-----	-----	-----	-----	-----	-----	1.24E 1.29T	
0.7	-----	-----	1.23P	-----	1.16V	-----	1.51E 1.45M 1.41H 1.47P	1.57P
0.725	-----	-----	-----	1.59V	-----	-----	1.81E	
0.741	-----	-----	-----	-----	-----	-----	2.05E 2.26T	
0.75	-----	-----	2.07P	1.91V	-----	-----	2.21E 2.29M 2.18H 2.32P	2.53P

Table 4.4 (Continued). Compressibility factor data. Source codes are M (Barker's Monte Carlo), E (Barker's equation), H (Henderson), T (Tsien), P (Phillips), V (Toxvaerd), and F (Fehder).

ρ	<u>Temperature</u>							
	0.792	0.8	0.838	0.845	0.88	0.896	0.9	0.927
0.45	-----	0.76P						
0.4993	-----	-----	0.98F	-----	1.08F			
0.5	-----	0.73H 0.80P	-----	-----	-----	-----	1.00H	
0.55	-----	0.91P						
0.5824	0.94F	-----	-----	1.21F				
0.6	-----	0.96H 1.06P	-----	-----	-----	-----	1.32H	
0.6319	-----	-----	-----	-----	-----	1.57F	-----	1.69F
0.65	-----	1.38P						
0.7	-----	1.97H 1.84P	-----	-----	-----	-----	2.30H	
0.75	-----	2.66H 2.72P	-----	-----	-----	-----	3.10H	

Table 4.4 (Continued). Compressibility factor data. Source codes are M (Barker's Monte Carlo), E (Barker's equation), H (Henderson), T (Tsien), P (Phillips), V (Toxvaerd), and F (Fehder).

ρ	<u>Temperature</u>						
	0.95	1.0	1.015	1.067	1.099	1.175	1.25
0.45	-----	1.03E 1.04M					
0.4993	-----	1.14E	-----	-----	1.38F		
0.5	-----	1.15E 1.11H	-----	-----	-----	-----	1.43H
0.538	1.35T	1.27E					
0.55	-----	1.31E 1.27M					
0.5824	-----	1.46E	1.56F	-----	-----	1.77F	
0.6	-----	1.56E 1.49H	-----	-----	-----	-----	1.84H
0.6319	-----	1.77E	-----	1.97F			
0.65	-----	1.91E 1.94M					
0.67	2.07T	2.09E					
0.7	-----	2.42E 2.39M 2.31H	-----	-----	-----	-----	2.76H
0.741	3.05T	3.02E					
0.75	-----	3.18E 3.19M 3.13H	-----	-----	-----	-----	3.59H

Fig. 4.9. Pressure isotherms from Barker's equation and Henderson's Monte Carlo data. Barker's equation is a Padé approximant (Eq. 4.17). Henderson's data were used to generate cubic isotherms. Higher order fits lead to excessive fluctuations in the derivative, $(\partial P/\partial \rho)_T$.

Fig. 4.10. Pressure isochores from Barker's equation and Henderson's Monte Carlo data. The single isochore from Barker was obtained by fitting a quadratic to the values of Barker's isothermal equations at $\rho = 0.6$. A cubic fit was unsuitable because it produced excessive fluctuation in $(\partial P/\partial T)_\rho$. Henderson's data were used to generate quadratic equations for the isochores.

Fig. 4.11. Specific heat from Henderson's Monte Carlo energy data. The curves are based on quadratic fits to the energies at $\rho = 0.5$ and 0.6, and on a cubic fit to the energies at $\rho = 0.7$. The curves include both the kinetic and the configurational contributions.

Table 4.5. Equations derived from Barker's pressure equation and Henderson's Monte Carlo data. Both kinetic and configurational contributions are included.

$$E = \begin{cases} -0.9221 + 1.8171T - 0.19740T^2 & , \rho = 0.5 \\ -0.7644 + 1.6418T - 0.12772T^2 & , \rho = 0.6 \\ -0.9661 + 1.3799T + 0.01102T^2 - 0.00721T^3 & , \rho = 0.7 \end{cases}$$

$$c_V = \left(\frac{\partial E}{\partial T}\right)_V = \begin{cases} 1.8171 - 0.39480T & , \rho = 0.5 \\ 1.6418 - 0.25544T & , \rho = 0.6 \\ 1.3799 + 0.02204T - 0.021631T^2 & , \rho = 0.7 \end{cases}$$

$$P(T)_\rho = \begin{cases} -0.66563 + 1.25280T - 0.01824T^2 & , \rho = 0.5 \\ -0.99998 + 1.91659T - 0.01631T^2 & , \rho = 0.6 \\ -1.61384 + 3.48088T - 0.20996T^2 & , \rho = 0.7 \end{cases}$$

$$P(T)_\rho = -0.81032 + 1.51861T + 0.22655T^2 \quad , \rho = 0.6$$

Barker

$$\left(\frac{\partial P}{\partial T}\right)_\rho = \begin{cases} 1.25280 - 0.03648T & , \rho = 0.5 \\ 1.91659 - 0.03262T & , \rho = 0.6 \\ 3.48088 - 0.41992T & , \rho = 0.7 \end{cases}$$

Henderson

$$\left(\frac{\partial P}{\partial T}\right)_\rho = 1.51861 + 0.45309T \quad , \rho = 0.6$$

Barker

$$\left(\frac{\partial P}{\partial \rho}\right)_T = \begin{cases} -4.68013 + 8.49535T - 2.3956T^2 + 0.58100T^3 & , \rho = 0.5 \\ -6.66520 + 15.2262T - 4.5570T^2 + 0.95618T^3 & , \rho = 0.6 \\ 0.92390 + 0.87770T + 13.540T^2 - 4.21899T^3 & , \rho = 0.7 \end{cases}$$

Henderson

$$\left(\frac{\partial P}{\partial \rho}\right)_T = kT \left\{ \left[\left(1 + \sum_1^5 (1+i) f_i \rho^{i+1}\right) / \left(1 + \sum_1^4 g_j \rho^j\right) \right] - \right. \\ \left. \left[\left(\rho + \sum_1^5 f_i \rho^{i+1}\right) \left(\sum_1^4 j g_j \rho^{j-1}\right) / \left(1 + \sum_1^4 g_j \rho^j\right)^2 \right] \right\}$$

Barker

(f_1 through g_4 are listed in Table 4.2)

$$= \begin{cases} 0.55 & , \text{ at } T = 0.55 \text{ and } \rho = 0.6 \\ 2.24 & , \text{ at } T = 0.70 \text{ and } \rho = 0.6 \\ 5.04 & , \text{ at } T = 1.00 \text{ and } \rho = 0.6 \end{cases}$$

of vaporization is about six times the well depth. If just-melted lithium is taken as the reference point, the heat required for vaporization is the cohesive energy (23.03 MJ/kg) less the heat required to convert room temperature lithium to just-melted lithium (1.03 MJ/kg).

$$6c = (23 - 1.03) \text{ MJ/kg}$$

or

$$c = 3.667 \frac{\text{MJ}}{\text{kg}} / 8.679 \times 10^{25} \frac{\text{atom}}{\text{kg}} = 4.225 \times 10^{-20} \text{ J/atom} \quad (4.18)$$

The zero-potential interatomic separation, σ , can be found from the liquid density as follows. First, a hexagonal close packed (HCP) structure with a fixed layer spacing corresponding to the density of lithium at 500°C is assumed. The HCP lattice has a two-atom unit cell that contains portions of four atoms on each of two base planes, and one atom on an intermediate plane (Fig. 4.12). The intermediate plane atom and three base plane atoms form a tetrahedron. The HCP lattice constant, r_L , is twice the atomic radius, and the layer spacing is

$$r_h = \{r_L^2 - [(2/3)(\sqrt{3}/2)r_L]^2\}^{1/2} = (2/3)^{1/2} r_L. \quad (4.19)$$

Hence, the cell volume per atom is

$$\begin{aligned} V &= r_L [(\sqrt{3}/2)r_L] [2(\sqrt{2}/\sqrt{3})r_L] / 2 \text{ atoms} \\ &= (1/\sqrt{2}) r_L^3. \end{aligned} \quad (4.20)$$

If the density is decreased by increasing the base bond lengths while maintaining the layer spacing (tetrahedron height),

$$V = [(\sqrt{3}/2)r_L^2](2r_h) / 2 = (\sqrt{3}/2)r_L^2 r_h. \quad (4.21)$$

Fig. 4.12. Unit cell for a hexagonal-close-packed lattice. In the two-dimensional model of 500°C lithium, the undistorted three dimensional lattice is matched to the known lithium density. The unit cell is shown with heavy lines. Atoms in the unit cell are indicated with heavy symbols.

Setting $r_h = (2/3)^{1/2} r_L$ at 500°C lithium density,

$$V = [(8.679 \times 10^{25} \text{ atom/kg})(485 \text{ kg/m}^3)]^{-1} \quad , \quad (4.22)$$

$$r_h = 2.633 \times 10^{-10} \text{ m}$$

and

$$r_o = r_L = 3.225 \times 10^{-10} \text{ m} \quad . \quad (4.23)$$

At the rest length, r_o , the potential is minimum and $\partial\phi/\partial r = 0$,

$$(\partial\phi/\partial r)_{r=r_o} = 0 = 4\epsilon [-12 \sigma^{12}/r_o^{13} + 6 \sigma^6/r_o^7] \quad . \quad (4.24)$$

Or,

$$\sigma = (2)^{-1/6} r_o = 2.873 \times 10^{-10} \text{ m} \quad . \quad (4.25)$$

To further simplify the molecular dynamics calculations, it is desirable to use non-dimensionalized quantities to eliminate as many irrelevant constants as possible. Accordingly, the distance was measured in units of σ , the energy in units of ϵ , the mass in units of the lithium atomic mass, and temperature in units of ϵ/k . These units were used to determine the scales for time, velocity, temperature, force, density and pressure (Table 4.6). In addition, the LJ potential was truncated at $r_t = 4\sigma$ (in early calculations) and $r_t = 2.5\sigma$ (in later calculations). Truncation saves time by ignoring the large number of very weak bonds. The change in truncation procedure had little effect on the atomic motion. This is apparent from the lattice energy per atom for various truncation distances and densities (Fig. 4.13). Therefore, the choice of truncation distance is not critical. Shifting the potential upward by $\phi(r_t)$ smooths the potential by eliminating step jumps in lattice

Table 4.6. SI values of the reduced units.

<u>Quantity</u>	<u>SI value for 500°C lithium</u>
distance	$2.873 \times 10^{-10} \text{ m } (\sigma)$
energy	$4.225 \times 10^{-20} \text{ J } (\epsilon)$
mass	$1.152 \times 10^{-26} \text{ kg } (1/N_m)$
velocity	$1915 \text{ m/s } ([\epsilon/m]^{1/2})$
time	$0.1500 \text{ ps } (\sigma/v = \sigma(m/\epsilon)^{1/2})$
temperature	$3061 \text{ K } (mv^2/k = \epsilon/k)$
force	$1.471 \times 10^{-10} \text{ N } (\epsilon/\sigma)$
density (2-D)	$1.212 \times 10^{19} \text{ atom/m}^2 (\sigma^{-2})$
pressure (2-D)	$0.5119 \text{ Pa } (\epsilon/\sigma^2)$

Fig. 4.13. Lattice energy per atom for several variations of the Lennard-Jones 6-12 potential. The curve labels indicate the truncation distance. The "shifted" curve indicates a potential that has been slightly increased to eliminate a step increase in potential at the truncation distance.

energy at densities that introduce additional atoms within range of the potential. This shifted potential was used in Ref. 29.

The potential and force functions for the simplified LJ potential are

$$\begin{aligned} \phi(r) &= \begin{cases} 4r^{-6} (r^{-6} - 1) & , r \leq r_t \\ 0 & , r > r_t \end{cases} \\ \vec{F}_{1j} &= \frac{\vec{x}_1 - \vec{x}_j}{r} \cdot \begin{cases} 24r^{-7} (2r^{-6} - 1) & , r \leq r_t \\ 0 & , r > r_t \end{cases} \end{aligned} \quad (4.26)$$

where r_t is the truncation distance.

4.3. Thermodynamic Paths Followed on the P-V Diagram During and After Isochoric Heating

Some insight into the liquid breakup can be obtained by examining the pressure-volume diagram for lithium. Figure 4.14 is a P-V diagram for lithium constructed using Young's equation of state (Section 4.1). The figure shows only a portion of the subcooled liquid region. The saturated liquid line is very shallow in this density range; it is almost indistinguishable from the abscissa. If the plot is extended far to the right, the saturated liquid line eventually rises to the critical pressure of 114 MPa at $0.011 \text{ m}^3/\text{kg}$ (91 kg/m^3).

The initial condition, before the fusion pulse, is on the saturated liquid line at 500°C (485 kg/m^3). The fusion neutrons isochorically add a maximum of 800 kJ/kg (HYLIFE inner jet inner edge). The liquid temperature and pressure quickly rise to 735°C and 380 MPa with no density change. As the relief wave moves into the jet, an adiabatic (isentropic) expansion begins. In an adiabatic expansion, energy is conserved, although some of the internal energy can be converted to kinetic and surface energies. During expansion to the saturation line (and $P = P_{\text{sat}} \sim 0$), the liquid temperature falls to 695°C . During the expansion, the internal energy falls by $\sim 16 \text{ kJ/kg}$ from the value after the isochoric heating. Use of Eqs. 2.3 and 2.4 shows that $\sim 15.2 \text{ kJ/kg}$ of kinetic energy is produced by the tensile wave, without considering any phase change. Hence, most of the "lost" internal energy is converted to kinetic energy.

The expansion can be continued into the two phase liquid-vapor region on the P-V diagram to bound the vaporization contribution (Fig. 4.15). After the isentrope enters this two phase region, it

Fig. 4.14. P-V diagram of the heating and initial expansion of a HYLIFE inner jet.

continues to expand to lower, even negative, pressures. The isentrope is not continued beyond the isentropic spinodal line where it has zero slope since the fluid is then unstable to phase separation back to the spinodal, probably on a sub-nanosecond time scale. Between the coexistence curve and the spinodal, the fluid is metastable, and it eventually separates into saturated liquid and vapor phases (on the coexistence curve) by the sequential processes of nucleation and growth or by vaporization from the free surfaces if hydrodynamic fragmentation is faster than nucleation and growth.

If the isentropic expansion continued all the way to the spinodal, the intersection of the isentrope and spinodal would be as shown in the lower right corner of Fig. 4.15. The specific volume would increase by 77%; and the vapor volume would be $\sim 0.0016 \text{ m}^3/\text{kg-liquid}$. If the vapor were in equilibrium with 735°C liquid, the vapor pressure would be $\sim 120 \text{ Pa}$ (0.9 torr) and the vapor specific volume $\sim 9690 \text{ m}^3/\text{kg-vapor}$. The quotient of the two specific volumes is $\sim 1.6 \times 10^{-7}$ ($160 \text{ }\mu\text{g-vapor/ kg-liquid}$), an extremely low vaporization fraction. Since vaporization requires 20.7 MJ/kg-vapor ($23.0 \text{ e}_{\text{coh}} - 1.0 \text{ H}_{\text{melt}} - 1.3 \text{ specific heat}$), only 3.4 J/kg-liquid are used for vaporization. This is about 4400 times less energy than the kinetic energy produced by the expansion; therefore, vaporization does not utilize sufficient energy to drive the expansion. Further, the 77% expansion required before spinodal decomposition can begin would probably cause fragmentation hydrodynamically. Phase separation from the spinodal will eventually produce saturated liquid plus a small amount of saturated vapor (at about the same temperature as the intersection of the isentrope and the saturation line: 695°C in the

Fig. 4.15. P-V diagram showing isentropic expansion to the isentropic spinodal line.

example).

By using the MATHSY macro and Young's equation of state, thermodynamic values were calculated for several states during the heating and expansion (Table 4.7).

The discussion of phase change as a fragmentation mechanism will be concluded in Section 4.6, following a more detailed review of spinodal decomposition and of nucleation and growth in Sections 4.4 and 4.5.

Table 4.7. Thermodynamic values of the inner MYLIFE jets before and after heating. These values assume a homogeneous expansion without phase separation, and hence surface energy has been ignored.

	<u>Initial Condition</u>	<u>After Heating</u>	<u>After Expansion to Coexistence Curve</u>	<u>After Expansion to Spinodal*</u>
T(°C)	500	735.1	695.4	308
$\rho(\text{kg}/\text{m}^3)$	484	484	465	274.2
$V(\text{m}^3/\text{kg})$	0.00206	0.00206	0.00215	0.00365
P(MPa)	0.000685	380	0.00337	-1559
E(kJ/kg)	2350	3149	3133	4935
A(kJ/kg)	-2988	-4723	-4429	398
S(J/kg·K)	6905	7809	7809	7809

* The isentropic spinodal

4.4. Spinodal Decomposition

Spinodal decomposition is an extensively researched process. A 1962 literature search revealed over 500 publications on the subject. Perhaps the most straightforward summary is contained in Cahn's 1967 Institute of Metals Lecture³⁰ which also cites many references. Reid³¹ has also published a very clear summary article.

The concept of spinodal decomposition dates back to Gibbs in 1871. The concept is usually applied to a multi-component system with concentration being the independent variable. However, it is equally applicable to a single component system with specific volume as the independent variable. The spinodal line is also called the limit of metastability, the superheat limit, and the cavitation limit.

Basically, spinodal decomposition is possible whenever the Gibbs free energy curve has a negative second derivative (Fig. 4.16). For a one-component fluid, this implies $(\partial^2 P / \partial V^2)_S > 0$. Consider a small separation into two equal masses of a composition between the spinodes (point 3 in Fig. 4.16). To conserve volume, the abscissa values (specific volumes) of the two constituents (points 2 and 4) must be equidistant from the original composition. Because of the negative second derivative, the decrease of free energy on the left side is larger than the increase on the right side. Since the overall free energy drops, the separation is energetically preferred. Separation continues until the energetics are no longer favorable; i.e. to the equilibrium lines (points 1 and 5).

Cahn has applied the diffusion equation to spinodal decomposition in a two component system (components A and B).

Fig. 4.16. In spinodal decomposition, there is no energy barrier to small phase separations.

$$\text{Let } \bar{J} = J_A = -J_B \quad (4.27)$$

$$-\bar{J} = M \nabla(\mu_A - \mu_B) \quad (4.28)$$

where M is the "diffusion mobility" (always positive). The quantity $(\mu_A - \mu_B)$ is the free energy change when an "A" atom is reversibly added and a "B" atom is reversibly removed. For a homogeneous system

$$\mu_A - \mu_B = \frac{\partial G}{\partial C_A} \quad (4.29)$$

Here, G is the Gibbs free energy and the derivative indicates an addition of "A" phase and equal deletion of "B" phase. Combining the two equations

$$-\bar{J} = \left(M \frac{\partial^2 G}{\partial C_A^2} \right) \nabla C_A \quad (4.30)$$

But, by definition

$$-\bar{J} = D_m \nabla C_A \quad (4.31)$$

Hence,

$$D_m = M \frac{\partial^2 G}{\partial C_A^2} \quad (4.32)$$

Since M is always positive, D_m takes its arithmetic sign from the free energy curvature, $\partial^2 G / \partial C_A^2$. For spinodal decomposition, there is negative curvature and a negative diffusion coefficient. Small concentration (or density) fluctuations tend to grow due to the

negative diffusion coefficient. In the nucleation and growth region of the P-V diagram, there is positive curvature and a positive diffusion coefficient. Small density fluctuations tend to die; only large fluctuations (nuclei) which span the free energy peak in Fig. 4.16 can grow.

For a system that is sufficiently inhomogeneous that the inhomogeneity is apparent within the atomic interaction range, the chemical potential is modified.

$$\mu_A - \mu_F = \frac{\partial G}{\partial C} - 2K_s \nabla^2 C_A \quad (4.33)$$

The additional term represents the inhomogeneity effect on the chemical potential which is a function of the concentration's curvature. The constant K_s is positive and a function of the interaction energy and the interaction distance. When Eq. 4.33 is substituted into Eq. 4.28,

$$\vec{J} = M \frac{\partial^2 G}{\partial C^2} \nabla C - 2M K_s \nabla^3 C \quad (4.34)$$

By taking the divergence, the diffusion equation for spinodal decomposition is produced,

$$\frac{\partial C}{\partial t} = \frac{\partial^2 G}{\partial C^2} \nabla^2 C - 2M K_s \nabla^4 C \quad (4.35)$$

As can be seen by back substitution, the diffusion equation has the solution,

$$C - C_0 = e^{at} \cos(\vec{r}) \quad (4.36)$$

where

$$a(\vec{\beta}) = -M \beta^2 \left[\frac{\partial^2 G}{\partial C^2} + 2K_s \beta^2 \right] \quad (4.37)$$

The second term in the bracket is positive. Outside the spinodal, the curvature is also positive and the amplification factor, $a(\vec{\beta})$ is negative; i.e. the fluctuations shrink exponentially with time.

Inside the spinodal region, the free energy curvature is negative, leading to positive amplification factors and growing fluctuations.

At large enough frequency β , the second term in the brackets dominates and the fluctuations again die out. Thus, there is a range of fluctuation spatial frequencies that grow in time. One specific spatial frequency grows faster than all others, resulting in a very regular and periodic structure in the decomposing material.

The dominant wavelength is found by maximizing the bracketed term in Eq. 4.37. Thus

$$\vec{\beta}_{\text{dominant}} = -\left(\frac{\partial^2 G}{\partial C^2}\right) / 4K_s \quad (4.38)$$

Cahn estimates dominant wavelengths ~ 5 nm, and notes that in the early stages both phases are highly connected (rather than isolated bubbles) unless the minority phase is less than 15%.³²

Cahn and others have extended the analysis to include crystal anisotropy, coherency stresses, and applied magnetic and elastic fields. These phenomena add further nonlinear terms to Eq. 4.35, but they only affect the expression for the amplification factor Eq. 4.37; the form of the solution Eq. 4.36 remains unchanged.³⁰

For liquids, the decomposition time is submicrosecond³⁰ (less than 10 ps in Ref. 33) while for solids near the melting point it is

milliseconds.³⁰ For cooler solids and glasses, the decomposition time is long enough to allow experimentation and practical application in materials processing.

For a one component system, flash condensation and homogeneous-nucleation-in-boiling are manifestations of spinodal decomposition. The homogeneous-nucleation-in-boiling process can be observed by heating a glass container of water in a microwave oven. Because the container is smooth and heat addition is homogeneous, boiling does not originate from cavities at the water-container interface (pool boiling); instead homogeneous nucleation (spinodal decomposition) begins in the bulk fluid. At this point, the water temperature is much further (perhaps 50°C) above the normal H₂O boiling point than is the case in pool boiling (which has superheats of less than 5°C)*. Once rapid boiling is underway, the container is removed from the oven, and boiling quickly ceases as the water temperature falls below the spinodal temperature. If a tea bag or other set of nucleation sites is placed in the water before the temperature falls below the pool boiling temperature (about 5°C superheat), vigorous phase change will resume, but by nucleation and growth rather than by spinodal decomposition.

* An experiment using a thermometer with a 225°F upper limit indicated no superheat during a rolling boil and at least 13°F superheat after microwave heating. The equilibrium pressure rise of saturated water between 212 and 225°F is 30 kPa (4 psi). Since the water was not ejected from the container, the actual pressure rise was negligible, indicating a non-equilibrium state under the two-phase dome.

4.5. Nucleation and Growth

Nucleation and growth are the processes by which almost all phase changes not involving shock or detonation occur. The references in Section 4.4 briefly discuss these processes in contrast to spinodal decomposition. Two additional references containing excellent descriptions of nucleation and growth are Chapter 19 by Gerum et. al. in Heat Transfer in Boiling³⁴ and Frenkel's 1946 book Kinetic Theory of Liquids (especially Chapters 6 and 7).³⁵

A single phase material that is placed in a density-pressure condition in the metastable region under the two-phase dome will eventually separate into two distinct phases by the processes of nucleation and growth. Nucleation refers to the formation of a minority species nucleus of the critical size. This size can be found from a free body diagram of a spherical vapor bubble (Fig. 4.17). The expansion force due to the internal and external pressures ($\pi r_c^2 P_v - \pi r_c^2 P_l$) must equal the restraining surface force ($\gamma 2\pi r_c$). Equating the two forces determines the critical nucleus radius, r_c .

$$r_c = \frac{2\gamma}{P_v - P_l} \quad (4.39)$$

In the equation, P_v is the equilibrium vapor pressure at the vapor's temperature, and P_l is the surrounding liquid pressure. The equilibrium is unstable; vapor clusters smaller than the critical size collapse, and larger clusters grow. This is because the confining pressure on the vapor bubble, $P_l + 2\gamma/r$, is smaller than the equilibrium vapor pressure for $r > r_c$, and the bubble grows. For subcritical radius nuclei, the surface forces are so large that they

Fig. 4.17. Free body diagram of a critical nucleus. The internal minus external pressure forces are balanced by the surface forces.

collapse the bubble. In two dimensions, $2r_c P_v - 2r_c P_l = 2\gamma$,
or $r_c = \gamma/(P_v - P_l)$.

A second way of thinking about the critical nucleus size is in terms of free energy. The free energy of a drop (or bubble) is approximately the sum of two terms. The first term is the population times the free energy per atom in an infinite system. The second is the surface free energy,

$$A = N A_{\infty} + (\pi r^2 \gamma - NTS_e) \quad (4.40)$$

In the brackets, S_e is the excess entropy per atom contributed to the system due to the free surface. Hoover³⁶ has shown that for solid crystals with parabolic potentials, this quantity does not vary sharply for systems with more than 100 atoms. To simplify the argument, NTS_e will be absorbed in the first term. Then

$$A = \frac{4}{3}\pi r^3 \rho A_{\infty}^* + \pi r^2 \gamma \quad (4.41)$$

The quantity, A_{∞}^* is negative and roughly constant (A_{∞} is strictly constant). The surface tension is constant and positive. Enough information has been specified to draw a free energy vs. radius curve (Fig. 4.18). A similar curve is plotted in Ref. 37 for sodium. The curvature at the origin is $2\pi\gamma$, and the curve peak indicates the critical radius. The free energy at the peak represents an activation energy for nucleation. Nuclei smaller than the critical radius move to lower (more favorable) free energies by shrinking. Nuclei larger than the critical radius lose free energy by growing; the critical

radius is an unstable equilibrium point.

The preceding argument intentionally avoids providing numbers because, for very small systems, the properties change. As stated earlier, Ref. 36 shows that the excess entropy is a steep function at radii of a few σ or less. Brodskaya³⁸ and Thompson²⁹ have both shown that the surface tension falls rapidly from its macroscopic value to zero as the system radius decreases from the 3 to 7σ range to zero. This is required by the simple model of Fig. 4.18. In Fig. 4.19, the free energy has been replotted on an energy per atom basis. The high values at small sizes are incorrect. For a single atom, there is no internal energy, and the curve must fall to the origin as it will if the surface tension falls to zero at the origin. Thus, the small radius portion of the free energy curve is surely distorted, although its shape is probably correct. Conversely, if the curve is constructed using free energy values measured at radii larger than 6σ , using the curvature at $r=0$ to calculate the ($r > 6\sigma$) surface tension is reasonable, with the primary error due to the weak number dependence of excess entropy at these radii.

According to Gerum³⁴, vapor nuclei can form around small (10 nm or larger) cavities in the container surface (as in pool boiling) or around small ($< 1 \mu\text{m}$) insoluble solid particles. Various types of radiation (α , γ , n , p , fission fragments, etc.) have also been suggested as nucleating mechanisms,³⁷ either by depositing the required activation energy in a liquid volume smaller than the critical size, or by creating a vapor jet that breaks up into discrete regions larger than the critical nucleation size. Kottowski³⁷ concludes that high energy neutrons in an LMFBR would not cause

Fig. 4.18. Free energy as a function of system size. The maximum defines the critical nucleus size and the nucleation activation energy.

Fig. 4.19 Free energy per atom as a function of system size for constant and size-dependent surface tension.

nucleation at 260°C superheat in the bulk sodium, but that they could increase the nucleation in wall cavities. Gerum and coworkers³⁴ conclude that nucleation from cosmic rays could not account for the measured superheats in their H₂O-Si oil and CO₂ experiments.

Frenkel³⁵ determined the amount of superheat in a vaporizing liquid as a function of the nucleus size. He began with the Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{H_v}{T(V_v - V_l)} \quad (4.42)$$

The pressure difference between the inside (the vapor pressure) and the outside is $dP = 2\gamma/r_N$ where the vapor pressure is at temperature T which is dT above the saturation temperature. Also, $V_v \gg V_l$ and $V_v \sim kT_{sat}/P$. Hence

$$T - T_{sat} = \frac{2\gamma kT_{sat}^2}{PH_v r_N} \quad (4.43)$$

For large superheat ($T - T_{sat}$), Eq. 4.42 must first be integrated

$$\int \frac{dP}{P_l} = \int \frac{H_v}{kT^2} dT \quad (4.44)$$

$$\ln \left(\frac{P_l + 2\gamma/r_N}{P_l} \right) = \frac{H_v}{k} \left(\frac{1}{T_{sat}} - \frac{1}{T} \right)$$

Thus,

$$T - T_{sat} = \frac{kT_{sat}}{H_v} T \ln \left(1 + \frac{2\gamma}{P_l r_N} \right) \quad (4.45)$$

The resulting superheat ($T - T_{sat}$) is shown in Fig. 4.20 for

Fig. 4.20. If no large nuclei are present, high superheat is possible before boiling begins.

water at 100 kPa (1 atm) pressure with the following properties:

$$\begin{aligned}\gamma &= 0.07 \text{ J/m}^2 && \text{(surface tension)} \\ H_v &= 7 \times 10^{-20} \text{ J/molecule} && \text{(heat of vaporization)} \\ k &= 1.38 \times 10^{-23} \text{ J/molecule-K} && \text{(Boltzmann's constant)} \\ T_{\text{sat}} &= 373 \text{ K} && \text{(saturation temperature)}\end{aligned}$$

If no large nuclei ($r \geq 10 \text{ }\mu\text{m}$) exist, superheats of tens and even hundreds of degrees are possible. Experiments on water³⁹ at 100 kPa have produced superheats of 200-210°C, and superheats approaching 1000°C have been calculated for sodium.³⁷ The ultimate limit of superheat is reached when the spinodal decomposition regime is entered, i.e., the system becomes unstable to small density fluctuations. However, superheat is further limited because the probability of forming small nuclei ($< \text{nm}$) by density fluctuations is high enough to occur in reasonably short times.

Fluids have been maintained in metastable states by insuring a lack of nucleation sites (for water, at negative pressures up to 27 MPa for periods of several seconds or more^{40,41}, and at negative pressures of 12 MPa for over a week⁴²). The growth process cannot begin until nuclei larger than the critical size are formed.

Once nucleation has occurred, the vapor bubbles grow to macroscopic size.³⁹ At early times, growth rate is controlled by the inertia of the surrounding liquid, and is described by the Rayleigh equation,

$$\frac{dR_B}{dt} = \left[\frac{2}{3} \frac{(P_v - P_{lm})}{\rho_{lm}} \right]^{1/2} \quad (4.46)$$

where ρ_{lm} is the mass density of the liquid. This equation assumes the bubble vapor pressure corresponds to the saturation temperature of

the bulk liquid. Since the bubble growth velocity, dR_B/dt is a constant, the growth rate in this "inertially limited growth regime" is independent of time.

As the growth progresses, the heat of vaporization of the newly created vapor requires energy from the liquid interface faster than the heat transfer rate from the bulk liquid. Hence, the interface liquid temperature and the vapor pressure both drop. In this "thermally limited growth regime", the bubble growth rate is approximated³⁹ by

$$\frac{dR_B}{dt} = N_J(\alpha_t/t)^{1/2} \quad (4.47)$$

where α_t is the thermal diffusivity and

$$N_J = \frac{\rho_L c_L (T_L - T_{sat})}{\rho_V H_V} \quad (4.48)$$

For the thermally limited growth regime, the pressure inside the bubble is almost the same as in the bulk liquid, the vapor temperature corresponds to that pressure, and the bubble radius increases with the square root of time. Both regimes are shown in Fig. 4.21.

For 100 kPa water³⁹, the inertial growth period is $< 250 \mu s$ with velocities ~ 50 m/s, and the thermal growth period lasts for ms with velocities of only a few m/s. These velocities are considerably lower than the expected hydrodynamic disassembly velocity in the HYLIFE lithium jets. Thus, bubble growth is too slow to drive the expansion and consequent fragmentation.

Fig. 4.21. Bubble growth slows with time (from Ref. 39). At early times ($< 250 \mu\text{s}$ for 100 kPa water), the surrounding fluid inertia determines the growth rate. At later times, growth is further limited by the rate of heat transfer from the bulk liquid to the interface.

4.6. Evaluation of the Rapid Vaporization Approach to Liquid Fragmentation

For the 10 cm radius HYLIFE inner jets, the outward liquid velocity due to the pressure relief wave is ~ 180 m/s (Table 2.2). If the fluid expanded homogeneously until the spinodal line is reached, its specific volume would increase by $\sim 77\%$. Its radius would increase by 33%, and ~ 180 μ s would elapse during the expansion. When the ~ 40 μ s wave transit time is added; the time is still less than the growth time examples given in Section 4.5 (250 μ s for the high growth rate initial phase). Hence, nucleation and growth are too slow to drive the expansion and consequent fragmentation. If the spinodal line is reached, spinodal decomposition is certainly fast enough, but it has insufficient energy to drive the expansion. Further, hydrodynamic fragmentation would probably occur before the fluid reaches the spinodal line.

It is unlikely that the spinodal line would be reached in a liquid lithium inertial fusion reactor. At the spinode, the liquid tension would be ~ 1560 MPa, much larger than the tensile strength of solid lithium or the tension induced in extremely clean water during carefully controlled experiments. If spinodal decomposition did occur, a characteristic wavelength of coexisting vapor-rich and liquid-rich regions would be $\sim 5\sigma$, according to simulations⁴³ by Abraham. In an ICF reactor, the entrained gas, target debris, and corrosion products will provide an abundance of potential nucleation sites, allowing a more gradual phase change by the processes of nucleation and growth or by vaporization from the free surfaces of the hydrodynamically fragmented liquid. However, the growth time is

longer than the liquid's expansion time, and vapor growth cannot drive the fragmentation; instead, the expansion leads to fragmentation (as in a solid). The consequent voids equilibrate by filling with vapor from three potential sources (flow from the vapor originally existing outside the liquid jet or drop, vaporization from the new free surfaces, and small vapor bubbles that by move by chance from the fragment bulk to the new surfaces).

Since rapid phase change does not drive the fragmentation process, at least not for high energy density reactors like HYLIFE, hydrodynamic models are devised and molecular dynamics simulation are described in the following chapters.

Chapter 5: Force and Energy Balance Models for Fragmentation

Four force and energy balance models are described in this chapter. The first balances the isochoric heating pressure by surface tension. The second balances the post-relaxation dynamic pressure by surface tension. The third minimizes the sum of the surface energy density and the fragment non-translational kinetic energy density. (In general, the fragment translational kinetic energy is much larger than the non-translational, dilational, kinetic energy.) The fourth model is a modification of the third model in which only the dilational kinetic energy near the fragment surface is considered.

These models differ by balancing different portions of the suddenly added energy against the surface tension. The first model naively requires the surface tension to balance the instantaneously increased pressure. The second model allows pressure relief and balances only the resulting expansion kinetic energy (dynamic pressure) against the surface tension. The third model uses only the fraction of the dynamic pressure associated with fragment dilation; fragment translational energy is properly ignored. Even this model considers only equilibrium situations and round fragments; thus, experimental verification is required. The fourth model uses only a portion of the fragment dilational energy.

In this chapter, all four models are described. The first model is reviewed and applied to HYLIFE. Then an improvement leads to the second model which is also applied to HYLIFE. The previously published derivation of the third model is expanded (in two and three dimensions), and extended to include radially dependent velocity divergence. The third model is also applied to several reactor designs, and reformulated

to allow comparison with the molecular dynamics results. The fourth model is briefly developed as a perturbation of the third model's derivation. Finally, the shortcomings of the models are discussed.

5.1. Balancing the Isochoric-Heating Pressure by Surface Tension

An early model (model 1) of fragment size was proposed⁴⁴ in 1979. In this model, the pressure increase was balanced against the surface tension,

$$\begin{cases} \Delta P(\pi a^2) = \gamma(2\pi a) & , \text{3-D} \\ \Delta P(2a) = \gamma(2) & , \text{2-D} \end{cases} \quad (5.1)$$

where γ is the surface tension, a is the drop radius, and ΔP is $\rho_m \Gamma_e$ as defined by Eq. 2.3. The surface tension, γ , is 0.35 and 0.435 J/m² for Li and Li₁₇Pb₈₃, respectively (Table 2.1). Eq. 5.1 reduces to

$$a = (D-1) \gamma / (\rho_m \Gamma_e) \quad (5.2)$$

where D indicates 2 or 3 dimensions. For the HYLIFE leading edge, $a = 1.8$ nm, corresponding to a fragment containing ~ 1030 atoms.

The calculation resembles a critical nucleus size computation except that the internal pressure is determined by the isochoric heating rather than by thermodynamic equilibrium. The model ignores pressure relief in the original liquid drop which is achieved by generating expansion momentum. Instead, it assumes that the original liquid somehow fragments such that the added pressure within the liquid can be contained by the surface pressure, $2\gamma/r$. The calculation also does not predict the original drop size that would be stable against fragmentation since, if the original drop had radius a , its original internal pressure would be $\sim 2\gamma/a$ before the isochoric heating and $\sim 4\gamma/a$ after heating.

5.2. Balancing the Post-Relaxation Dynamic Pressure by Surface Tension

A second estimate (model 2) of the fragment drop size uses the dynamic pressure ($\rho_m v^2/2$) of the expanding liquid drop after the isochoric-heating pressure has been relieved. Using Eqs. 2.3 and 2.4,

$$\Delta P = \frac{1}{2} \rho_m v^2 = \frac{1}{2} \rho_m \left[\frac{\rho_m \Gamma_0}{\rho_m c} \right]^2 = \frac{1}{2} \rho_m \left(\frac{\Gamma_0}{c} \right)^2 \quad (5.3)$$

Using this pressure in Eq. (5.1).

$$a = \frac{2(D-1)\gamma}{\rho_m} \left(\frac{c}{\Gamma_0} \right)^2 \quad (5.4)$$

where D is the number of dimensions. Using the HYLIFE example again $a = 90$ nm, corresponding to 129 million atoms in each fragment. The fragment size is larger than the previous model because the driving pressure is reduced from the isochoric-heating value to the dynamic expansion pressure. The model assumes that the original drop fragments such that each fragment has an expansion velocity about its center of mass that is identical to the expansion velocity of the original drop. The fragment's surface pressure, $2\gamma/a$, resists the dynamic pressure, and the fragment alternately dilates and contracts until the dynamic dilational pressure is converted to a homogeneous internal static pressure. The difficulty with this model is that the original expansion kinetic energy is partitioned between fragment translation and fragment dilation (in addition to fragment rotation). The model ignores the partition, resulting in an overestimate of the driving pressure and an underestimate of the fragment size.

5.3. Minimizing the Sum of the Surface Energy and the Local Dilation Kinetic Energy (The Grady-Glenn Model)

The previous two models ignore the translational and rotational energies of the fragments. To improve the models, the fraction of the kinetic energy (or dynamic pressure) that must balance the surface forces must be estimated. Grady's original effort⁴⁵ was extended by Glenn⁴⁶. Their efforts are described and further extended in this four part section. First, the model (model 3) is derived in two and three dimensions. Then, the radially averaged result is extended to include variation with radial position within the original drop. Finally the model is applied to ICF reactors and to the microscopic molecular dynamics simulations.

5.3.1. Model Derivation in Two and Three Dimensions

Grady uses the fragment size as the independent variable and splits the kinetic energy into the motion of the fragment center of mass and the dilation about the fragment center of mass (Fig. 5.1). The dilational kinetic energy is added to the surface energy, and the sum is minimized with respect to the fragment size. This energy minimization process is similar to the Griffith Theory of Fracture⁴⁷ which is familiar to material scientists. The surface energy density is

$$s = \begin{cases} \frac{4\pi a^2 \gamma}{\frac{4}{3} \pi a^3} & , \text{ 3-D} \\ \frac{2\pi a \gamma}{\pi a^2} & , \text{ 2-D} \end{cases} = D \gamma / a \quad (5.5)$$

where D = 2 or 3 for two or three dimensions.

The fragment dilational energy density is

$$K_v = \begin{cases} \int_0^a \left(\frac{1}{2} \rho_m v^2 \right) 4\pi r^2 dr / \frac{4}{3} \pi a^3 & , \text{ 3-D} \\ \int_0^a \left(\frac{1}{2} \rho_m v^2 \right) 2\pi r dr / \pi a^2 & , \text{ 2-D} \end{cases} \quad (5.6)$$

To perform the integration, the dilation velocity must be specified as a function of the radius from the fragment center. This is accomplished by using the continuity equation in spherical or circular coordinates with no angular dependence,

$$\dot{\rho}_m = \frac{\partial \rho_m}{\partial t} = - \nabla \cdot (\rho_m \vec{v}) \quad , \quad \vec{v} \text{ is purely radial}$$

Fig. 5.1. Geometry used in the Grady-Glenn energy minimization model.

Or

$$\dot{\rho}_m = \begin{cases} -\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho_m v) = -\frac{\partial}{\partial r} (\rho_m v) - \frac{2\rho_m v}{r}, & 3-D \\ -\frac{1}{r} \frac{\partial}{\partial r} (r \rho_m v) = -\frac{\partial}{\partial r} (\rho_m v) - \frac{\rho_m v}{r}, & 2-D \end{cases} \quad (5.7)$$

For a homogeneously diverging drop, $\dot{\rho}_m$ is a constant. Then, $\frac{\partial}{\partial r} (\rho_m v)$ must be a multiple of $\rho_m v/r$. But $\rho_m v = 0$ at $r = 0$ by symmetry; hence,

$$\frac{\partial}{\partial r} (\rho_m v) = \frac{\rho_m v}{r} \quad (5.8)$$

and

$$\dot{\rho}_m = -D \frac{\rho_m v}{r} \quad (5.9)$$

Using this result, Eq. 5.6 becomes

$$K_v = \begin{cases} \int_0^a \frac{2}{9} \pi (\dot{\rho}_m^2 / \rho_m) r^4 dr / \frac{4}{3} \pi a^3, & 3-D \\ \int_0^a \frac{\pi}{4} (\dot{\rho}_m^2 / \rho_m) r^3 dr / \pi a^2, & 2-D \end{cases} \quad (5.10)$$

Since it is assumed that ρ_m and $\dot{\rho}_m$ don't vary within the fragment, the integration can be performed,

$$K_v = (a \dot{\rho}_m^2) / (D_2 \rho_m) \quad (5.11)$$

where $D_2 = 2D(D+2)$.

As illustrated in Fig. 5.2, the sum of the surface energy density and fragment dilational energy density is minimized by differentiation,

$$\frac{\partial}{\partial a} (K_v + s) = 0 \quad (5.12)$$

Fig. 5.2. Grady's model selects a fragment size that minimizes the sum of the surface plus fragment dilational energy densities.

which leads to

$$0 = \frac{2a\rho_m^2}{D_2\rho_m} - \frac{D\gamma}{a^2} \quad (5.13)$$

Grady has successfully compared this result to oil shale fragmentation and breakup of explosively loaded pipes (Fig. 5.3).⁴⁵

To use Grady's result for ICF reactor design, the dilation rate, $(\dot{\rho}/\rho)$ is required. Glenn⁴⁶ carried out a series of hydrodynamic calculations of isochorically heated (pressurized) spheres. In these calculations, tensile fragmentation was not allowed, and the density varied smoothly. The velocity profile was quite flat for $r/R > 0.1$ (Fig. 5.4). Hence, for most of the liquid mass, Eq. 5.9 can be used with $v = v_s = \Gamma e/c$, the surface (or jump-off) velocity. Then, Eq. 5.13 can be modified to predict a representative fragment size as a function of initial size (R), energy loading (e), Grüneisen parameter (Γ), sound speed (c), surface tension (γ), and liquid mass density (ρ_m). The result is

$$a = \left[\frac{D_3}{\rho_m} \gamma \left(\frac{Rc}{\Gamma e} \right)^{2/3} \right] \quad (5.14)$$

where $D_3 = D+2$ and D is the number of dimensions.

In most cases, Eq. 5.14 predicts much larger fragments than models 1 and 2. However, this model includes a new variable, the system size, R . If the sphere size is chosen to avoid fragmentation ($a = R$), model 3 agrees well with model 2 because then all the kinetic energy is dilational. For example, with HYLIFE loading, the stable (when $a = R$) drop size is 114 nm, within 25% of the model 2 prediction. The stable drop size predictions of models 1 and 2 were 1.8 and 90 nm,

Fig. 5.3. Comparison of Grady's model and laboratory experiments (from Ref. 45). Strain rate is $\dot{\rho}/(3\rho)$ and fracture toughness is $(2\rho\gamma_c^2)^{1/2}$.

Fig. 5.4. Glenn's calculated velocity profile for uniformly heated spheres. The dashed lines are analytic approximations which are discussed in Section 5.3.2.

respectively.

The three models balance a decreasing sequence of forces against the surface tension. The first model uses the entire isochoric pressure while the second model uses the dynamic pressure calculated from the jump-off velocity. Finally, the third model selects only the small portion of the dynamic pressure confined within the fragment, properly ignoring the portion associated with motion of the fragment as a whole. When the system size and heating level are such that fragmentation is minimal, models 2 and 3 naturally converge. Similarly, when fragmentation is extensive, models 1 and 2 naturally fail.

Another model (model 4) can be derived from model 3 by assuming only the dilational energy contained in the surface region of the fragment must be contained by the surface tension. Equation 5.6 is integrated only from $(a-\delta)$ to a , rather than from 0 to a , where δ is the distance in from the surface beyond which the dilational energy is ignored. The result of the model is identical in two and three dimensions,

$$a = \left[\frac{2\gamma}{\rho \delta} \left(\frac{R_C}{r_C} \right)^2 \right]^{1/2} . \quad (5.15)$$

Model 4 predicts no fragmentation for the HYLIFE example conditions.

5.3.2. Effect of Considering the Velocity Distribution Rather Than The Average Disassembly Velocity in Model 3

In Section 5.3.1, the fragmentation model (model 3) was derived in two and three dimensions. These derivations used the surface disassembly velocity and constant velocity divergence to predict fragment size. In this section, the derivation is extended to include the velocity divergence as a function of radial position within the original drop rather than a single value. In the derivation, the radial dependence of the velocity divergence is taken from Glenn's hydrodynamic calculations⁴⁶.

Glenn approximated⁴⁶ the velocity profile by an exponential expression.

$$v = v_s(1 - e^{-\mu r/R}) \quad (5.16)$$

where v_s is the surface velocity. As shown in Chapter 2

$$v_s = \Gamma e/c \quad (5.17)$$

The approximation (Fig. 5.4) has the correct limiting values at $r = 0$ and $r = R$, but is flatter than the calculated velocity profile. The approximation was chosen because it provides a very good fit to the velocity divergence ($-\dot{\rho}/\rho$) as shown in Fig. 5.5. From $r/R = 0.1$ to 0.9 , the approximation and the calculation are within 10% of each other. At $r = 0$ and $r = R$, the error is $\sim 20\%$. The small radius error is insignificant because the small liquid mass at small radius. The error at the outer radius is evaluated in this section.

The constant, μ , is found by requiring the velocity divergence

Fig. 5.5. Glenn's calculated velocity divergence ($-\dot{\rho}/\rho$) and analytic approximation.

$(\nabla \cdot \vec{v} = -\dot{\rho}/\rho)$ to match the hydro-code calculations at $r = 0$ and $r = R$.

$$\begin{aligned} -\dot{\rho}/\rho = \nabla \cdot \vec{v} &= \begin{cases} \frac{1}{r^2} \frac{\partial}{\partial r}(r^2 v) & , \text{ 3-D} \\ \frac{1}{r} \frac{\partial}{\partial r}(rv) & , \text{ 2-D} \end{cases} \\ &= \begin{cases} \frac{v_s}{r^2} \frac{\partial}{\partial r}(r^2 - r^2 e^{-\mu r/R}) & , \text{ 3-D} \\ \frac{v_s}{r} \frac{\partial}{\partial r}(r - r e^{-\mu r/R}) & , \text{ 2-D} \end{cases} \\ &= \frac{v_s}{R} [\mu e^{-\mu r/R} + \frac{D_4 R}{r} (1 - e^{-\mu r/R})] \end{aligned} \quad (5.18)$$

where D_4 is $D-1$ and D is the number of dimensions.

The two limits are

$$\begin{cases} -\frac{\dot{\rho}}{\rho} |_{(r=R)} = \frac{v_s}{R} [D_4 + (\mu - D_4)e^{-\mu}] \\ -\frac{\dot{\rho}}{\rho} |_{(r=0)} = \frac{v_s}{R} [\mu + D_4\mu] = \frac{v_s}{R} (D\mu) \end{cases} \quad (5.19)$$

where L'Hôpital's rule was used to evaluate the second term in the second limit.

The ratio of the two limits is

$$[(\frac{\dot{\rho}}{\rho})_{(r=R)} / (\frac{\dot{\rho}}{\rho})_{(r=0)}] = [D_4 + (\mu - D_4)e^{-\mu}] / D\mu \quad (5.20)$$

For $\mu \gg 1$, the case of interest, the ratio becomes $D_4/(D\mu) = (1 - 1/D)/\mu$, or $2/(3\mu)$ in 3-D and $1/(2\mu)$ in 2-D.

$$\mu = (1 - \frac{1}{D}) \frac{(\frac{\dot{\rho}}{\rho})_{(r=0)}}{(\frac{\dot{\rho}}{\rho})_{(r=R)}} \quad (5.21)$$

For Glenn's 3-D examples, μ was 10.4 and 7.9 at mach numbers of 0.01 and 0.1, respectively. The mach number, v_s/c , is much less than one for cases of interest here. The value of μ can be substituted in Eq. 5.18 to produce a radially-dependent velocity divergence. In Section 5.3.1., this quantity was approximated as Dv_s/R everywhere. For the exponential velocity profile, the surface velocity divergence is $(D-1)v_s/R$.

Including the full velocity divergence equation produces a correction factor, v , in the fragment size equation

$$a = v \left[\frac{D_3}{\rho_m} \gamma \left(\frac{R_0}{r_e} \right)^{2/3} \right] \quad (5.22)$$

where $D_3 = D+2$. The correction factor, v , is a function of the dimensionless position, r/R , within the original liquid

$$v = \left\{ \frac{1}{D} \left[\mu e^{-\mu r/R} + \frac{D_4 R}{r} (1 - e^{-\mu r/R}) \right] \right\}^{-2/3} \quad (5.23)$$

where $D_4 = D-1$ and D is the number of dimensions.

The correction factor is plotted in Fig. 5.6 for $\mu = 10$. To illustrate the insensitivity to μ , the curves are also plotted at $\mu = 5$ and $\mu = 20$ (boundaries of the bands). The fragments near the drop center will be up to an order of magnitude smaller than the prediction based on the surface velocity. Based on the 3-D velocity approximation, the outermost fragments will be up to ~ 31% larger than the prediction based on the average velocity divergence. However, the velocity approximation underestimates the velocity divergence at the surface, leading to an overprediction in fragment size. When the actual hydro-code $(-\dot{\rho}/\rho)$ value at $r = R$ is

Fig. 5.6. Fragment size correction factor for the Grady-Glenn model. The correction accounts for the fragment's original position within the liquid drop.

used, the fragment size overprediction from the averaged equation is only 13%.

Even after this correction, the theory still assumes local homogeneity within the fragment (see Eqs. 5.8 and 5.9). Hence, for large fragment size (a approaching R), the model continues to break down because $\dot{\rho}$ is not constant in the original (homogeneous) liquid.

5.3.3. Application to Several ICF Reactors

Table 5.1 shows the predicted fragment sizes from Eq. 5.14 for the various ICF reactor geometries described in Table 2.2. (Simple hydrodynamic calculations of the velocity divergence would also allow radially dependent fragment size predictions using the methods of Section 5.3.2.) Table 2.2 also compares the fragment dilational kinetic energy to the fragment translational energy. These values are calculated from the fragment specific kinetic energy (kinetic energy per unit mass),

$$K_m = \frac{1}{2} v^2 = \frac{1}{2} \left(\frac{\Gamma_e}{c} \right)^2 \quad (5.24)$$

and the fragment dilational specific kinetic energy calculated from Eqs. 5.9 and 5.11 with $v = v_s$,

$$\frac{K_v}{\rho_m} = \frac{1}{\rho_m} \frac{(\dot{a}\rho_m)^2}{D_2 \rho_m}; \text{ and } \dot{\rho}_m = -D\rho_m v_s/R \quad (5.25)$$

$$\frac{K_v}{\rho_m} = D_5 \left(\frac{\Gamma_e}{Rc} \right)^2 = D_5 \left(\frac{\gamma \Gamma_e}{\rho_m R c} \right)^{2/3}$$

where $D_2 = 2D(D+2)$, $D_5 = D/[2(D+2)]$, and $D_6 = D(D+2)^{1/3}/2$.

The fragment translational specific kinetic energy is the difference $K_m - K_v/\rho_m$. As Table 5.1 shows, almost all the kinetic energy is translational; only a small fraction is in dilation of the fragments.

The low energy density reactor concepts are predicted to have little or no fragmentation. For the high energy density MYLIFE inner jets, the model (Table 5.1) predicts fragment diameters of ~ 1% of

Table 5.1. Predicted fragmentation in several ICF reactors. The fragmentation was calculated from the formula for unconstrained spheres.

Reactor	Fluid ^{††}	Thick. (cm)	Fragm. Diam. (cm)	Suddenly added specific energy (J/kg)	Transl. specific kinetic energy (J/kg)	Dilational specific kinetic energy (J/kg)
HYLIFE inner jet	Li	20	0.21	800,000	15,800	1
HYLIFE outer jet	Li	20	1.3	50,000	61.6	0.16
HIBALL (inner jet, ignoring SiC sock)	LiPb	3	1.8	500	0.14	0.013
Modified Wetted Wall ^{†††}	Li	4	2.7	3500	0.22	0.081
EAGLE	Li	0.05	0.14 [†]	3700	0 [†]	0.34 [†]
Pulse*Star	LiPb	1	0.53	1000	0.58	0.042

[†] No breakup predicted by the energy minimization model.

^{††} LiPb is $\text{Li}_{17}\text{Pb}_{83}$

^{†††} Liquid motion is not in diverging geometry.

the jet diameter. The overall MYLIFE fragmentation will increase the liquid surface area by about two orders of magnitude during the period that the hot gas caused by ablation blows through the jet array (60-300 μ s after the fusion pulse). After the hot gas blows through the fragmenting array, the fragment translational energy distribution (higher velocities for the fragments from the inner jets) causes the fragments to coalesce at several ms after the pulse. Then, the coalesced liquid again fragments due to its uniform motion in a diverging geometry. The fragment size distribution during this later period determines the condensation rate, at least until homogeneous nucleation begins. The fragment size distribution during the period the gas transits the array influences the early stages of gas cooling and the structural load imposed when the gas reaches the wall.

5.3.4. Application to Small Lennard-Jonesium systems

The fragment size predictions of this chapter have been in terms of system and fragment radii. In this section, the models are reformulated into the variables observed in the molecular dynamics experiments to be discussed in Chapter Seven.

For the molecular dynamics runs, the fragment data is in terms of population rather than radius.

$$N_C = \rho \left(\frac{D+1}{D}\right)^{D-2} \pi R^D, \quad N = \rho \left(\frac{D+1}{D}\right)^{D-2} \pi R^D \quad (5.26)$$

The reduced molecular dynamics units allow replacement of the mass density, ρ_m , with the atomic density, ρ . Finally, the equation of state data (Section 4.2) provides the pressure increase directly as a function of density and temperature.

$$P \sim \Delta P = \rho \Gamma e \quad (5.27)$$

Thus, the four model predictions become

$$N_C = \pi \left(\frac{D+1}{D}\right)^{D-2} \rho \left[\frac{(D-1)\gamma}{P}\right]^D \quad (\text{Model 1}) \quad (5.28)$$

$$N_C = \pi \left(\frac{D+1}{D}\right)^{D-2} \rho^{D+1} [2(D-1)\gamma]^D \left(\frac{e}{P}\right)^{2D} \quad (\text{Model 2}) \quad (5.29)$$

$$N_C = [\pi (D+2)^D \left(\frac{D+1}{D}\right)^{D-2} \gamma^D \rho^{D+1} \left(\frac{e}{P}\right)^{2D}]^{1/3} N^{2/3} \quad (\text{Model 3}) \quad (5.30)$$

$$N_C = \left(\frac{2e\gamma}{\delta}\right)^{D/2} \left(\frac{e}{P}\right)^D N \quad (\text{Model 4}) \quad (5.31)$$

In two and three dimensions, model 3 is

$$N_C/N = \left[\frac{16\pi}{N} \gamma^2 \rho^3 \left(\frac{e}{P}\right)^4\right]^{1/3} \quad (5.32)$$

$$N_C/N = \left[\frac{500\pi}{3N} \gamma^3 \rho^4 \left(\frac{e}{P}\right)^6\right]^{1/3} \quad (5.33)$$

The second test of model 3 by the molecular dynamics results is kinetic energy generation. The planar result (Eq. 5.24) is,

$$K/N = \frac{1}{2} \left(\frac{\Gamma e}{c} \right)^2 = \frac{1}{2} \left(\frac{P}{\rho c} \right)^2 \quad (5.34)$$

Glenn's⁴⁶ results show that this equation also approximately applies in spherical geometry. However, the kinetic energy to be measured is the translational energy of the fragments; some of the kinetic energy of the jump-off velocity is manifested as dilational energy of the fragments, thus making Eq. 5.34 an upper-bound for the translational energy generation. In two and three dimensions, model 3 (Eqs. 5.24 and 5.25) predicts,

$$I_{tr} = \begin{cases} \frac{1}{2} \left(\frac{P}{\rho c} \right)^2 \left[1 - \frac{3}{5} \left(\frac{N_c}{N} \right)^{2/3} \right] & , \text{ 3-D} \\ \frac{1}{2} \left(\frac{P}{\rho c} \right)^2 \left[1 - \frac{1}{2} \left(\frac{N_c}{N} \right) \right] & , \text{ 2-D} \end{cases} \quad (5.35)$$

These equations approach the correct upper bound under extreme fragmentation ($N_c \rightarrow 0$). However, they do not approach the correct lower bound of zero for no-fragmentation; this is a consequence of the assumption of a homogeneous expansion in model 3.

Because calculation of the surface tension requires use of the molecular dynamics model, numerical predictions are not made until Chapter Seven, after the molecular dynamics model is introduced in Chapter Six. Also, although the pressure is used directly in Eqs. 5.28 to 5.35, the specific energy increase, e , and the Grüneisen parameter, Γ , are also evaluated in Chapter Seven to allow comparison of the factors in the molecular dynamics simulations with the analogous factors in the ICF reactor predictions.

5.4. Evaluation of the Force and Energy Balance Models

The development of the Grady-Glenn model was very exciting because it gave intuitively reasonable estimates of fragment size. However, the model is too simple in that it only considers the lowest final energy state and it only considers spherical or circular (cylindrical) fragments. The model does not attempt to find the path between the initial state and the optimum final state. There could be potential barriers; that is, the path between the states might pass through a state of higher energy. In that case, the optimum state might not be reached during the time of interest.

Isochorically heated drops could begin to break up in two ways. In the first, the growing relief wave could cause cavitation at some depth into the drop, and an onion skin fragment would result. Since the skin area increases as it expands outward, it will stretch and break, perhaps by some surface instability mechanism. The drop size might then be of order the onion skin thickness. (This mode is expected for films on surfaces, such as the MWW or the liquid on the outsides of the HIBALL socks.) The second breakup mode would be to fragment the drop into wedges with radial fracture lines (see Fig. 7.21 for snapshots during breakup). If the wedges are longer than they are wide, they could either collapse into spheres, or they could fragment further due to velocity gradients or surface waves. Breakup by either of these initial modes could change the local kinetic energy density and, thus, require revised calculations using the Grady-Glenn model. Or, they could lead to further non-spherical breakup.

Because the circumferential strain is identical to the radial

strain in a homogeneous expansion, neither the onion skin nor the wedge modes are expected to dominate (and neither mode does dominate in the molecular dynamics experiments - see Fig. 7.21).

Chapter 6: Molecular Dynamics Experiment Development

In Chapter Five, models were developed to predict fragment size and velocity distributions. Grady has tested model 3 for solid fragmentation, no other tests have been attempted. In this chapter, a molecular dynamics (MD) technique is developed; it will be used to test models 1 to 4 at a microscopic scale in Chapter Seven.

In Section 6.1, previous MD calculations are summarized. In Section 6.2, the equations of motion are formulated in finite difference form. In Section 6.3, the model is applied using a parabolic (harmonic) potential energy function, and the failure of this potential energy function is explained. In Section 6.4, the Lennard-Jones potential is used to test the MD model. In Section 6.5, a new startup procedure is developed to produce an equilibrium circular system. This procedure begins with a zero-temperature expanded hexagonal crystal. Surface tension implodes and melts the crystal and a moving repulsive wall confines the melted atoms in a circle of the appropriate size. (Without the wall, the system would fragment before the desired initial conditions are reached.) Then, by repeatedly adjusting the velocities, the desired initial (equilibrium) temperature is established. The resulting configuration and velocities are used to initiate the fragmentation problem with no restraining wall. (Removal of the wall is necessary to allow expansion and fragmentation.) In Sections 6.6 and 6.7, graphic and tabular output from the molecular dynamics calculations are described. Finally, in Section 6.8, memory utilization and computational efficiency are discussed.

6.1. Previous Molecular Dynamics Modeling of Liquids

Molecular dynamics allows study of fluids at the atomic level. Once a potential energy function is specified, the equations of motion for all the atoms can be solved and the motion determined as a function of time. Solution of the equations is straightforward. However, even with the ultra-fast CRAY-1 computer, only a few thousand atoms can be considered. For example, in this study, 14491 atoms were followed for a reduced time of ~ 110 (17 ps) at an expenditure of ~ 10.5 hours of CRAY CPU time. Abraham⁴⁸ has followed over 161,000 atoms for ~ 200 ps at an expenditure of ~ 70 hours of IBM/370-3081 CPU time, yet even this large effort only considered $\sim 10^{-17}$ g of material. Thus, macroscopic systems cannot be directly simulated.

Fortunately, study of small systems has shown that macroscopic properties can be calculated at microscopic scale.^{49,50} Most molecular dynamics calculations avoid consideration of artificial surfaces around the microscopic calculation region by using periodic boundary conditions. This method works well if the wavelength of the phenomenon of interest does not exceed the size of the periodic system, the usual case. Reference 51 includes a list of molecular dynamics publications, most of which use periodic boundary conditions. Hoover^{49,50} has provided several clear examples of the usefulness of molecular dynamics calculations using as few as two atoms with periodic boundary conditions.

A much smaller number of molecular dynamics studies have considered finite systems with actual surfaces. Brodskaya and Rusanov^{38,52} studied three-dimensional systems with 32 to 500 atoms for periods of ~ 50 ps. They found that the surface tension

increases from zero to its macroscopic (asymptotic) value as the drop radius increases to $\sim 3.5\sigma$. More recently, Thompson, et al.²⁹ studied three-dimensional systems with 54 to 2048 atoms for much longer periods (70 times more time steps). They found that although the drop configuration is non-spherical at any instant, the time averaged configuration is spherical. Thompson's study also showed that for drop radii greater than 7.5σ , there is less than 3% error in the internal pressure due to assumption of constant surface tension and replacement of the radius of tension by the slightly larger equimolar radius (i.e. replacing $P_{\text{inside}} - P_{\text{outside}} = 2\gamma_s/R_s$ by $2\gamma_m/R_e$), and that there is negligible error for radii $> 10\sigma$.

For ICF reactor situations, macroscopic drops are expected to fragment into smaller macroscopic drops; in this regime, the surface tension is independent of system size. The molecular dynamics simulations should ideally be conducted in a system large enough that the properties are size independent, but computer limitations do not permit such a constraint. In this study, the molecular dynamics calculations used systems with initial radii of $\sim 10\sigma$, 20σ , 40σ and 90σ . For the smaller fragments from these systems, the predicted surface energy (based on constant γ) is too large, raising the predicted fragment size above the correct value (Fig. 6.1).

One should also note that the size dependence of surface tension also affects the critical nucleus size. Since the surface forces are smaller than predicted by constant γ for critical nuclei with radii less than 7σ , the unstable equilibrium occurs at a higher than expected size, and homogeneous nucleation will be slower than anticipated (see Fig. 4.19).

Fig. 6.1. For small fragments, the surface energy is lower than predicted by constant γ , leading to smaller fragments than expected.

6.2. Solving the Equations of Motion

The molecular dynamics model was developed in two, rather than three, dimensions for three reasons. First, a larger region can be considered without increasing computation time. Second, two dimensional motion is easily presented graphically. Finally, for cylindrical jets found in several ICF reactors, expansion in the axial direction is initially negligible compared to the two-dimensional radial expansion. However, extension of the model to three dimensions is straightforward.

The acceleration for each atom is simply the force per unit mass,

$$\frac{\vec{x}_+ + \vec{x}_- - 2\vec{x}_0}{(\Delta t)^2} = \frac{\vec{F}}{m} \quad (6.1)$$

$$\rightarrow \vec{x}_+ = 2\vec{x}_0 - \vec{x}_- + \vec{F}(\Delta t)^2/m$$

where $\vec{x}_+$ is the atom location after the next time step, $\vec{x}_0$ is the current location, and $\vec{x}_-$ is the location before the previous time step. The force is found from the potential

$$\vec{F} = -\frac{\partial \Phi}{\partial \vec{r}} \quad (6.2)$$

The force equation is applied to each of the $\binom{N}{2} = N(N-1)/2$ pairs of nodes, where N is the number of atoms. Of course, for most pairs, the force is zero because a limited range is assumed for the interatomic potential. For example, before fragmentation, only ~10% and 0.5% of the pairs are non-zero for two-dimensional 127 and 2611 atom systems, respectively. Each pair is checked only once, and $(\vec{F}_{ij})$ is set to $(-\vec{F}_{ji})$. When neighbor listing is employed, only a

subset of the possible pairs is checked. When adequate motion has occurred, the neighbor list is reconstructed to insure non-zero pairs are not overlooked (see Section 6.8).

For startup, the array $\vec{X}_-$ must be specified.

$$\vec{X}_- = \vec{X}_0 - \vec{V}\Delta t \quad (6.3)$$

Hence, the problem may be started by initially setting the velocities to zero and setting the bonds to non-rest lengths, or vice versa.

If the velocities are zero, it is a zero temperature problem and the node array will initially retain radial symmetry if the problem starts with radial symmetry (unless either melting or computer round-off errors destroy the symmetry). In this case, the initial node positions are adjusted from their rest positions

$$\begin{aligned} x_1 &= x_1(1 + \epsilon_{xx}) + y_1(1 + \epsilon_{xy}) \\ y_1 &= y_1(1 + \epsilon_{yy}) \end{aligned} \quad (6.4)$$

where x_1 and y_1 are the components of $\vec{x}_1$ and the strains are functions of the displacement vector,

$$\begin{aligned} \epsilon_{xx} &= du_x/dx \\ \epsilon_{yy} &= du_y/dy \\ \epsilon_{xy} &= (du_x/dy) + (du_y/dx) \end{aligned} \quad (6.5)$$

If the temperature is non-zero, the velocity components of all N particles must be randomly assigned. First, a random number, r_1 , between $(-10 (kT/m)^{1/2})$ and $(+10 (kT/m)^{1/2})$ is generated. Then a second number, r_2 , between 0 and 1 is generated. If $r_2 < \exp(-\pi r_1^2/2kT)$, the velocity component under consideration is set to value r_1 ; if not, two new random numbers are generated. This

procedure results in the Maxwell-Boltzmann velocity distribution shown in Fig. 6.2.

Once all the initial velocities are selected, they are adjusted so the array has no net initial momentum.

$$v_{\text{new}} = v_{\text{old}} - \frac{1}{N} \sum_1 v_{\text{old}} \quad (6.6)$$

Then, the velocities are adjusted so $(1/2mv^2)_{\text{avg}} = 1/2 kT$ for each velocity component,

$$v_{\text{new}} = v_{\text{old}} \left[\left(\frac{kT}{m} \right) / \frac{1}{N} \sum v_{\text{old}}^2 \right]^{1/2} \quad (6.7)$$

where the equation is applied separately to the x and y components of the velocities. Summing the squares of the new velocities produces $v_{\text{avg}}^2 = kT/m$ for each component.

The time step was set by requiring that energy conservation be maintained. Since the atoms are moved to their new positions based on the forces and velocities at their current positions, the motion during one time step must be small enough that the forces don't drastically change. From an energy viewpoint, if a time step reduces an atomic separation into the range where the potential energy function is steeply repulsive, energy is spuriously added to the system. On subsequent steps, the energy will be transferred to these very particles, resulting in motion of the energized atom past many other atoms in a single time step.

Equation 6.1 can be written as

$$\vec{x}_+ - \vec{x}_0 = \vec{x}_0 - \vec{x}_- + \frac{\vec{F}(\Delta t)^2}{m} \quad (6.8)$$

Fig. 6.2. Velocity distribution function used to randomly generate the initial velocities.

The quantity $\vec{x}_0 - \vec{x}_1$ is $-\vec{v}(At)$. If it is assumed that motion, $(\vec{x}_1 - \vec{x}_0)$, is limited to 10% of some specified interatomic spacing, d , the equation becomes

$$\vec{d}/10 = \vec{v}(At) + \vec{F}(At)^2/m \quad (6.9)$$

This quadratic equation has the solution

$$At = (-\vec{v} + [\vec{v}^2 - 4(\frac{\vec{F}}{m})(\frac{\vec{d}}{10})]^{1/2}) / \frac{2\vec{F}}{m} \quad (6.10)$$

To utilize the equation, values of $\vec{v}$, $\vec{F}$ and $\vec{d}$ are required. The velocity, $\vec{v}$, is

$$\vec{v} = (\frac{2kT}{m})^{1/2} \quad (6.11)$$

The distance, $\vec{d}$, is the equilibrium spacing for a perfect crystal at the given density or strain (using Eq. 6.4). There are two choices for the force. If the equilibrium crystal spacing is small so that a large repulsive force exists, that force is used. If the equilibrium crystal spacing is large so the force is attractive, the maximum possible attractive force for the potential function is used; i.e., the force at the interatomic separation for which

$$-\frac{\partial F}{\partial r} = \frac{\partial^2 \phi}{\partial r^2} = 0 \quad (6.12)$$

In the computer code, the default time step was reduced by another factor of ten. Then a time step reduction factor was input during each run. After some experimentation using the LJ potential, a value of 0.4 was found to consistently conserve energy while smaller values did not. Thus, the normal time step is the product of Eq. 6.10 and $1/(10 \cdot 0.4)$, i.e., 25% of equation 6.10 (0.003 ps is typical).

6.3. The Unsuitability of the Parabolic Potential

A simplified potential energy function for a lithium bond is shown in Fig. 6.3. The function was constructed by first assuming two parabolic forms that have equal first derivatives at the connection point. This procedure works well for molecular dynamics calculations of solids.

The low point on the potential curve is at the bond rest length (r_0), and it was set so that the interparticle spacing is consistent with the specific volume at the melt temperature (453.7 K). As shown in Section 4.2, $r_0 = 3.123 \times 10^{-10}$ m for lithium. The point at which the two parabolas in the potential join, r_j , is set by the specific volume at the isothermal spinodal, v_j . (In retrospect, the isentropic spinodal would have been a better choice.) The spinodal point is the place where $(\partial P / \partial V)_T = 0$. Since pressure is proportional to force or $(-\partial \phi / \partial r)$, the spinodal point corresponds to the inflection point in the potential curve, i.e., r_j . If the lithium is expanding isentropically from an initial condition reached by adding 800 J/g to 500°C saturated liquid, the spinodal line is reached at a specific volume of

$$v_j = 0.00325 \text{ m}^3/\text{kg} = 3.745 \times 10^{-29} \text{ m}^3/\text{atom}$$

as shown in Section 4.3. Or,

$$r_j = 4.051 \times 10^{-10} \text{ m} \quad (6.13)$$

where equation 4.21 was used to specify the hexagonal-close-packed layer spacing. Thus, the parabolas join at a bond length of 130% of the rest length.

Fig. 6.3. The lithium parabolic potential energy function and its associated force function. Positive forces are repulsive (compression) and negative forces are attractive (tension).

Since the simplified potential function is constructed from two identical parabolas, only their curvature, $\partial^2\phi/\partial r^2$, is required to specify the potential function. This quantity can be obtained from the isentropic bulk modulus

$$B = -V \left(\frac{\partial P}{\partial V} \right)_S \quad (6.14)$$

Equation 6.14 can be manipulated

$$B = -V \left(\frac{\partial P}{\partial r} \right) \frac{\partial r}{\partial V} = - \left(\frac{Nr^3}{\sqrt{2}} \right) \frac{\partial P}{\partial r} \left(\frac{-\sqrt{2}}{3Nr^2} \right) = - \left(\frac{r}{3} \right) \frac{\partial P}{\partial r} \quad (6.15)$$

The static pressure is

$$P = - \frac{\partial E}{\partial V} = -6N \left(\frac{\partial \phi}{\partial r} \right) \frac{\partial r}{\partial V} = - \left(\frac{2\sqrt{2}}{r^2} \right) \frac{\partial \phi}{\partial r} \quad (6.16)$$

where the multiplier, $6N$, indicates that each of the 12 bonds per atom is shared between two atoms. Equations 6.15 and 6.16 can be combined

$$B = \left(\frac{r}{3} \right) \frac{\partial}{\partial r} \left[\frac{2\sqrt{2}}{r^2} \frac{\partial \phi}{\partial r} \right] = \frac{2\sqrt{2}}{3r} \left[\frac{\partial^2 \phi}{\partial r^2} - \frac{2}{r} \frac{\partial \phi}{\partial r} \right] \quad (6.17)$$

At the bond rest position (again taken as being at T_m), $r = r_0$ and $(\partial\phi/\partial r) = 0$. Then $(\partial^2\phi/\partial r^2) = 3 r_0 B_m / 2\sqrt{2}$ for all r since a parabolic potential function has a constant curvature. The bulk modulus at the melting point is,

$$B_m = -V_m \left(\frac{\partial P}{\partial V} \right)_S \quad (6.18)$$

The factor $(\partial P/\partial V)_S$ is the slope on a P-V diagram of the isentrope passing through the intersection of the saturated liquid curve and the T_m isotherm. When this diagram was constructed in Section 4.3,

$$\left(\frac{\partial P}{\partial V}\right)_S = -5.464 \times 10^{12} \text{ Pa}/(\text{m}^3/\text{kg})$$

$$B_m = 10,550 \text{ MPa} \quad (6.19)$$

$$\frac{\partial^2 \phi}{\partial r^2} = 3.495 \frac{\text{J}}{\text{m}^2}$$

The equation for the potential is

$$\phi = \begin{cases} \frac{1}{2} b (r-r_0)^2 - \epsilon & , \quad r \leq r_j \\ -\frac{1}{2} b (r-r_b)^2 & , \quad r_j < r < r_b \\ 0 & , \quad r \geq r_b \end{cases} \quad (6.20)$$

where $r_b = r_j + (r_j - r_0) = 4.979 \times 10^{-10} \text{ m}$ and b is $\partial^2 \phi / \partial r^2 = 3.495 \text{ J/m}^2$. The curves join at $r = r_j = 4.051 \times 10^{-10} \text{ m}$. The value of ϵ is found by setting the two equations equal at that point,

$$\epsilon = b(r_j - r_0)^2 = 3.01 \times 10^{-20} \text{ J} \quad (6.21)$$

The potential also has a continuous slope where the two parabolas join.

A check on the value of ϵ can be made by realizing that complete vaporization of one atom requires breaking about twelve bonds (in three dimensions) with each bond being shared by two atoms, i.e., breaking about six bonds per atom. Thus, six times the depth of the potential well ($6\epsilon = 1.81 \times 10^{-19} \text{ J/atom} = 15.7 \text{ kJ/g}$) should be and is comparable to the known cohesive energy of lithium (23.03 kJ/g) less the heat required to convert room temperature lithium to just melted lithium (1.03 kJ/g), i.e., comparable to 22.0 kJ/g. Therefore, the value of ϵ computed from the bulk modulus and the spinodal density is consistent with the heat of vaporization.

To simplify the initial calculations, reduced units (in which r_0 , m , b , and Boltzmann's constant are numerically 1.0) were used. In addition, r_j was set to $1.15 r_0$ (compared to $1.3 r_0$ in the actual potential), and r_b was set to $1.3 r_0$ (compared to $1.6 r_0$ in the actual potential). These latter changes reduced the number of weak attractive bonds and decreased the calculation time.

The resulting simplified parabolic potential is

$$\phi = \begin{cases} \frac{1}{2} (r-1)^2 - 0.0225 & , r \leq 1.15 \\ -\frac{1}{2} (r-1.3)^2 & , 1.15 < r < 1.3 \\ 0 & , r \geq 1.3 \end{cases} \quad (6.22)$$

The well depth of 0.0225 is dictated by requiring the potential to be 50% of the well depth at $r = 1.15 r_0$ ($r_0 = 1$).

The simple parabolic potential was used with an initial condition of 10% compression of each bond for a 127 atom system. A movie of the atom locations clearly shows the motion of a tensile relief wave from the surface into the center of the atomic array. A second movie of the two-dimensional strain along one axis of the array shows that the tensile wave grows in magnitude as it converges to the center of the array and that the pressure behind the wave is zero. When the wave reaches the center, the bonds linking the central atom with the first surrounding hexagonal row of atoms are broken. A compression wave then moves out to the surface, reflecting as a tensile wave, and the process is repeated. Only the first passage of the wave is easily followed since the various reflected waves interfere; however, when the second tensile wave reaches the center, the large magnitude of the

strain and the breaking of bonds are easily recognized.

Since the initial calculation demonstrated the ability to follow waves and break bonds, the lithium properties (r_j and r_b) were reincorporated into the simple parabolic potential for a 127 atom system. A 13.4% compression initial condition was imposed, corresponding to 1600 J/g if the energy is only in planar bonds or 800 J/g if the energy is in all the bonds (3-D). For this initial condition, each lithium atom was repulsively connected to the six atoms in the first row of neighbors and attractively connected to the six of the twelve atoms in the second row of neighbors. The initial motion of the outer row of atoms was outward, as before. However, the next row moved inward since it saw balanced repulsion forces and unbalanced (inward) attractive forces. The inward motion compressed a ring and connected other second neighbor bonds, accelerating the implosion. The outer row turned around, and all the atoms moved to a small central region until over 5000 of the 8001 possible bonds were formed. At this density, many of the bonds were so short that the total of the repulsive forces was large enough to halt the implosion. At late times, there was a tight, non-symmetrical, pulsating core with a number of ejected atoms moving away at high speeds (up to 30 km/s). This configuration is not realistic, as will be discussed shortly.

The lithium parabolic potential was also used with an initial condition of 445°C instantaneous temperature rise, where the energy was distributed randomly to all bonds in the 2-D mesh. This temperature rise corresponds to 800 J/g deposited into 3-D atomic kinetic energy. The velocities moved some of the atoms close enough for second neighbor attractive bonds to form in several regions. The

attractive bonds pulled more atoms into the compressed regions, and the regions themselves converged and coalesced. At late times, the mesh looked qualitatively like the result of the compression initial condition--a pulsating compressed mass and high velocity ejected atoms.

Since suddenly heated liquids should not implode, the Hooke's law (parabolic) lithium potential must be too simple. One major source of trouble is the small potential at zero spacing due to the insufficiently steep parabolic equations. To see if the potential is stable against implosion, the energy per atom of an infinite mesh having the bonds at the rest position was compared to the energy of the same mesh having two or more atoms per site. In the first case, each atom has six bonds at the well depth, and each bond is shared with another atom. Thus, the total 2-D potential per atom is three times the well depth. In the case with n atoms per site, each atom has one-half share of $6n$ well depths (ϕ_w) and $(n-1)$ y-intercepts (ϕ_0).

$$n\text{-atom per site mesh: } \phi = -\frac{6n}{2} \phi_w + \frac{(n-1)}{2} \phi_0 . \quad (6.23)$$

The potential is unstable if it decreases when the number of atoms per site increases; this condition is satisfied when $\phi_0 < 6 \phi_w$.

For the simplified potential, $\phi_0 = 21.2 \phi_w$, and the potential was stable.

For the lithium potential, $\phi_0 = 4.65 \phi_w$. Because this value is below the stability limit, implosion to multiple atoms per site is favored. However, the situation is more complex, as can be seen by considering the four infinite mesh configurations in Table 6.1. The atomic mesh was initially compressed (#2 in

Table 6.1). The potential with all bonds at their rest lengths (#1 in Table 6.1) is energetically favored, but the forces move much of the mesh in the opposite direction, toward multiple atoms per site (#4) which is energetically favored over both the initial configuration and the rest positions. However, there is an intermediate configuration with single atoms per site and highly compressed bonds (#3) that is favored over all of the other three configurations because there are no bonds with positive potential and many bonds with negative potential. Thus, the mesh implodes, but not completely to multiple atoms per site. The occasional ejection of a few atoms of the mesh is caused by stress concentrations due to the reflecting tensile waves and by thermal fluctuations.

Because of the failure of the parabolilc potential, the more realistic Lennard-Jones potential is used in the remainder of the molecular dynamics simulations.

Table 6.1. Potential per atom. The totals are the number of bonds per atom divided by two (for sharing) times the potential.

Description	Bond Length	Number per atom	Potential ($\times 10^{-20}$ J)	Total (10^{-20} J/atom)
#1 All bonds at rest length	3.123	6	-3.01	-9
	5.409	6	9	<u>0</u>
				-9
#2 All bonds at (0.866) rest length	2.705	6	-2.75	-8.25
	4.685	6	-0.2	-0.6
	5.4	6	0	<u>0</u>
				-8.85
#3 All bonds at (0.583) rest length	1.82	6	0	0
	3.152	6	-3.0	-9
	3.64	6	-2.6	-7.8
	4.815	12	-0.03	-0.18
	5.46	6	0	<u>0</u>
				-16.98
#4 Two atoms per site, rest length	0	1	14.0	7.0
	3.123	12	-3.01	-18.06
	5.409	12	0	<u>0</u>
				-11.06

6.4. The Lennard-Jones (6-12) Potential

In the previous section, the lithium equation of state was represented by a simple parabolic potential. The potential was unsatisfactory because it was insufficiently repulsive at small interatomic spacings. In this section, the steeper Lennard-Jones (LJ) potential is added to the model.

The Lennard-Jones potential and force functions were shown in Fig. 4.5, and the equations were presented in both SI and reduced units in Section 4.2. That section also showed the P- ρ and T-P phase diagrams for two-dimensional Lennard-Jonesium as derived by Barker.²²

The LJ molecular dynamics model (Eqs. 4.25 which use $\sigma = \epsilon = k = m = 1.0$) was tested for a number of initial density and temperature combinations using a 127 atom system. These calculations all began with a perfect solid crystal at the appropriate density and with a randomly generated velocity distribution that produced the correct kinetic energy corresponding to the temperature. The evolution of the system in time was then observed. The initial conditions for the test runs are shown in Fig. 6.4.

The first test run (A on Fig. 6.4) was for a cold solid ($\rho = 0.92$, $T = 0.3$). Figure 6.5 shows the paths followed by the atoms during the first 10.2 reduced units of time (1.5 ps). The lattice remained hexagonal with the atoms moving in small displacements around their equilibrium positions.

The next test run (B) was for a vapor ($\rho = 0.03$, $T = 0.45$). Figure 6.6 shows a set of four time exposures of the atom paths. The total elapsed time is 63 reduced units (9.2 ps). The long mean free

Fig. 6.4. Initial conditions for the calculations that tested the molecular dynamics model against the published phase diagram.

Fig. 6.5. Time evolution of a solid. The atoms never move far from their equilibrium positions, and the system retains its shape. The diamonds mark the final positions of each atom at the end of the time exposure. The two parallel lines at the upper left of the frame are scale lines that should be ignored. The length scale of 10 reduced units corresponds to 2.8 nm.

Time 0 to 10.23

Fig. 6.6. Time evolution of a gas. The four sequential time exposures indicate long mean free paths and an expanding system.

paths and expanding system are characteristic of the vapor phase.

Test run C was for a liquid ($\rho = 0.75$, $T = 0.45$). Figure 6.7 shows four sequential time exposures of the atom paths covering 38 reduced time units (5.5 ps). The vibrations around the equilibrium lattice points are large enough to allow atoms to escape from those equilibrium locations; i.e., to diffuse through the fluid. A few atoms near the edge escape the fluid altogether (to establish vapor pressure). Some atoms stay in a crystalline form; this is because the system has relaxed from its initial liquid state to below the triple line.

Test run D was for a solid-vapor mixture ($\rho = 0.75$, $T = 0.35$). Figure 6.8 shows four sequential time exposures covering 63 reduced time units (9.2 ps). The edge of the initially uniform system is expanding into vapor while the bulk of the system remains as a crystalline solid.

Test run E was for a liquid-vapor mixture ($\rho = 0.4$, $T = 0.45$). Figure 6.9 shows four sequential time exposures covering 15 reduced time units (2.2 ps). The initial uniform density region quickly separates into liquid drops and isolated vapor atoms.

Test run F was for a solid-liquid mixture ($\rho = 0.85$, $T = 0.6$). Figure 6.10 shows four sequential time exposures covering 32 reduced time units (4.6 ps). The core remains solid while the outer atoms move around the outer edge like a liquid film.

The purpose of these test runs was to qualitatively observe the evolution of systems beginning in various regions of the phase diagram. Test runs A, B, E, and F (solid, vapor, liquid-vapor and solid-liquid) evolved into the expected equilibrium figurations. Test

Fig. 6.7. Time evolution of a liquid. The four sequential time exposures show the diffusion of liquid atoms throughout the system, establishment of vapor pressure and relaxation to below the triple line (since some regions appear to be solid).

Time = 0 to 9.42

9.42 to 18.80

-10 0 10

-10 0 10

18.80 to 28.18

28.18 to 37.56

Fig. 6.8. Time evolution of a solid-vapor state.

Fig. 6.9. Time evolution of a liquid-vapor state.

Fig. 6.10. Time evolution of a solid-liquid state.

Time 0 to 7.9

7.9 to 15.7

15.7 to 23.6

23.6 to 31.5

-10 0 10 -10 0 10

runs C and D, (liquid and solid-vapor) looked similar because the systems both evolved into the solid-vapor region. At a long enough time, no liquid regions would remain in these two examples.

6.5. Establishing the Initial Density Starting With a Zero Temperature Solid

The molecular dynamic fragmentation experiments require an initial circular configuration with the desired density and temperature, and with the potential and kinetic (thermal) energies being in equilibrium. As a method of achieving the correct initial configuration, an easily described expanded-hexagonal solid at zero temperature was allowed to implode from its own surface tension. A surrounding repulsive wall was also converged until the appropriate average density was achieved. Then, the temperature was set by repeatedly adjusting the velocities until equilibrium was established.

The atoms were initially set up as a perfect hexagonal crystal at the appropriate density and with zero temperature (no initial velocities). A reduced density of 0.6 was chosen because it is near neither the critical nor the triple point density. At a density of 0.6, all the initial bonds are attractive. When time begins, the unbalanced forces on the outer atoms (i.e., surface tension) drives a collapsing process (Fig. 6.11 and 6.12). The induced atomic motion increases the temperature and melting is clearly observable; i.e., the atoms no longer remain in a fixed arrangement. To insure the desired final density, the initial hexagon is surrounded by a circular wall with an inward motion as described below. The potential between the atoms and the wall is purely repulsive and directed toward the array center.

Fig. 6.11. Circularization for a 271 atom system. The initial collapse is driven by surface tension, rather than the moving wall. The wall motion stops when the desired final (circular) area is enclosed.

Time 0 to 5

5 to 10

-15

0

15

-15

0

15

10 to 15

15 to 20

Fig. 6.12. Circularization for a 2611 atom system. The moving wall appears to be thick because it is drawn at several sequential times in each picture.

$$\begin{aligned} \phi &= \begin{cases} 4r^{-12} & , r \leq r_r \\ 0 & , r > r_r \end{cases} \\ F &= \begin{cases} 48 r^{-13} & , r \leq r_r \\ 0 & , r > r_r \end{cases} \end{aligned} \quad (6.24)$$

where r is the radial distance between the particle and the wall, F is directed radially inward, and r_r is the wall-particle force cut off distance. Here, $r_r = d_0$, where d_0 is the initial lattice spacing

$$d_0 = 1.12246 (0.91649/\rho)^{1/2} = 1.387 \text{ for } \rho = 0.6 \quad (6.25)$$

In Eq. 6.24, 1.12246 is the rest length (radius at the well depth), and 0.96149 follows from the hexagonal lattice density at the rest length

$$\rho\sigma^2 = 2/[\sqrt{3}(1.12246)^2] = 0.91649\sigma^2$$

The wall prevents any atoms from escaping (as vapor or as fragments) before the isochoric heating. During the calculation, the wall slowly moves inward until it reaches the point where the average density within the circle is the desired value. The initial wall radius is

$$R_i = (n_r + 1)d_0 \quad (6.26)$$

where n_r is the number of rows in the original hexagonal lattice.

The number of atoms in the lattice is

$$N = 1 + 3 n_r (n_r - 1) \quad (6.27)$$

In Fig. 6.11, the wall is initially one lattice spacing from the lattice while in all other runs, the wall was initially two lattice spacings away. Since the initial motion is determined by the unbalanced forces on the surface atoms (as shown in Figs. 6.11 and 6.12), the initial wall position is not critical.

The outer radius of the final circular array defines the same area as the initial hexagonal array (out to the final atom row, rather than the wall).

$$\pi(R_f - d_0)^2 = 6 \left(\frac{1}{2} [(n_T - 1)d_0] \left(\frac{\sqrt{3}d_0}{2} (n_T - 1) \right) \right) \quad (6.28)$$

where R_f is the final wall radius. This final wall position is one lattice spacing, d_0 , from the desired outer circle of atoms, and the repulsive force was chosen to be zero for this and larger standoffs. Equation 6.28 can be solved for R_f ,

$$R_f = d_0 \left[1 + (n_T - 1) \left(\frac{\sqrt{3}}{2} \right)^{1/2} \right] \quad (6.29)$$

The magnitude of the wall motion duration was set equal to the number of rows (in reduced time units). The wall velocity can then be found from equations 6.26 and 6.29,

$$v_w = -d_0 [0.090608 + 0.90939/n_T] \quad (6.30)$$

For 30 rows (2611 atoms), $v_w = 0.121$ (230 m/s). This is much slower than the wave speed measured during the early collapse which was 4.5 (8600 m/s). For 500°C lithium the sound speed is ~4500 m/s.

The time step was set to 0.01 reduced units (1.5×10^{-15} s) for the circularization calculation. Although this step was a bit small,

the low number of these calculations didn't merit searching for the largest allowable time step.

At the end of the circularization, the reduced temperature is ~ 0.54 (1650 K) for the 271 atom system. This temperature is in the liquid region on the phase diagram, and the final frame of Fig. 6.11 appears to be a fairly homogeneous liquid. For the 2611 atom system, the temperature after circularization is ~ 0.7 (2140 K). This temperature is also in the liquid region on the phase diagram, but the final frame of Fig. 6.12 indicates a non-equilibrium configuration. Almost all the atoms are in a ring of liquid that is against the confining wall. If the system continues to evolve with no further wall motion, a homogeneous configuration would eventually be formed, but at a different temperature than 0.7. However, it is better to equilibrate to the desired temperature as described in the next section. The only purpose of the circularization is to produce a circular area containing all the atoms at the correct average density.

6.6. Temperature Modification and Isochoric Heat Addition

The purpose of the equilibration calculation is to produce an equilibrium configuration with the correct average density and correct temperature. The non-equilibrium, but correct average density, configuration produced by the circularization code is the starting point for the equilibration calculation. The circularization and equilibration calculations are linked by a data file written at the conclusion of the circularization calculation. This file contains the positions and velocities of all the atoms. The two-point velocities are crude since they are based only on the current and previous atom positions,

$$\vec{v}_1 = [\vec{X}_1(t) - \vec{X}_1(t-\Delta t)]/\Delta t \quad (6.31)$$

These crude velocities are adequate to restart the calculation. Splitting the circularization and equilibration calculations allows investigation of numerous starting temperatures with only one circularization calculation. The same technique is used to link the equilibration calculation results to the fragmentation calculations.

The now motionless confining wall maintains the desired average density and prevents fragmentation or vapor pressure generation during thermal equilibration. At each time step, the velocities are adjusted to correct the temperature. This procedure changes the calculation from energy conserving to isothermal. First, new trial positions are calculated from the original difference equation

$$\vec{X}_+ = 2\vec{X}_0 - \vec{X}_- + \vec{F}\Delta t^2/m \quad (6.32)$$

Then, the new and old positions are used to calculate the velocities,

$$\vec{v} = (\vec{x}_+ - \vec{x}_-)/2\Delta t \quad (6.33)$$

Next, the velocities are adjusted to produce the correct temperature,

$$\vec{v} = \vec{v}_0 [2K/(m \sum v_0^2)]^{1/2} \quad (6.34)$$

where K is the desired kinetic energy, NkT . The adjusted velocities are used to influence the particle motion by correcting both the old and the new positions ($\vec{x}_-$ and $\vec{x}_+$), although the correction in $\vec{x}_-$ is not directly seen since that information has already been output at the time of the adjustment. The adjustment is straightforward. Equations 6.32 and 6.33 are used to eliminate $\vec{x}_-$, and the resulting equation is solved for $\vec{x}_+$,

$$\vec{x}_+ = \vec{x}_0 + \vec{v}\Delta t + \vec{F}\Delta t^2/(2m) \quad (6.35)$$

The equilibration calculation used to start the isochoric heating calculation for the 2611 system evolved into the procedure described above. In the original calculation, the post-circularization configuration was allowed to equilibrate for 128 reduced time units (6000 time steps). However, the temperature was only adjusted once every 500 steps. The desired temperature was 0.55, and the adjustments were designed to overshoot this mark to attempt to anticipate equipartition of added or removed energy between the kinetic and potential energies. This procedure was not perfect, and the temperature oscillated around the desired value (Fig. 6.13).

For a density of 0.6, the phase diagram (Fig. 4.6) indicates a saturation temperature of 0.53. The isothermal model with temperature adjustments at every time step was started from the 6000 step

Fig. 6.13. Temperature oscillation during the initial 6000 step equilibration (18.6 ps).

configuration (Fig. 6.14). Five isothermal equilibration calculations were run for 1000 time steps each (~28 time units) for temperatures bracketing the saturation temperature (0.42, 0.45, 0.5, 0.55 and 0.55). The final configurations for these five calculations are shown in figures 6.15-6.17. The low temperature results are clearly in the two phase region with outer gas pockets surrounding central liquid. The higher temperature results appear to be pure liquid although voids of up to ~5 σ in diameter are scattered within the liquid and at the edges. Fehder²⁷ also saw small voids in molecular dynamics studies of liquids at ρ, T conditions of (0.68, 0.93), (0.68, 1.44), and (0.46, 1.15).

The small voids could indicate that either the system is in the two phase liquid-vapor region or it has not yet reached mechanical equilibrium (that is, more equilibration time is needed). To test the first possibility, an equilibration calculation was run at a very high reduced temperature, 1.153, which is above the critical point. The configuration after 3000 time steps (11 ps) is shown in Fig. 6.18. Even at this high temperature, small voids exist within the liquid. This result is analogous to Thompson's study of small drops²⁹ which showed that drops are non-spherical at any instant of time, but the time average of the drop shape is spherical. In the two-dimensional liquid, instantaneous voids exist, but the time average of the density at any location is the bulk density.

The possibility that the voids are symptomatic of an unequilibrated system can also be dismissed. In Fig. 6.19, the potential energy per atom is plotted as a function of time for the equilibration calculations. In each case, constant potential energy

Fig. 6.14. Configuration at the end of 6000 equilibration time steps (18.6 ps).

Fig. 6.15. Final configuration after 1000 isothermal time steps (~4.4 ps) at temperatures of 0.42 and 0.45.

Fig. 6.16. Final configuration after 1000 isothermal time steps (~4.4 ps) at temperatures of 0.5 and 0.53.

Fig. 6.17. Final configuration after 1000 isothermal time steps (~4.4 ps) at a temperature of 0.55.

Fig. 6.18. Configuration of a 721 atom system equilibrated to a temperature of 1.153 for 3000 time steps (11 ps).

Fig. 6.19. Potential energy per atom as a function of time for seven equilibration runs. Mechanical equilibrium seems to be reached at ~10 time units (1.5 ps) in each case. Solid lines are for 2611 atom systems while dashed lines indicate 721 atom systems.

(mechanical equilibrium) is reached in ~ 10 time units (1.5 ps). The decreasing potential energy magnitude ($|E_p/N|$) with increasing temperature can be attributed to either fewer bonds or to less energy per bond. For the 2611 atom runs in the 0.42 to 0.55 temperature range, the change was almost entirely due to the change in the number of bonds. For the 721 atom runs (at temperatures of 0.5 and 1.153), the change in potential energy per atom was due to roughly equal contributions from fewer bonds and less energy per bond.

Thus, it appears that the small voids are real. Their existence will influence the fragmentation process and the molecular dynamics simulations. Fragmentation in ICF reactors will produce fragments that are much larger than the void spacing, and the molecular dynamics experiments should be designed to produce fragments that contain at least several voids. That is, fragments smaller than ~ 150 atoms should not be trusted since their shapes and sizes will be primarily determined by the individual voids rather than the hydrodynamics. For larger fragments, the statistical distribution of the voids will be more important than individual voids.

The isothermal equilibration worked well for most of the systems studied. However, it is possible to misuse this technique. For example, a 721 atom system was equilibrated to $T = 0.5$, and the resulting configuration appeared to be two-phase liquid-vapor. A further equilibration to $T = 0.55$ was attempted in order to move vertically into the liquid region on the T - ρ diagram. Instead, the system followed a path up and to the right, all the way into the solid region, as indicated by the frozen structure in Fig. 6.20 which appears to have about a half-dozen nuclei and interesting crystal

Fig. 6.20. Final configuration of a 721 atom system that froze during temperature equilibration.

grains. The potential energy per atom is -2.5 compared to a value of -1.8 for the liquid in Fig. 6.17 which is at the same temperature; the large decrease is consistent with freezing as the atoms assume their closer spacing deeper in the potential well. Evidently, the response to each adjustment increased both temperature and density, causing further adjustments to continue the process. This sequence of events could have been caused by a radial oscillation of the system, i.e., if most of the atoms happened to be moving inward at the beginning of the equilibration run, increasing density would be expected.

The isochoric heat addition was input by specifying a heated temperature and adjusting the velocities (and hence the temperature) using Eq. 6.33. In early runs, an attempt was made to compensate for the overshoot due to equipartition (conversion of a portion of the added kinetic energy into potential energy). However, the actual temperature immediately following the energy addition is available in the output, and that value was used when the runs were evaluated in Chapter Seven. In later runs, the desired heated temperature was produced without overshoot.

Since the velocity adjustment procedure multiplies an already equilibrated velocity distribution, it is also equilibrated. However, the atoms are not spatially equilibrated for about ~ 10 time units. Since this time is of the same order as the wave transit time across the system, the equilibration calculations were rerun at the temperature desired after isochoric heating. These results provide the initial conditions for the fragmentation runs which begin when the confining wall is suddenly removed.

The actual energy distribution in an ICF reactor is dependent on

the neutron moderation and absorption processes, and is probably highly non-uniform. Yet, in the macroscopic fluid, the added energy reaches spatial and velocity equilibria in a time short (sub-ns) compared to either the energy addition time (μ s) or the pressure relief time ($\sim 40 \mu$ s in HYLIFE). Thus, the microscopic fragmentation runs should start from a configuration equilibrated at the heated temperature (rather than the saturation temperature). The results discussed in Chapter Seven all begin from configurations equilibrated at the heated temperature.

6.7. Graphic Output

Although a voluminous data output can be produced by each run (as described in the next section), a graphical display allowed quick evaluation of the results and also provided hints as to which numerical data would be most interesting. Four types of graphical output were produced during the evolution of the molecular dynamics models.

- o Early runs used frequent snapshots of the atomic positions, with bonds indicated by lines connecting the atoms. When run as film strip, this output allowed easy visualization of both tensile and compressive waves.

- o Later film strips eliminated the bond lines; this also proved to be effective. A complete film sequence of the circularization, equilibrium, and fragmentation of a 2611 atom system was produced as a part of this work. The author is willing to lend a copy of the film upon request.

- o Because producing many frequent frames is very expensive, a time-exposure that showed the trajectories of the atoms for tens and even hundreds of time steps proved to be quite economical. The trajectories were drawn about ten times per frame, i.e., the motion of an atom for a few to a few tens of steps was drawn as a single straight line. In practice, this procedure saved considerable computer time while preserving an adequate amount of trajectory information. At the end of each time exposure frame, a small diamond was drawn at the end of each trajectory; this allowed determination of the directions of the trajectories.

o The most economic graphic output drew diamonds at the atom locations once per frame (no trajectories were drawn). Even this limited graphic output proved to be quite useful.

6.8. Tabular Output

At selected time steps during circularization, equilibration, and fragmentation, data were written to an output file. These results fell into two categories: data summarized over all atoms and data summarized by cluster (fragment). Data output included bond count, potential and kinetic energies, translational and rotational energies, temperature, density and PV product.

6.8.1. Data Summarized Over All Atoms

At selected time steps, a number of overall quantities were computed and sent to the output data file.

o Bond Count - During the calculation of the interatomic forces, the bond count was incremented whenever the interatomic separation was less than the cutoff distance (4σ for early calculations and 2.5σ for later calculations). The number of bonds in the system decreased when the density decreased and when atoms were ejected as vapor pressure.

o Kinetic Energy - The kinetic energy in each coordinate direction was computed.

o Potential Energy - The total potential of all the bonds was calculated at the same time as the forces. The potential was also output as the delta potential above the perfect potential. The perfect potential is defined as the potential energy for a perfect hexagonal crystal when all the first neighbor interatomic separations correspond to the bottom of the potential well, i.e., when $d\phi/dr = 0$ or $r_0 = 1.12246\sigma$. The potential energy increased during circularization and when particles were ejected from the system. For a completely vaporized state, the potential would be approximately zero since virtually no atoms are within the bond range at any given time.

o Total Energy - During the fragmentation calculations, conservation of the sum of the kinetic and delta potential energies to within 2% of the initial value was required. The energy quantity checked was the sum of the kinetic and delta-potential energies to avoid problems when the actual energy is small and negative. Poor

energy conservation was usually due to the choice of an excessively long time step. When energy conservation was a problem, the velocities were adjusted or the time step was decreased. For the circularization and equilibration calculations, energy was not rigorously conserved because of work done by the wall and because of velocity adjustments used to correct the temperature.

o Wall Data - During circularization and equilibration, the wall interacted with the outer particles. At output times, the code totaled the wall-atom bond forces and potentials. The pressure on the wall was also computed by dividing the force (which is radial) by the wall perimeter. This two-dimensional pressure has units of force per unit length or, equivalently, energy per unit area.

6.8.2. Data Summarized by Cluster

A cluster is defined as a set of atoms that have bonds with each other but with no other atoms. In this study, the potential was truncated at either 2.5σ or 4.0σ , allowing straightforward determination of the cluster identities when the forces were calculated. First, all atoms were assigned to cluster number $(N+1)$ where N is the number of atoms in the system. Then the nested do loops that calculate the forces were entered. The outer do loop incremented the first atom, N_1 , from 1 to $(N-1)$. The inner do loop incremented the second atom identification, N_2 , from (N_1+1) to N . On each cycle of the outer do loop, the first atom in the atom pair was assigned to its own cluster. On each cycle of the inner do loop that calculated a non-zero bond force, the second atom was assigned to a cluster. If its current cluster number was $(N+1)$, it was assigned to the same cluster as the first atom. If the second atom was in neither cluster $(N+1)$ nor the same cluster as the first atom, the maximum ($N_{\max}$) and minimum ($N_{\min}$) of the cluster assignment of both atoms were calculated. Then the cluster assignments of all the atoms were reviewed, and atoms in cluster $N_{\max}$ were reassigned to cluster $N_{\min}$.

After the nested do loops were completed, the cluster assignments were reviewed. First, atoms with no assignment were assigned to new clusters. Then, the population of each cluster was calculated. Because of the reassignment procedures, some cluster numbers had zero population. Hence, the cluster assignments were reviewed one last time to adjust the cluster numbering to count only non-zero population clusters.

Once the cluster assignments were complete, the center of mass, translational energy, rotational energy, thermal energy, and temperature of each cluster were calculated. The values of these quantities were calculated simultaneously for each cluster. This was accomplished by looping through the atom list (index j) and incrementing the quantity, $f[N_1(j)]$, where f is the quantity of interest and $N_1(j)$ is the cluster assignment (1) for atom j .

The center of mass for a given cluster is $\langle \vec{X} \rangle = (\sum \vec{X})/N_c$ where the sum is over the N_c atoms in the cluster. In this and the following cluster quantity formulas, the atomic mass, m , was ignored since it was set to 1.0.

The cluster kinetic energy is $\sum v^2/2$. The cluster translational energy can be found from either the motion of the center of mass or the average velocity. Using the latter method,

$$\vec{v} = \sum \vec{v} / N_c$$

and the translational energy is

$$N_c \vec{v}^2 / 2 = (\sum \vec{v})^2 / (2N_c)$$

The cluster rotational energy is $L^2/2I$. The angular momentum is

$$L = \sum [(x - \langle x \rangle)v_y - (y - \langle y \rangle)v_x],$$

and the moment of inertia is

$$I = \sum (\vec{X} - \langle \vec{X} \rangle)^2$$

The thermal energy of the cluster was found by subtraction since it includes all the kinetic energy except the center-of-mass translation and rotation. The cluster temperature was found by dividing the thermal energy by $(N_c k)$.

The cumulative density was calculated as a function of radial distance from the atom nearest the center of mass of each cluster containing more than 20 atoms. For these clusters, a cumulative density profile,

$$\left[\sum_i \langle 1 | (r_1 > r_p) \right] / \pi r_p^2$$

was plotted in radial increments of $\sigma/4$.

The virial theorem was used to calculate PV for each cluster

$$PV = \frac{1}{D} [\sum v^2 + \sum_{i<j} (\vec{r}_{ij} \cdot \vec{F}_{ij})] \quad (6.36)$$

where D is the number of dimensions, $\vec{r}_{ij}$ is the vector between atoms i and j, and $\vec{F}_{ij}$ is the force on atom i due to atom j. The right hand side of the equation should be time averaged; however only instantaneous values were calculated at energy edit times. Time averaging was done afterwards for the limited number of energy edits.

Once all of the above cluster quantities were calculated and output, they were summed and output for the entire system.

6.9. Computational Efficiency

Once the computer codes were tested for a small system (127 atoms), the run time was analyzed and extrapolations were made to see what size system could be reasonably analyzed. Then, methods of increasing the calculational efficiency were considered.

For the test run, the average step time on the CRAY-1 computer was 19 ms/step. This calculation considered all atom pairs at each time step. Most of the run time was used in the nested do loops that calculated the interatomic forces. Because these loops contained "if" statements to circumvent part of the loop when the interatomic separation was larger than the cutoff distance, they would not vectorize. Vectorized do loops run up to an order of magnitude faster than non-vectorized loops.

An easy way to vectorize the nested loops is to eliminate the bond cutoff and calculate the forces for all atom pairs. This increases the number of bonds by a factor of five for the 127 atom system. The average step time for the fully vectorized code was 54 ms/step, indicating that this tactic would not be useful, particularly for larger systems.

For the non-vectorized code, another run was made for a 271 atom system. Comparison of memory usage indicated that a 120,000 atom system could be calculated with 85% of the machine's memory. Unfortunately, the run time for such a large system would be unreasonable. If run time were proportional to the system population, over 50 CPU hours would be required to study a 120,000 atom system. It is likely that considerably more time would be required since run time increases faster (as $N \ln N$) than the system population. Hence, a

major improvement in calculational efficiency was required.

One of the earliest methods of increasing calculational efficiency, suggested by Alder⁵³, was to infrequently compute the projected collision times, if any, of all possible pairs of atoms. Then, the time step was adjusted after each step to cover the projected time until the next collision. In the same publication, Alder suggested dividing the region into grids and only consider atoms pairs in nearby grids; this was the precursor to neighbor listing. In 1967, Verlet⁵⁴ introduced a neighbor listing scheme (called Verlet tables by some authors). Recently, Thompson⁵⁵ has optimized and automated neighbor listing. In Thompson's method, a list is constructed for each atom that includes all atoms within some range r_q , of the atom. The range must be larger than the potential's truncation range, r_t , and it should be smaller than the radius of the system. Once the list is established, only those atoms on the list are considered when calculating the interatomic forces. The greatly reduced set of atom pairs to be considered at most time steps correspondingly decreases the run time. Conversely, the neighbor list array is large, between N and N^2 , depending on the choice of r_q .

The neighbor list becomes invalid when the atoms have moved far enough that they have interactions with other atoms not on the list. The list lifetime depends on the atomic motion in Thompson's scheme. When the neighbor list is built, an array that has dimension equal to the number of atoms is set to zero. After each time step, the array entries are increased by the scalar distance traveled by the atoms. Before the next time step, the maximum of the distance array is compared to a test quantity. If the maximum distance is less than the

test quantity, another time step using the current neighbor list is allowed. The test quantity is $0.95[1 - 1/(n_q+1)](r_q-r_t)$ where n_q is the number of time steps the list has been used. The variable test quantity anticipates whether the next step will move the atoms past the list range. The anticipation is based on the number of steps already accomplished since the last list update. In this study, the total path length was used since vaporizing atoms travel in straight paths. In a more confined system, it would be better to consider the net distance traveled, allowing use of the list for longer periods.

Thompson tested the neighbor list procedure for three dimensional 256 and 500 atom systems.⁵⁵ He used a reduced density of 0.8, a reduced temperature of 0.76, 1000 time steps, and a Lennard-Jones potential truncated at 2.5σ . In both cases, he found that the step time sharply increased for list radii less than 2.6σ ; this was because the list was updated too frequently. Thompson also found a gradual rise in step time for list radii above 2.9σ ; this was because the list became excessively long, and time was wasted on each step in checking too many non-interacting atom pairs. Thompson's optimum list radii were 2.7σ (2.1 CPU seconds per step) for the 256 atom system and 2.8σ (4.4 CPU seconds per step) for the 500 atom system. His data was collected using a PDP 11/70 minicomputer that has approximately 18% of the speed of an IBM 370/168.

The neighbor list procedure was integrated into the computer programs developed in this study. The step time is shown as a function of the list radius for a 2611 atom system in Fig. 6.21. The optimum list radius is about 4.0σ , and the step time is in the 220

Fig. 6.21. Step time dependence on list radius for a 2611 atom system.

to 330 msec/step range depending on the type of calculation. For comparison, without neighbor listing, the circularization calculation required 1.5 sec/step. The circularization calculation was the fastest because it had a minimum of atomic mixing while it was solid.

Figure 6.22 shows the list update frequency as a function of the list radius. Equilibration and fragmentation calculations used each list for about 25 time steps while circularization neighbor lists were valid for about 120 time steps. The memory price paid for the increased speed is shown in Fig. 6.23 which plots the neighbor list array size as a function of the list radius. An array of about 40,000 dimension is required; this is about 3% of the CRAY memory.

Because it takes longer for waves to traverse large systems, the 2611 atom calculations require more time steps than the smaller systems. A typical problem required 19 minutes of CPU time during circularization, 37 minutes during equilibration, and 24 minutes during fragmentation.

The step time, list size, and list update intervals are summarized in Table 6.2 for fragmenting 169, 721, 2611, and 14491 atom systems. The 6.7 ms/step time for the 169 atom system was considerably better than the 19.7 ms/step measured in the smaller 127 atom test run without neighbor listing. Although it was unreasonable to run a test problem without neighbor listing at 14491 atoms, the improvement at that size was probably many orders of magnitude. Even with neighbor listing, computer time rather than memory placed the system size limit at ~ 15,000 atoms (10.5 Cray CPU hours were consumed by the single 14491 atom fragmentation run, but less than 1/6 of the available memory was used by the code.)

Fig. 6.22. List update interval for a 2611 atom system.

Fig. 6.23. List size for a 2611 atom system.

Table 6.2. Computational efficiency measures during fragmentation runs on various sized systems.

Size (atoms)	Time Per Step (sec)	List Update Interval (steps)	List Size
169	0.0067	25	2,170
721	0.042	18	9,870
2611	0.35	18	37,700
14491	6.3	21	212,000

Chapter 7: Two-Dimensional Molecular Dynamic Experiment Results

In this chapter, the molecular dynamics results are presented and analyzed in terms of the four models derived in Chapter Five. First, the input parameters required by the models are determined. The relationship between the quantity of isochoric heat added and the temperature rise is calculated. (The temperature rise, ΔT , is an independent variable in some of the plots of the results.) The material properties (Grüneisen parameter, wave speed, and surface tension) are estimated. These four input functions are incorporated into the models, and predictions are generated for the fragment size and translational temperature. The molecular dynamics results are discussed and then compared to the predictions. Finally, the effect of the zero vapor pressure initial condition is estimated.

7.1. Partition of Isochoric Heating Energy Between Kinetic and Potential Energies

A series of isothermal molecular dynamics calculations was run at temperatures ranging from saturation (~ 0.5) to 1.2 for 169, 721, 2611 and 14491 atom systems confined by a repulsive wall to $\rho_{\text{avg}} \sim 0.6$, a value roughly midway between the critical and liquid triple point densities. The calculations began with the wall-confined $T \sim 0.5$ configuration, and velocity adjustments at each time step maintained the desired temperature increase. The potential energy increased with time and then oscillated; the change from increase to oscillation occurred by the first energy compilation (~ 1.5 ps) in each case. Because this "energy equilibration time" is both size independent and much less than the wave traversal time in an ICF reactor liquid region, the molecular dynamics fragmentation runs should begin with an equilibrated configuration. The equilibration calculations were for times ranging between 25 and 80 reduced time units (4 to 12 ps) with six to ten intermediate energy compilations.

The results are summarized in Fig. 7.1 which shows the increases in kinetic energy and potential energy per atom as a function of temperature increase. The values are for an average of the energy values at the compilation times. Time averaging is required since the energies fluctuate with the atomic motion; however, the number of times used in these averages is not adequate for high precision. If the calculations were repeated, energies would be calculated at more intermediate times to improve the average. The curve labeled "fit" is described by the equation

$$\Delta E/N \equiv e = 1.45 (\Delta T)^{0.847} \quad (7.1)$$

Fig. 7.1. Increase in potential and kinetic energies in the $\rho = 0.6$ molecular dynamics runs after the temperature is increased and maintained at a higher value. The energies are normalized to zero at saturation ($T = 0.53$). Henderson's Monte Carlo data are also shown; they have been slightly adjusted to match the molecular dynamics results at $kT/\epsilon = 1.0$.

This equation has the correct limiting value of zero at zero ΔT , and it fits the molecular dynamics data reasonably well.

Henderson²⁴ reported internal energies derived from Monte Carlo calculations at $\rho = 0.6$ for temperatures between 0.55 and 1.25. When the molecular dynamics energies are adjusted to match Henderson's value at $T = 1.0$, the agreement is within 4% for the lower seven temperatures. For a temperature of 1.25, the error is 7% in the opposite direction indicating that Equation 7.1 should not be extrapolated beyond its last data point of $T = 1.15$. The unadjusted values of the molecular dynamics energies also agree with Henderson's Monte Carlo data. For example, at $T = 0.75$, for 2611 atoms, the configurational plus thermal energy per atom is -0.93 compared to ~ -0.95 from Henderson. The higher energy in the molecular dynamics calculation is probably due to the wall which acts as an artificial surface and increases the interior pressure and energy.

7.2 Material Properties

To calculate the liquid fragmentation using the Grady-Glenn model, three properties are required: The Grüneisen parameter (Γ), wave speed (c), and surface tension (γ). These properties are calculated below for the two-dimensional Lennard-Jonesium material using the literature and using molecular dynamics as a calculational tool.

7.2.1 The Grüneisen Parameter

Three methods were used to determine the Grüneisen parameter, Γ : analytic theory for gases and solids, calculation from published liquid temperature-density-pressure data, and calculation from a molecular dynamics simulation.

For a gas,

$$P = \rho kT \quad (7.2)$$

and

$$\frac{E}{N} = \frac{D}{2} kT \quad (7.3)$$

where D is the number of dimensions. By definition,

$$\Gamma = \frac{1}{\rho} \left[\frac{\partial P}{\partial (E/N)} \right]_V \quad (7.4)$$

These equations can be combined

$$\begin{aligned} \Gamma &= \frac{1}{\rho} \left[\frac{\partial (\rho kT)}{\partial (DkT/2)} \right]_V \\ &= \frac{1}{\rho} \left[\frac{\rho k \Delta T}{Dk \Delta T/2} \right] = \frac{2}{D} \end{aligned} \quad (7.5)$$

Hence, for a gas, the Grüneisen parameter is 1.0 in 2D and 0.67 in 3D.

For a solid, the analytic theory begins with a result from Slater,⁵⁶

$$\Gamma_i = - \left[\frac{\partial (\ln \nu_i)}{\partial (\ln V)} \right]_T \quad (7.6)$$

The logarithmic derivative is independent of multiplicative factors, allowing replacement of the frequencies, ν_i , by angular frequencies, ω_i , where i specifies the vibration mode. Also,

$\partial/\partial(\ln V) = -\partial/\partial(\ln \rho)$. If all the modes have equal frequencies, then

$$\Gamma = \left[\frac{\partial(\ln \omega)}{\partial(\ln \rho)} \right]_T \quad (7.7)$$

For harmonic vibration, $\omega = (\kappa/m)^{1/2}$, and $\kappa = \partial^2 \phi / \partial r^2$. If the repulsive part of the potential is proportional to r^{-n} , κ is proportional to $r^{-(n+2)}$. The density, ρ , is proportional to r^{-D} where D is the number of dimensions; thus

$$\begin{aligned} \omega &\sim \kappa^{1/2} \sim [r^{-(n+2)}]^{1/2} \\ &\sim [\rho^{-1/D}]^{-(n+2)/2} \sim \rho^{(n+2)/2D} \end{aligned} \quad (7.8)$$

And

$$\Gamma = \left[\frac{\partial(\ln \omega)}{\partial(\ln \rho)} \right]_T = \frac{n+2}{2D} \quad (7.9)$$

For an r^{-12} repulsive potential, Γ is 3.5 and 2.3 for two and three dimensional solids, respectively.

The published Lennard-Jonesium liquid temperature-density-pressure equation from Barker²² was discussed in Section 4.2. The equation is cross plotted at $\rho = 0.6$ in Fig. 7.2 which also shows Henderson's Monte Carlo data (Section 4.2) and the molecular dynamics pressure data computed from the isothermal equilibration runs described in Section 7.1. Barker's cross-plotted equation and Henderson's data were fit to quadratic forms (see Table 4.5).

The molecular dynamics pressures include values computed from the radial repulsive forces between the atoms and the wall and, in three cases, PV data (using Eq. 6.36). In most cases, the pressures were

Fig. 7.2. Pressures from the molecular dynamics runs, Barker's theoretical and Monte Carlo calculations²², and Henderson's Monte Carlo calculations²⁴.

time averaged from only six to ten widely separated instantaneous values; therefore, they are imprecise. (In two cases, the data were averaged over ~ 185 time steps.) However, all the molecular dynamics data lie above the Monte Carlo data. This trend is probably due to the molecular dynamics boundary conditions. The repulsive wall represents an artificial surface which increases the internal liquid pressure to a value higher than for the theoretical and Monte Carlo calculations; however, the wall is required to confine the system during the time averaging period. The alternative, periodic boundary conditions, does not allow circular surfaces. Also, since the wall is purely repulsive, there is no opportunity for mutual cancellation of negative and positive forces, as would be observed by a test surface within the bulk liquid.

The Grüneisen parameter is

$$\Gamma = \frac{1}{\rho} \left(\frac{\partial P}{\partial E} \right)_V = \frac{1}{\rho} \left(\frac{\partial P / \partial T}{\partial E / \partial T} \right)_V \quad (7.10)$$

The pressure derivative is available from both Barker's pressure equation and Henderson's data (see Table 4.5). The energy derivative, $c_V \equiv (\partial E / \partial T)_V$ is also available from Henderson's data (Table 4.5 and Fig. 4.11). These derivatives were used to plot the Grüneisen parameter as a function of the temperature for three densities (Fig. 7.3). This figure also shows the solid and gas results and the known Grüneisen parameters of liquid lithium and lead.

The liquid results should eventually decline to the ideal gas value at high temperature. The lower density (0.5 and 0.6) results are dominated by the specific heat ($\partial P / \partial T$ is roughly constant). However, the high density (0.7) result is dominated by the pressure

Fig. 7.3. Grüneisen parameter from the Monte Carlo data of Henderson and Barker. Solid, gas and liquid metal results are also presented. The values plotted include the factor $(D/2)$ where D is the number of dimensions. Thus, two dimensional results can be read directly while the values should be multiplied by $2/3$ to obtain three dimensional numbers.

derivative (c_v is roughly constant). The shift in the dominant factor is responsible for the sign change in the slope of the Grüneisen parameter.

As density increases, the liquid Grüneisen parameter approaches the solid value. However, considerably higher temperatures are apparently required before the liquid values converge to the ideal gas limit.

Since the molecular dynamics results are concerned with the final pressure produced, rather than the local (in temperature) value of the Grüneisen parameter, a cumulative Grüneisen parameter was also calculated from the Monte Carlo data of Henderson²⁴ and Barker²² (Fig. 7.4).

$$\Gamma_c = \frac{1}{\rho} \left[\frac{P - P_{\text{sat}}}{E - E_{\text{sat}}} \right] \quad (7.11)$$

The final Grüneisen calculation used two molecular dynamics calculations with energy and wall pressure compilations at each time step (~0.004 ps). The isothermal equilibration code was used with a stationary repulsive wall and temperature adjustments on each time step. Beginning with a $T = 0.53$ equilibrated liquid, 300 steps were run at both $T = 0.53$ and $T = 0.7$. The pressure on the wall was calculated at each time step by summing the repulsive forces between the atoms and the wall. The higher temperature run took ~110 time steps to partition the added energy into potential plus kinetic energy. After this time (~3 reduced time units or 0.5 ps), both runs displayed fluctuating pressures and energies around average values (Figures 7.5 and 7.6). The pressures were averaged over the

Fig. 7.4. Cumulative Grüneisen parameter defined by the pressure and energy differences between the heated state and the saturated liquid at the same density. This plot also shows the single cumulative Grüneisen parameter calculated from the two molecular dynamics runs.

Fig. 7.5. Pressure as a function of time for two constant volume and temperature molecular dynamics calculations.

Fig. 7.6. Configurational plus kinetic energy per atom for two 2611 atom liquids confined by walls. The density was 0.6 for both the $T = 0.7$ and $T = 0.53$ (saturated) cases. The energy zero is at zero temperature with all first neighbor bonds at a minimum potential (- ϵ).

last ~5 time units and values of 0.592 and 0.207 were obtained for the $T = 0.7$ and 0.53 runs, respectively. The time averaged energy increase was 0.3 reduced units (1.76 AT), about 8% lower than the relatively crude prediction of Fig. 7.1. The Grüneisen parameter is then,

$$\Gamma_c = \frac{1}{\rho} \frac{\Delta P}{\Delta E} = \frac{1}{0.6} \left(\frac{0.592 - 0.207}{0.3} \right) = 2.1 \quad . \quad (7.12)$$

This result agrees with the results calculated from Barker's and Henderson's data as shown in Fig. 7.4. The Henderson pressure (and derived Grüneisen parameter) data were used in the comparison of the molecular dynamics fragmentation data with the four hydrodynamic models from Chapter Five (Section 7.4).

7.2.2 Wave Speed

The wave speed was evaluated at the heated temperature since that is the temperature at which the wave travels. Two approaches to calculating the wave speed were taken. First, the Henderson²⁴ and Barker²² pressure data (Section 4.2) were used to compute the sound speed. Then, the molecular dynamics runs were used to estimate the wave convergence time, $\tau = R/c$.

The sound speed is

$$c = [(\frac{\partial P}{\partial \rho})_S]^{1/2} \quad (7.13)$$

Thermodynamic relationships can be used to convert equation 7.13 to more measurable quantities

$$(\frac{\partial P}{\partial \rho})_S = \frac{c_P}{c_V} (\frac{\partial P}{\partial \rho})_T \quad (7.14)$$

where c_P and c_V are the specific heats at constant pressure and volume, respectively.

$$c_P = c_V + TV \alpha_V^2 B_T \quad (7.15)$$

where α_V is the volumetric coefficient of thermal expansion, $(\partial V/\partial T)_P/V$, and B_T is the isothermal bulk modulus, $-V(\partial P/\partial V)_T$. The coefficient of expansion can be eliminated by using

$$(\frac{\partial P}{\partial V})_T (\frac{\partial V}{\partial T})_P (\frac{\partial T}{\partial P})_V = -1 \quad (7.16)$$

and $\partial/\partial V = -\rho^2 \partial/\partial \rho$ can be used to eliminate the volume.

Finally,

$$c_V = \left(\frac{\partial E}{\partial T} \right)_V \quad (7.17)$$

Then,

$$c = \left\{ \left(\frac{\partial P}{\partial \rho} \right)_T \left(1 + \left[T \left(\frac{\partial P}{\partial T} \right)_V \right]^2 / \left[\rho^2 \left(\frac{\partial P}{\partial \rho} \right)_T \left(\frac{\partial E}{\partial T} \right)_V \right] \right) \right\}^{1/2} \quad (7.18)$$

Equation 7.18 was evaluated at temperatures of 0.55, 0.7, and 1.0 using Barker's²² pressure equation (Eq. 4.17 and Fig. 4.9) and its crossplot (Fig. 4.10 and Table 4.5) in conjunction with specific heats derived from Henderson's²⁴ Monte Carlo data (Fig. 4.11 and Table 4.5). However, intermediate temperatures could not be directly evaluated using Barker's equation since the constants in Eq. 4.17 (f_1 through g_4) are specified only at four temperatures. Henderson's Monte Carlo data were also used to evaluate the sound speed (Eq. 7.18) at a range of pressures and temperatures (using the analytic fits summarized in Table 4.5). The results are shown in Fig. 7.7, and the values of the various terms in Eq. 7.18 are listed in Table 7.1 for the three points using Barker's pressure data. The agreement in the sound speeds calculated from the two references is satisfactory.

The molecular dynamics runs were examined every thirty time steps following the removal of the confining wall. Plots of the density and cumulative density,

$$\int_0^r (\rho(r) \Delta V) / \int_0^r \Delta V$$

(and in some cases, the cumulative radial velocity), as functions of radial position were generated at each time. In two cases, a movie of

Fig. 7.7. Sound speed computed from Henderson's²⁴ Monte Carlo pressure and energy data and from Barker's²² pressure equation.

Table 7.1. Calculation of the sound speed (Eq. 7.18) for a constant density of 0.6 and temperatures of 0.55, 0.7 and 1.0. Source codes are "H" for Henderson and "B" for Barker. Reduced variables are used ($T=kT/\epsilon$, $\rho=\rho\sigma^3$, $P=P\sigma^2/\epsilon$, and $c=c\sqrt{m/\epsilon}$).

		Temperature		
		0.55	0.7	1.0
P	B	0.132	0.356	0.936
$(\partial P/\partial T)_V$	B	1.77	1.84	1.97
$E-E_{0.55}$	H	0.030	0.252	0.680
$(\partial E/\partial T)_V$	H	1.57	1.55	1.51
$(\partial P/\partial \rho)_T$	B	0.55	2.24	5.04
$(\frac{\partial P}{\partial \rho})_T^{1/2}$	B	0.74	1.50	2.24
c		1.90	2.55	3.49
$c/(\frac{\partial P}{\partial \rho})_T^{1/2}$		2.56	1.70	1.55

the atomic positions was produced. A typical density result is shown in Fig. 7.8.

For most of the molecular dynamics runs, the time that the relief wave reached the center can be estimated to be between two compilation times. Although the runs were intended to begin at exactly $\rho = 0.6$, the actual densities varied between 0.61 and 0.73. The wave traversal time (R/c) data were adjusted to remove the influence of the density. The adjustment was derived from the variation of the previously generated sound speed curves with density (Fig. 7.7). The ratio of the ($\rho = 0.7$) curve to the ($\rho = 0.6$) curve is almost identical to the ratio of the ($\rho = 0.6$) curve to the ($\rho = 0.5$) curve. A fourth order equation,

$$F_\rho = 3.4862 - 5.7303T + 5.9473T^2 - 2.7619T^3 + 0.4712T^4 \quad (7.19)$$

is midway between the two ratio curves. This equation was used to produce a normalized sound speed,

$$c^* = \begin{cases} c / (1 - \rho^* + \rho^* F_\rho) & , \rho \leq 0.6 \\ c / (1 - \rho^* + \rho^* F_\rho) & , \rho > 0.6 \end{cases} \quad (7.20)$$

where

$$\rho^* = \begin{cases} (0.6 - \rho) / 0.1 & , \rho \leq 0.6 \\ (\rho - 0.6) / 0.1 & , \rho > 0.6 \end{cases} .$$

The results of density-normalizing the sound speed curves and the molecular dynamics data are indicated in Fig. 7.9. The convergence of the sound speed curves justifies the normalization, at least for $0.5 \leq \rho \leq 0.7$. The vertical range for each molecular dynamics run indicates the difficulty in reading the wave traversal time from the

Fig. 7.8. Density and cumulative density profiles 330 steps (time = 9.06 reduced units or 1.4 ps) after removal of the wall from a liquid equilibrated at $kT/\epsilon = 0.65$. The initial cumulative density profile is also shown. Comparison of the two cumulative density profiles indicates the tensile relief wave has penetrated to $r \sim 15$ reduced units (4 nm).

Fig. 7.9. Average wave speed for each of the molecular dynamics runs. The sound speed curves from Fig. 7.7 are repeated. All speeds have been adjusted to the value expected at $\rho\sigma^2 = 0.6$. The variation in the curves shows the accuracy of the adjustment. The vertical ranges in the molecular dynamics results are due to the difficulty in separating the wave motion from the background thermal motion.

molecular dynamics results.

Although the molecular dynamics results do not disagree with the sound speed curves, they also do not confirm them. Further, in some cases, the molecular dynamics data could be interpreted as indicating an acceleration in the rarefaction wave as it converged.

To investigate the unexpected possibility of an accelerating rarefaction wave, two additional sets of calculations were carried out. The first set began with an 823 atom circular crystal at zero temperature. Densities of 1.01 and 0.6 were used, producing a strong expansion wave and a somewhat weaker compression wave. The results are shown in Fig. 7.10. The position tracks indicate the location where the particle velocity increases to 10^{-1} reduced units as a function of time. These tracks are essentially straight except when the wave slows as it approaches the center (where no new atoms are available to the wave). The two cumulative velocity amplitude curves have maxima at about the times that the wave reaches the center. At later times, the outer regions reverse and the crystal motion begins to rebound; this behavior is due to the ability of the material to sustain tensions of this level without fracturing.

The second set of calculations used the AFTON hydrodynamics code¹⁸. Two compressed materials were released in both slab and cylindrical geometries. For both the perfect gas and the Lennard-Jones liquid, the expansion wave had identical tracks on the radius-time graph for both geometries, indicating that the ability of the Lennard-Jones liquid to sustain tension has no impact on its wave speed in a converging geometry.

Fig. 7.10. Wave front tracks and particle velocity magnitudes for converging expansion and compression waves.

These two experiments (molecular dynamics and hydrodynamics code) verify that converging rarefaction waves do not accelerate. Thus, the sound speeds read from the molecular dynamics fragmentation runs must be regarded as inexact due to the obscuring thermal motion. However, even these inexact results do not disagree with the equation-of-state derived sound speeds. The sound speeds derived from Henderson's data are used as data in the comparison of the molecular dynamics results to the four hydrodynamic models from Chapter Five (Section 7.4). The sensitivity to a factor of two change in the sound speed is also evaluated.

7.2.3. Surface Tension

Little effort has been made to calculate the two-dimensional surface tension for the Lennard-Jones potential. Two authors have performed Monte Carlo or molecular dynamics calculations with periodic boundary conditions to simulate two-dimensional Lennard-Jones liquids with free surfaces^{23,57}. However, neither author calculated the information required to specify the surface tension. Further, Croxton's⁵⁷ molecular dynamics simulation did not adequately isolate the surface from the boundary⁵⁸.

In three-dimensions, more work has been published. Falls⁵⁹ used a series of simplifying approximations to develop a theory capable of predicting equilibrium density and pressure profiles in small droplets. The theory predicts that the surface tension is lower than for a planar interface when the droplet radius is less than about ten molecular radii. Falls also offers a good intuitive explanation for this phenomenon. Consider two cones with vertices on an atom that is near, but not on, the drop surface (Fig. 7.11). One cone (the normal cone) opens outward across the droplet interface while the other (the tangential cone) is parallel to the surface. For a planar interface, as well as for large and small drops, the normal cone contains only a few atoms because of the surface. For a planar interface or for a large drop, the tangential cone contains many more particles. This asymmetry produces unequal normal and tangential forces (and pressures) on the reference atom. These unequal pressures can be described as surface tension. For small drops, the tangential cone intersects the surface, and the normal and tangential forces become more isotropic, reducing the surface tension.

Fig. 7.11. Cones of particles interacting with a reference atom for a planar interface, a large drop, and a small drop.

Brodskaya^{38,52} used molecular dynamics to compute the density and pressure profiles in small three dimensional Lennard-Jonesium drops. The calculations used time averages over about 20 reduced time units ($t \sqrt{\epsilon/M} / \sigma$). Recently, Thompson²⁹ published an extensive molecular dynamics study of surface tension that used time averages of up to 1400 reduced time units.

The results of the three studies (Falls, Brodskaya, and Thompson) are compared in Fig. 7.12. The qualitative results are similar: decreasing surface tension with decreasing drop size and with increasing temperature ($\gamma = 0$ at the critical point and for isolated atoms). However, the quantitative results are only approximately similar. Because of the extraordinary care and long time averages taken by Thompson, that study²⁹ is probably more accurate than the earlier Soviet studies^{38,52}. Thompson²⁹ discussed the approximations inherent in Falls' theory⁵⁹ and concluded they are responsible for some "unphysical" behavior in Falls' results ($P_T > P_N$ across much of the profile for small drops, implying negative surface tension). Falls attributes this behavior to being in the unstable (spinodal) region of the phase diagram, but Thompson was able to simulate stable drops of the same size (with $P_T < P_N$ and positive surface tension).

Because of Thompson's success in calculating three-dimensional surface tension²⁹, an effort was made here to repeat the calculations in two dimensions. A wall-confined liquid at the desired density and temperature was the starting point. The wall radius was suddenly increased and the system evolved into one or more liquid drops and associated vapor. The wall was centered on the system

Fig. 7.12. Three-dimensional surface tension as a function of temperature and drop size. The data is plotted as a function of $(N_l)^{-1/3}$ because surface tension is expected to have radius and area dependent contributions. Straight lines are used to connect data points to group the similar data. Planar limits are indicated by shaded regions.

center of mass, and the velocities were adjusted for an isothermal situation to accommodate energy loss from the liquid during vapor pressure formation. Thompson²⁹ showed that both isothermal and constant energy calculations are valid.

If the liquid region fragmented, the velocities were adjusted to increase the inward radial kinetic energy. The azimuthal velocities were then adjusted to preserve the overall temperature. Once the fragments coalesced, time averaging of the density and pressure profiles was reinitiated.

The surface tension calculation requires time averaged pressure and density profiles. The instantaneous density was calculated in concentric rings of width $\sigma/4$. The instantaneous normal pressure was calculated at concentric surfaces centered in the rings.

$$P_N(r) = \rho(r) k T + \frac{1}{2\pi r} \sum_k F_k \quad (7.21)$$

where the sum is the total of the normal components (with respect to the system center of mass) of all the interatomic bonds crossing the surface. Using a straight line force between the particles to determine the configurational pressure was originally proposed by Irving and Kirkwood⁶⁰. Choice of a different force line produces a different pressure tensor, as demonstrated by Harasima⁶¹.

As in the atomic motion calculation, two nested do-loops are used to determine which particles have interactions. For each interaction, the minimum and maximum radii (with respect to the system center of mass) of the bond are determined,

$$r_{\max} = \max (r_i, r_j) \quad (7.22)$$

$$r_{\min} = \begin{cases} \frac{1}{2} [2(r_i^2 + r_j^2) - r_{ij}^2 - \frac{(r_i^2 - r_j^2)^2}{r_{ij}^2}]^{1/2}, & |\lambda_{\min}| \geq 1 \\ \min (r_i, r_j), & |\lambda_{\min}| < 1 \end{cases} \quad (7.23)$$

where λ defines the vector $\vec{r}$ in terms of the position vectors of the two particles ($\vec{r}_i, \vec{r}_j$) and the interparticle vector ($\vec{r}_{ij}$) as shown in Fig. 7.13.

$$\vec{r} = \frac{1}{2} (\vec{r}_i + \vec{r}_j + \lambda \vec{r}_{ij}) \quad (7.24)$$

The value of λ when r is minimized, $\lambda_{\min}$, is computed where $\vec{r}$ and $\vec{r}_{ij}$ or its extension meet at a right angle. Then

$$\lambda_{\min} = (r_i^2 - r_j^2) / r_{ij}^2 \quad (7.25)$$

When $r_{\min}$ does not lie between points i and j , $|\lambda_{\min}| \geq 1$, and the minimum radius surface intersects the smaller radius point.

Once the minimum and maximum radii of the bond are specified, the surfaces affected by the bond are determined. For each of these surfaces, the values of λ at the surface-bond intersections are computed

$$\lambda_{\pm} = \left[\frac{r_i^2 - r_j^2}{r_{ij}^2} \right] \pm \left[\left(\frac{r_i^2 - r_j^2}{r_{ij}^2} \right)^2 + 1 - 2 \left(\frac{r_i^2 + r_j^2}{r_{ij}^2} \right) + \frac{4r_{ij}^2}{r_{ij}^2} \right]^{1/2} \quad (7.26)$$

The normal force is

Fig. 7.13. Geometry used to calculate $\lambda_{\min}$. The arcs define the radial limits within which test surfaces are affected by the bond between atoms i and j .

$$\vec{r} = \frac{1}{2} (\vec{r}_i + \vec{r}_j + \lambda \vec{r}_{ij})$$

$$\begin{aligned}
 F_k &= |\hat{r} \cdot \hat{r}_{1j}| \left(-\frac{\partial \phi_{1j}}{\partial r_{1j}} \right) \\
 &= -|\vec{r} \cdot \vec{r}_{1j}| \left(\frac{\partial \phi_{1j}}{\partial r_{1j}} \right) / (r_{1j} r)
 \end{aligned}
 \tag{7.27}$$

Symmetry requires the same contribution from each intersection,

$$|\vec{r} \cdot \vec{r}_{1j}| = \frac{1}{2} r_{1j}^2 \left[\left(\frac{r_1^2 - r_{1j}^2}{r_{1j}^2} \right) + 1 - 2 \left(\frac{r_1^2 + r_{1j}^2}{r_{1j}^2} \right) + \frac{4r_1^2}{r_{1j}^2} \right]^{1/2}. \tag{7.28}$$

This final term must be doubled when there are two intersections;

i.e., when both $|\lambda_-|$ and $|\lambda_+| \geq 1$ (Fig. 7.14). Equations

7.27 and 7.28 can be used in Eq. 7.21 to find the pressure profile.

Although the instantaneous density and pressure profiles (and the liquid shape) are very irregular, time averaging produces reasonable profiles (Fig. 7.15) and a circular shape.

The pressure profile has been used to compute the surface tension in both one dimensional (planar interface) and three dimensional geometries⁶²,

$$\gamma_s = \begin{cases} \int_{-\infty}^{\infty} (P_N - P_T) dz & , \text{1-D} \\ \int_{-\infty}^{\infty} (P_N - P_T) \left(\frac{r}{R_s} \right)^2 dr & , \text{3-D} \end{cases} \tag{7.29}$$

The same methodology is used below to derive the surface tension in two dimensions.

First, the relationship between P_N , $\partial P_N / \partial x$, and P_T is required. Consider a two dimensional volume element as shown

Fig. 7.14. Relationship between the bond and the surface.

Fig. 7.15. Instantaneous atom positions and time averaged density and pressure profiles.

in Fig. 7.16. For zero motion,

$$\begin{aligned} \Sigma F_z &= 0 \\ &= 2P_N r \theta - 2(P_N + \frac{\partial P_N}{\partial r} dr)(r+dr)r + 2P_T \sin \theta \, dr \end{aligned} \quad (7.30)$$

For small angles, $\sin \theta \sim \theta$, and

$$0 = -P_N - \frac{\partial P_N}{\partial r} r - \frac{\partial P_N}{\partial r} dr + P_T \quad (7.31)$$

The dr term can be made arbitrarily small, thus,

$$P_T = P_N + r \frac{\partial P_N}{\partial r} \quad (7.32)$$

The comparable expression in three dimensions is

$$P_T = P_N + \left(\frac{r}{2}\right) \frac{\partial P_N}{\partial r} \quad (7.33)$$

Equation 7.32 has the alternative forms,

$$\frac{\partial}{\partial r}(r P_N) = P_T \quad (7.34)$$

$$\frac{\partial}{\partial r}(r^2 P_N) = r(P_N + P_T) \quad (7.35)$$

Next, the actual tangential force on one side of a radial line is equated to the tangential forces on the same line in the hypothetical situation where the pressure profile is a step function at the surface (Fig. 7.17).

$$\begin{aligned} - \int_{R_1}^{R_2} P_T dr &= - \int_{R_1}^{R_2} P_{12} dr + \gamma_s \\ \rightarrow \gamma_s &= \int_{R_1}^{R_2} (P_{12} - P_T) dr \end{aligned} \quad (7.36)$$

Fig. 7.16. Two dimensional volume element used to derive the relationship between P_N , $\partial P_N / \partial r$, and P_T . All forces are shown as positive (compressive).

Fig. 7.17. Hypothetical strip used to determine the force balance that specifies the surface tension. The pressure arrows indicate two dimensional pressure (force/length) times incremental radius (dr) while the surface tension, γ_s , has force units in two dimensions.

where P_{12} is $P_1(P_1)$ for $r = a_s$ and $P_2(P_2)$ for $r = a_s$.

Similarly, the moments about $r = 0$ are equated for the two situations,

$$-\int_{R_1}^{R_2} P_T r dr = -\int_{R_1}^{R_2} P_{12} r dr + \gamma_s a_s \quad (7.37)$$

$$\rightarrow \gamma_s = \frac{1}{a_s} \int_{R_1}^{R_2} (P_{12} - P_T) r dr$$

Next, equations 7.34 and 7.35 are integrated, and the isotropy of the pressure away from the interface is used.

$$\int_{R_1}^{R_2} P_T dr = (r P_N) \Big|_{R_1}^{R_2} = R_2 P_2 - R_1 P_1 \quad (7.38)$$

$$\int_{R_1}^{R_2} (P_N + P_T) r dr = (r^2 P_N) \Big|_{R_1}^{R_2} = R_2^2 P_2 - R_1^2 P_1 \quad (7.39)$$

These equations can be further manipulated by noting that

$$\int_{R_1}^{R_2} P_{12} dr = R_2 P_2 - R_1 P_1 + a_s \Delta P \quad (7.40)$$

$$2 \int_{R_1}^{R_2} P_{12} r dr = R_2^2 P_2 - R_1^2 P_1 + a_s^2 \Delta P \quad (7.41)$$

where $\Delta P \equiv P_1 - P_2$. Then, Eqs. 7.38 and 7.39 become

$$\int_{R_1}^{R_2} P_T dr = \int_{R_1}^{R_2} P_{12} dr - a_s \Delta P \quad (7.42)$$

and

$$\int_{R_1}^{R_2} (P_N + P_T) r dr = 2 \int_{R_1}^{R_2} P_{12} r dr - a_s^2 \Delta P \quad (7.43)$$

The pressure difference can be eliminated from these two equations to obtain

$$\int_{R_1}^{R_2} (P_{12} - P_T) dr = \frac{1}{a_s} \int_{R_1}^{R_2} [(P_{12} - P_T) + (P_{12} - P_N)] r dr \quad (7.44)$$

But, the first two terms were evaluated using the force and moment balances (Eqs. 7.36 and 7.37). Thus

$$\gamma_s = \gamma_s + \frac{1}{a_s} \int_{R_1}^{R_2} (P_{12} - P_N) r dr \quad (7.45)$$

Since the last term is clearly zero, its sign can be reversed. Then, Eq. 7.44 becomes

$$\gamma_s = \int_{R_1}^{R_2} (P_{12} - P_T) dr = \frac{1}{a_s} \int_{R_1}^{R_2} [(P_{12} - P_T) - (P_{12} - P_N)] r dr$$

or

$$\gamma_s = \int_{R_1}^{R_2} (P_N - P_T) \left(\frac{r}{a_s} \right) dr \quad (7.46)$$

This result is parallel to the one and three dimensional equations (Eq. 7.29). In general,

$$\gamma_s = \int_{-\infty}^{\infty} (P_N - P_T) \left(\frac{r}{a_s} \right)^{D-1} dr \quad (7.47)$$

where D is the number of dimensions. The extension of the limits to infinity is permissible since $P_N - P_T = 0$ except near the interface.

A force balance between the inside and outside of the drop relates γ_s , a_s , and ΔP (Fig. 4.17).

$$a_s = (D-1)\gamma_s / \Delta P \quad (7.48)$$

Then,

$$\gamma_s^D = \left(\frac{\Delta P}{D-1} \right) \int_{-\infty}^{\infty} (P_N - P_T) r^{D-1} dr \quad (7.49)$$

In two and three dimensions (Eqs. 7.32 and 7.33),

$$P_N - P_T = - \left(\frac{r}{D-1} \right) \left(\frac{\partial P_N}{\partial r} \right) \quad (7.50)$$

Then,

$$\gamma_s = - \left[\frac{\Delta P^{D-1}}{(D-1)^D} \right] \int_0^{\infty} \frac{\partial P_N}{\partial r} r^D dr \quad (7.51)$$

This equation is identical to Eq. 15 (Ref. 29) in three dimensions,

$$\gamma_s^3 = - \left[\frac{\Delta P^2}{8} \right] \int_0^{\infty} \frac{\partial P_N}{\partial r} r^3 dr \quad (7.52)$$

In two dimensions,

$$\gamma_s^2 = - \Delta P \int_0^{\infty} \frac{\partial P_N}{\partial r} r^2 dr \quad (7.53)$$

This result can be numerically evaluated using the time-averaged pressure profile obtained from the molecular dynamics calculation (Eqs. 7.21, 7.27, and 7.28).

A series of two dimensional molecular dynamics calculations was performed on systems ranging from 70 to 700 atoms at temperatures below (0.25) the triple point, near it (0.35 to 0.4), and above it

(0.45). Time averages were taken for up to 1450 reduced time units ($t \sqrt{\epsilon/\mu} / \sigma$) in a few cases, with typical averaging periods being 400 to 700 time units.

Analysis of the results indicates that the sub-triple point runs had not reached equilibrium. (Low densities and negative pressures typical of the two-phase solid-vapor region were measured.) For the high temperature runs (which were only about 0.1 reduced temperature units below the critical point of ~ 0.55), fluctuations and occasional drop fragmentation obscured the results. Fortunately, near the triple point, reasonable results were obtained. This experience, which used ~ 6 CRAY CPU hours, indicates that the relatively small 2-D temperature range between the triple and critical points makes 2-D free-surface simulation very difficult.

Once a reasonable two-dimensional surface tension vs. system size curve was generated, scaling arguments were used to convert the three dimensional results to two dimensions. A simple way of thinking about surface tension is in terms of excess energy due to missing bonds for surface atoms. Then,

$$\gamma = \left(\frac{\text{missing bonds}}{\text{surf. atom}} \right) \left(\frac{\text{surf. atoms}}{\text{surf. area}} \right) \left(\frac{\text{energy}}{\text{bond}} \right) = \left(\frac{\text{energy}}{\text{surf. area}} \right) \quad (7.54)$$

In two dimensions,

$$\gamma_2 = 2 \left(\frac{1}{r_2} \right) (-\phi_2) \quad (7.55)$$

In three dimensions,

$$\gamma_3 = 3 \left(\frac{2}{\sqrt{3} r_3^2} \right) (-\phi_3) \quad (7.56)$$

where r_3 is the bond length for the given density (ρ^3). For equal densities, r_2 does not equal r_3 since $\rho_3 = \sqrt{2} / r_3^3$ and $\rho_2 = 2/(\sqrt{3} r_2^2)$.

Application of Eq. 7.56 at $T_2 = 0.41$ ($\rho = 0.75$) gives $\gamma_3 = 1.84$, about four times the correct value of 0.43. The simple model is expected to produce high values of surface tension because the actual (smooth) density profile increases the energies of the remaining bonds; the simple model assumes a step decrease in density with no change in bond strength.

Using the density-bond length relationships and Eqs. 4.15, 7.55, and 7.56 allows calculation of the ratio of 3-D to 2-D surface tensions,

$$\frac{\gamma_3}{\gamma_2} = 1.14 \rho^{-5/6} [(\frac{\rho^2}{2} - 1) / (\frac{\rho^3}{1.54} - 1)] \quad (7.57)$$

As before, reduced units are used ($\rho = \rho_3 \sigma^3 = \rho_2 \sigma^2$, $\phi = \phi/c$, $r = r/\sigma$, $T = kT/c$, $\gamma_3 = \gamma \sigma^2/c$, and $\gamma_2 = \gamma \sigma/c$). The ratio, γ_3/γ_2 , varies from 1.9 at $\rho = 0.5$ to 1.4 at $\rho = 0.9$.

Figure 7.18 shows the results of the two dimensional molecular dynamics calculations at $T = 0.35$. The figure also shows the two dimensional planar limits (scaled from three dimensional values) and the $T = 0.41$ two dimensional surface tension scaled from the $T = 0.80$ three dimensional data. (The temperatures correspond to a reduced density of 0.75 in both dimensions.) For comparison, the predicted $T = 0.41$ surface tension curve is shown assuming the two dimensional surface tension varies linearly with temperature to zero at the critical temperature ($T = 0.56$). The accuracy of this assumption is

Fig. 7.18. Two dimensional surface tension from molecular dynamics calculations and from scaled three dimensional values. The data is plotted as a function of $1/\sqrt{N_\ell}$ because surface tension is expected to have a size dependence.

unimportant because the expansion and vapor pressure formation have reduced the temperature of most fragments to the 0.35 region at the time of fragmentation. Finally, the figure shows an analytical equation used to approximate the surface tension,

$$\gamma = 0.42 \left[1 - \left(\frac{T-0.35}{0.21} \right) \right] [0.281 \log N_L - 0.029] \quad (7.58)$$

where N_L is the number of liquid atoms and 0.42 is the surface tension for $N_L > 5000$ atoms at a temperature of 0.35. The equation is plotted at $T = 0.35$.

Because the surface tension is still somewhat uncertain, Eq. 7.58 is used, and the sensitivity to a factor of ten error is evaluated in the comparison between the molecular dynamics fragmentation runs and the four models from Chapter Five. Equation 7.58 has also been reformulated to eliminate the logarithmic dependence in favor of a more physically meaningful power-law relationship,

$$\gamma = 0.35 \left[1 - (N_L)^{-1/2} \right]^4 \left[1 - \left(\frac{T-0.35}{0.21} \right) \right] \quad (7.59)$$

This relationship is plotted in Appendix A, and it is not much different than Eq. 7.58.

As an alternative method of evaluating surface tension, the potential energy per atom was examined as a function of drop size for all the fragments with more than 19 atoms in the 169, 721, and 2611 atom fragmentation runs. The energy data were taken at the latest time available in each run. It was hoped that the ensemble would produce an energy curve that, coupled with reasonable entropy dependence on drop size³⁶, could be fit to a single equation with

surface tension being one of the fitting constants. However, the scatter in the energy data (Fig. 7.19) is too large to allow an accurate curve fit, probably because time averages were not used. The scatter did not disappear when the kinetic energy and surface energy (from Eq. 7.58) were added, confirming the need to time average. Unfortunately, the energy data were only compiled at infrequent intervals.

Fig. 7.19. Potential energy per atom as a function of drop size at times long after fragmentation. The scattered data does not allow determination of the surface tension by curve fitting these non-time-averaged data.

7.3. Molecular Dynamics Experiment Results

As a part of this study, molecular dynamics calculations were carried out on two dimensional circular liquid regions of up to 14491 atoms. These liquid regions were equilibrated within a confining wall at various temperatures between saturation (~ 0.5) and ~ 1.2 and then released. An additional three dimensional molecular dynamics study⁶³ of 250 atom cubical systems is discussed. This study equilibrated to various densities and temperatures using periodic boundary conditions and then released the boundaries.

7.3.1. Two Dimensional Molecular Dynamics Results

A series of fragmentation calculations began with wall-confined systems of 14491, 2611, 721 and 169 atoms that had been equilibrated at temperatures ranging from ~ 1.2 down to near saturation (~ 0.5 to 0.55). Although the calculations were intended to begin at constant density (~ 0.6), inspection of the cumulative density profile

$$\rho_C(r) = \int_0^r \rho(r) 2\pi r dr / \pi r^2 \quad (7.60)$$

indicated initial densities ranging from 0.61 to 0.73 . The initial conditions for the 13 fragmentation runs are shown in Table 7.2 and in Fig. 7.20.

As time evolved, snapshots of the atomic positions were used to visualize the fragmentation; an example sequence is shown in Fig. 7.21. A more quantitative description of the fragmentation process is contained in the next several figures which show four fragmentation quantities as a function of time, system population and heating level. The abscissa of each plot is the time divided by the pressure relief time ($t/\tau = t_c/R$). Four system sizes (14491, 2611, 721 and 169 atoms) are shown on each figure. The multiple curves for each system size indicate different amounts of isochoric heating. The amount of heating can be seen from the y-intercepts on Fig. 7.22 which shows the evolution of the thermal and translational temperatures with time. To decrease the impact of vapor pressure formation on the results, both temperatures are based on the total non-monomer atoms in the system. The translational temperature is defined as the total of

Table 7.2. Initial conditions for the fragmentation runs. Reduced units are used: r/σ , kT/ϵ , $\rho\sigma^2$, $P\sigma^2/\epsilon$, $c\sqrt{M/\epsilon}$, and $t_T=(R/c)(\sqrt{\epsilon/M}/\sigma)$.

Population	Radius	Temperature	Density	Pressure	Sound Speed	Relief Time
14491	86.7	1.01	0.61	1.02	3.7	23.6
2611	36.6	1.16	0.62	1.38	4.1	8.9
2611	36.6	0.76	0.62	0.53	3.1	11.9
2611	36.6	0.65	0.62	0.31	2.7	13.4
721	19.4	1.17	0.61	1.31	4.0	4.8
721	19.1	0.77	0.63	0.60	3.2	5.9
721	18.8	0.65	0.65	0.40	3.2	6.0
721	18.6	0.55	0.66	0.17	2.9	6.4
721	18.4	0.51	0.68	0.07	2.9	6.2
169	9.1	1.19	0.65	1.75	4.6	2.0
169	8.9	0.77	0.68	0.86	4.0	2.3
169	8.9	0.62	0.68	0.41	3.5	2.6
169	8.6	0.50	0.73	0.11	3.6	2.4

Fig. 7.20. Initial conditions for the two dimensional molecular dynamics fragmentation calculations.

Fig. 7.21. Snapshots of the atomic configurations at four times during the fragmentation process of a 14491 atom system ($T \sim 1.0$).

Fig. 7.22. Thermal and translational temperature evolution in the 2-0 fragmentation runs.

the center of mass kinetic energies of all the clusters with more than one atom, divided by the number of non-monomer atoms. The thermal temperature is defined as the total kinetic energy of non-monomer atoms less the cluster center of mass translational and rotational energies, all divided by the number of non-monomer atoms. The rotational temperature, defined by $T_{\text{rot}} = 2(L^2/2N_c I)$ (Section 6.8.2), was not plotted because it was always too low to show on the graphs.

The thermal temperature relaxed to a "post-fragmentation" level of about 0.35 to 0.4 (near the triple point) after about two or three pressure relief times (R/c) in all cases (Fig. 7.22). The translational temperature reached its "post-fragmentation" value at about the same time; however, the value was very dependent on the initial "pre-fragmentation" thermal temperature. For the highest heating level (to $T \sim 1.15$), the final translational temperature was ~ 0.4 , somewhat higher than the final thermal temperature. For the lower heating levels, the final translational temperature was 0.1 or lower. There was an observable system size dependence for the translational temperature, with the larger systems attaining higher values. (Increased fragmentation is expected from the lower surface to volume ratios in larger systems as shown in Chapter Five.) The total of the final translational and thermal temperatures was always less than the initial thermal temperature; the remaining energy was carried as kinetic energy by monomer atoms in the vapor, or stored as potential energy in the interatomic bonds. The system potential energy increased due to bond loss during both vapor pressure formation and surface area growth (fragmentation), and decreased due to the

increase in bulk density caused by the lower liquid temperature. (The increases in the potential energy were higher in magnitude than the decreases.)

The thermal temperature of the largest cluster is shown in Fig. 7.23. Comparison with Fig. 7.22 shows that the average and largest cluster temperatures were similar at all times.

The fractional size of the largest cluster is shown in Fig. 7.24. When fragmentation was extensive, it occurred at about two to four pressure relief times. In some cases, fragmentation did not occur (small heating in small systems). The top curve ($T \sim 0.55$) in the 721 atom graph is interesting; between 7.5 and 9.5 pressure relief times, about 20% of the atoms fragmented, but by the next compilation time ($t/\tau \sim 11.5$), the fragment had been recaptured due to its internal oscillation (which caused an elongation). The $T \sim 0.75$ runs appear to be borderline for the three smallest system sizes, with fragmentation occurring in steps over an extended period of time much longer than the thermal temperature relaxation time.

The largest cluster size is replotted in Fig. 7.25 using a normalizing factor from model 3 ($1/N^{2/3}$). If model 3 is correct, the curves starting from similar temperatures should coalesce after fragmentation. The larger degree of success of the normalization for high initial temperatures indicates that the model works best for vigorous fragmentation, and not as well for marginal fragmentation.

The final figure of the series, Fig. 7.26, shows the bond count per non-monomer atom. In each case, the initial values of five to six included ~ 3 first neighbor and ~ 3 second neighbor bonds per atom. The bond count fell due to fragmentation and vapor pressure

Fig. 7.23. Thermal temperature evolution of the largest cluster in the 2-D fragmentation runs. (The cluster identity sometimes changed with time.)

Fig. 7.24. Fractional size of the largest cluster in the 2-D fragmentation runs (size / non-monomer population). The cluster identity sometimes changed with time.

Fig. 7.25. Normalized size of the largest cluster in the 2-D fragmentation runs (size / system size^{2/3}). The normalization (from model 3) should cause the curves with similar temperatures to coalesce after fragmentation. When fragmentation was extensive, the curves do coalesce, supporting the validity of model 3.

Fig. 7.26. Bonds per non-monomer atom in the 2-0 fragmentation runs.

formation in about the same time as the temperature; "post-fragmentation" values were reached in two to four pressure relief times. (Since the temperature change was independent of the potential truncation distance, the temporal agreement between the temperature, the cluster size and the bond count indicates that the truncation distance was not inappropriate.) For the borderline cases ($T \sim 0.75$), the bond count was not affected by the late time fragmentation; this was because most of the bonds were broken in the early stages ($t/\tau \sim 2$ to 4), forming internal voids. However, the cluster separation was not complete until all bonds between the clusters were broken; when the fragmentation was borderline, this occurred much later due to the small translational velocities generated.

The paths followed on a T - ρ diagram are shown in Fig. 7.27 for two 2611 atom runs. The paths shown use spatially averaged densities up to the fragmentation point, but inspection of the position plots shows marked heterogeneity much earlier. (The definition of fragmentation used here requires a minimum fragment separation of 2.5σ .) Internal voids which eventually become fragment surfaces appear much earlier. The internal voids decrease the "pre-fragment" density; hence, density appears to increase upon fragmentation. Temperature also decreases; as a new daughter fragment is born, its "center-of-mass translational energy" is instantaneously subtracted from the "internal" energy of its parent cluster. Most of the fragment temperatures lie along the saturated liquid phase line. Finally, although the low temperature run appeared to penetrate the unstable region under the isothermal spinodal (and may have reached the isentropic spinodal which lies below the isothermal spinodal), the

Fig. 7.27. Pressure-density paths followed by two fragmentation runs. The densities were calculated in an average sense; actual local density in the fluid did not reach such low values.

regular density patterns^{64,65} characteristic of "spinodal decomposition" were not observed. This is because the fragmentation expansion is inhomogeneous. If the internal voids that precede fragmentation were not included in the density calculation, then the spinodal lines would not be reached.

The fragment size distribution for the 14491 atom run after fragmentation was evident is shown in Fig. 7.28. The solid lines show the population in clusters of the given size. The curves are the population in the bin (e.g. 10 to 14 atoms) divided by the bin width (e.g. 4 atoms). The abscissa is the fragment size divided by the total population; hence, the integral of each solid curve is 1.0. The jagged curve includes only one fragment size in each bin, but variable width bins are used to eliminate narrow spikes in a mostly-zero background. The smoother curve has wider bins, but the same integral. This smoother curve is probably similar to an ensemble average of a number of calculations beginning with slightly different configurations of identical energy and average density.

The dashed line in Fig. 7.28 shows the integrated distribution for the 14491 atom run; i.e. each curve value indicates the fraction of the total population in fragments of the given size or smaller. The population distribution was concentrated in small fragments, with one-half of the population in fragments that were less than 20% of the size (in atoms) of the largest fragment.

The integrated (cumulative) population distributions for three runs with similar heating levels and varying system sizes are shown in Fig. 7.29. The smallest (721 atom) system had a significant portion of the population concentrated in an intermediate fragment size range

Fig. 7.28. Fragment size distribution for the 14491 atom system at $t = 104.3$, just after fragmentation was well defined. The solid lines show the fractional population distribution as a function of fragment size; the integrals of both the raw and the smoothed curves are 1.0. The dashed line is the running integral of the raw curve.

Fig. 7.29. Integrated population distributions as a function of fragment size for three fragmentation runs with similar heating levels but different system sizes. The dashed lines give integrals as functions of the fractional fragment size, N_c/N , and the solid lines are normalized to the largest fragment size, i.e. the abscissa is $N_c/N_{c\text{max}}$. The fragment data were taken just as fragment sizes became well defined.

(indicated by the steep portion of the curve). The larger systems' populations were peaked at relatively lower fragment sizes and exhibited decreasing population density with increasing fragment size. The overall effect of increasing system size was to concentrate population in smaller fractional fragment sizes; 50% of the population was in fragments smaller than 36%, 18%, and 17% of the largest fragment size for the 721, 2611, and 14491 atom systems, respectively.

7.3.2. Three Dimensional Molecular Dynamics Results.

A series of three dimensional molecular dynamics calculations were carried out this year by an Italian and University of Illinois team⁶³. Each calculation began with periodic boundary conditions and a cubical 250 argon atom system (using the 6-12 Lennard-Jones potential with a cutoff at $r = 3\sigma$). The atoms were initially at the lattice points of a body-centered-cubic structure. The specific volume was set and maintained at 12, 24 or 48 cm³/gmole during equilibration from an initial randomly generated velocity distribution corresponding to 300, 600, 1200 or 2400 K. After 600 time steps (0.01 ps each) of constant energy equilibration, the periodic boundary conditions were released. The resulting evolution of the system was computed for 3000 time steps with energy compilations each 300 time steps. Each of the twelve runs was repeated three times to check the statistical fluctuation in the results.

Because the Italian study was primarily concerned with the velocity distribution in the vapor and small clusters, the authors did not report results for clusters larger than seven atoms. However, they were kind enough to privately provide full computer outputs for two runs: $V = 48$ cm³/gmole, $T = 300$ K; and $V = 24$ cm³/gmole, $T = 600$ K. For argon, the authors used the following parameters:

$$\begin{aligned} m &= 39.96/6.023 \times 10^{26} = 6.63 \times 10^{-26} \text{ kg/atom,} \\ \sigma &= 3.405 \times 10^{-10} \text{ m, and} \\ \epsilon/k &= 119.8 \text{ K} \end{aligned} \quad (7.61)$$

From these parameters,

$$\begin{aligned}
 \epsilon &= 119.8 (1.38 \times 10^{-23}) = 1.65 \times 10^{-21} \text{ J}, \\
 A\sqrt{\epsilon/m} / \sigma &= 10^{-14} \sqrt{\epsilon/m} / \sigma = 0.0046 \\
 \rho\sigma^3 &= 6.023 \times 10^{23} \sigma^3 / V \text{ (cm}^3/\text{gmole)} \\
 \left\{ \begin{aligned} &= 0.495 \quad , \quad V = 48 \text{ cm}^3/\text{gmole} \\ &= 0.991 \quad , \quad V = 24 \text{ cm}^3/\text{gmole} \end{aligned} \right. \quad (7.62) \\
 kT/\epsilon &= T / 119.8 \text{ K} \\
 \left\{ \begin{aligned} &= 2.50 \text{ for } T = 300 \text{ K} \\ &= 5.01 \text{ for } T = 600 \text{ K} \end{aligned} \right. .
 \end{aligned}$$

Reduced units ($\rho\sigma^3$, kT/ϵ , $P\sigma^3/\epsilon$, and E/ϵ) are used in the remainder of this section.

The computer output included cluster size distribution, overall temperature, and both thermal and translational temperatures for each cluster size, all at 300 time step intervals (1.38 reduced time units). After some examination, the total and thermal temperatures were determined to be in units of energy per atom while the translational temperatures were in different units (energy per cluster). Using this information, the system thermal and translational temperatures were determined,

$$T_{tr} = \frac{\sum_{S_c=2}^{\text{largest}} \{[T_{tr}(S_c)][N_s]\}}{(N - N_m)} \quad (7.63)$$

$$T_{th} = \frac{\sum_{S_c=2}^{\text{largest}} \{[T_{th}(S_c)][S_c][N_s]\}}{(N - N_m)} \quad (7.64)$$

where

S_c is the number of atoms in a cluster,

N_s is the number of clusters of size S_c ,

N_m is the number of monomer atoms,

N is the system population,

T_{tr} is the reduced translational temperature for the system (on a per atom basis),

$T_{tr}(S_c)$ is the reduced translational temperature for cluster size S_c (on a per cluster basis),

T_{th} is the reduced thermal temperature for the system (on a per atom basis), and

$T_{th}(S_c)$ is the reduced thermal temperature for cluster size S_c (on a per atom basis).

When Eqs 7.63 and 7.64 are modified to include monomers, the sum of T_{tr} and T_{th} equal the system temperature given in the computer output, which verifies the equations. (If $T_{tr}(S_c)$ is assumed to be on a per atom basis, the total temperature increases with time, an unreasonable result.)

To allow comparison with model 3, the pressure at boundary release time, the wave speed, and the surface tension are required. The three dimensional surface tension was discussed in Section 7.2.3. The pressure is available from a semi-empirical expression by Ree⁶⁶,

$$P = \rho T + B_{10} \rho^{11} T^{-3/2} + \sum_1^4 B_1 \rho^{1+1} T^{-1-0.251} - \sum_1^5 C_1 \rho^{1+1} T^{0.5-0.251} + \sum_1^5 A_1 \rho^{1+1} T^{-1/4} \quad (7.65)$$

where ρ , T , and P are reduced variables, and the constants A_1 to A_5 , B_1 to B_4 , B_{10} , and C_1 to C_5 are listed in Table 7.3.

The sound speed is calculated from Eq. 7.18. Ree's pressure equation can be used to determine the quantities needed to evaluate Eq. 7.18, $(\partial P/\partial \rho)_T$, $(\partial P/\partial T)_\rho$, and $(\partial E/\partial T)_\rho$.

$$\begin{aligned} \left(\frac{\partial P}{\partial \rho}\right)_T = & T + 11B_{10}\rho^{10}T^{-3/2} + \sum_1^4 (1+1)B_1\rho^1T^{1-0.251} \\ & - \sum_1^5 (1+1)C_1\rho^1T^{0.5-0.251} + \sum_1^5 (1+1)A_1\rho^1T^{-1/4} \end{aligned} \quad (7.66)$$

$$\begin{aligned} \left(\frac{\partial P}{\partial T}\right)_\rho = & \rho - 1.5B_{10}\rho^{11}T^{-5/2} + \sum_1^4 (1-0.251)B_1\rho^{1+1}T^{-1/4} \\ & - \sum_1^5 \frac{1}{2}(1-0.51)C_1\rho^{1+1}T^{-0.5-0.251} - \sum_1^5 \frac{1}{4}A_1\rho^{1+1}T^{-1-0.251}. \end{aligned} \quad (7.67)$$

The internal energy is

$$E = (3/2)\rho T + \partial(A^E/T)/\partial(1/T) \quad (7.68)$$

where the excess Helmholtz free energy per atom is

$$A^E = \frac{T}{\rho} \int_0^\rho \left(\frac{P}{\rho T} - 1\right) d\rho \quad (7.69)$$

Combining Eqs. 7.65, 7.68 and 7.69; and then differentiating produces

$$\begin{aligned} \left(\frac{\partial E}{\partial T}\right)_\rho = & \frac{3}{2}\rho + T - \frac{3}{22}B_{10}\rho^{10}T^{-5/2} + \sum_1^4 \left(\frac{1-0.251}{1+1}\right)B_1\rho^{1+1}T^{-1/4} \\ & - \sum_1^5 \left(\frac{1-0.51}{1+1}\right)\frac{1}{2}C_1\rho^{1+1}T^{-0.5-0.251} - \sum_1^5 \left(\frac{1}{4(1+1)}\right)A_1\rho^{1+1}T^{-1-0.251}. \end{aligned} \quad (7.70)$$

After equilibration, the two runs had decreased temperatures due

Table 7.3. Constants used in Ree's⁶⁶ pressure equation. (A_1 to A_5 were labeled D_1 to D_5 by Ree).

$B_1 = 3.629$	$C_1 = 5.3692$	$A_1 = -3.4921$
$B_2 = 7.2641$	$C_2 = 6.5797$	$A_2 = 18.6980$
$B_3 = 10.4924$	$C_3 = 6.1745$	$A_3 = -35.5049$
$B_4 = 11.459$	$C_4 = -4.2685$	$A_4 = 31.8151$
$B_{10} = 2.17619$	$C_5 = 1.6841$	$A_5 = -11.1953$

to the atomic structure changing from solid to liquid (increasing the potential energy at the expense of the kinetic energy). The $T = 2.50$ run actually began to fragment from a reduced temperature of 2.36; the $T = 5.01$ run began to fragment from a temperature of 2.50. The temperature, density, pressure, sound speed and cube half-width at the start of fragmentation are shown for both runs in Table 7.4. The cube half-width was calculated from

$$\rho = 250 \text{ atoms} / (2 L_{1/2}^3) \quad (7.71)$$

The conditions at the boundary release time are shown in Fig. 7.30.

The results of the two fragmentation runs are shown in Fig. 7.31 which has the same format as Figs. 7.22, 7.23, and 7.24. The top graph shows the evolution of the system translational and thermal temperatures, the middle graph shows the thermal temperature of the largest cluster, and the bottom graph shows the size of the largest cluster. The abscissa is time divided by the expected relief wave traversal time. In each case, monomer atoms have been excluded from both the energy and the population compilations in order to reduce the influence of vapor pressure formation on the fragmentation results.

The curves are qualitatively like their two dimensional counterparts although fragmentation was somewhat slower. The 3-D runs were for a very small system (less than one-half the radius of the smallest, 169 atom, 2-D runs). In 2-D, the fragmentation time was relatively independent of the initial conditions, but all those runs began at about the same density. In 3-D, the higher density system fragmented slower, probably because the denser atoms had to travel

farther before reaching the 3σ potential cutoff used to define the clusters.

Table 7.4. Thermodynamic and geometric quantities at the start of the 3-D fragmentation runs.

ρ	0.495	0.991
T	2.36	2.50
$T^\dagger$	(2.50)	(5.01)
P	1.49	17.89
$(\partial P / \partial T)_\rho$	1.25	6.18
$(\partial P / \partial \rho)_T$	6.70	81.71
$(\partial E / \partial T)_\rho$	3.72	5.88
$[(\partial P / \partial \rho)_T]^{1/2}$	2.59	9.04
c	3.28	9.91
$L_{1/2}$	3.98	3.16

† prior to equilibration

Fig. 7.30. Initial temperatures and densities for the two Italian 3-D molecular dynamics fragmentation calculations.

Fig. 7.31. Evolution of two pressurized cubes. The curves do not include monomers in either the energy or the population summations.

7.4. Comparison of the Molecular Dynamics Results to the Models Derived in Chapter Five

The hydrodynamic models, (1), (2), (3) and (4), from Chapter Five predict $N_C \sim N_P^{-2}$, N_P^{-4} , $N^{2/3}P^{-4/3}$, and NP^{-2} , respectively in two dimensions,. In three dimensions, the four models predict $N_C \sim N_P^{-3}$, N_P^{-6} , $N^{2/3}P^{-2}$, and NP^{-3} .

In this section, the two-dimensional molecular dynamic results (for the larger fragments) are plotted on log-log graphs to determine which power law applies. The result is that model 3 is the only model consistent with the molecular dynamics data. Then, quantitative predictions using model 3 are made for all the fragments with more than nine atoms (a size that eliminates an inconveniently large number of very small fragments); these predictions are a function of the observed fragment size because of the size dependence of the surface tension. The translational temperatures of the two-dimensional fragments are also compared with the upper bound prediction of simple hydrodynamics. Finally, the two available three dimensional molecular runs are compared to the predictions of model 3.

For a quantitative comparison of the molecular dynamics results to model 3, it is convenient to plot as figures of merit, the ratios of the observed to the predicted fragment fractional size and translational temperature. These quantities are

observed

predicted

$$\frac{N_C}{N} = \left[\frac{\pi}{N} (D+2)^D \left(\frac{D+1}{D} \right)^{D-2} \gamma^D \rho^{D+1} \left(\frac{c_s}{P} \right)^{2D} \right]^{1/3} \quad (7.72)$$

$$T_{tr} \left(= \frac{2}{D} \frac{K_C}{N_C} \right) = \frac{1}{D} \left(\frac{P}{\rho c} \right)^2 \quad (7.73)$$

where N_c and K_c are the population and translational energy of the observed cluster. The system population, N , does not include monomers in order to remove some of the influence of vapor pressure formation. When the ratio of observed to predicted fragment size or temperature is greater than one, an underprediction was made. It should be noted that the translational temperature prediction is an upper bound since it assumes that all the kinetic energy produced by the relief wave is translational, actually, a portion of the kinetic energy is initially dilational (and eventually thermal). For extensive fragmentation, Eq. 5.35 shows that model 3 predicts a reduction in the translational temperature of $[1-0.6(N_c/N)^{2/3}]$ in three dimensions and of $[1-0.5(N_c/N)]$ in two dimensions. Because the average observed quantities were always above the upper bound, the upper bound prediction was used for simplicity unless otherwise noted.

The time of the observation influences the figures of merit. The observation time should be late enough that fragmentation is essentially complete, but as early as possible to minimize the influence of vapor pressure formation. Because the energy compilations were intermittent, only a limited set of observation choices existed. The times selected are listed in Table 7.5. In cases where fragmentation was marginal, considerably more time (in relief time units) elapsed before fragmentation. Examination of the atomic position plots for these cases indicates that some regions oscillated (changed overall shape) several times before fragmenting.

For convenience, only fragments with ten or more atoms were considered; smaller fragments were too numerous and too easily

Table 7.5. Times at which the fragment sizes and translational temperatures were compared to the predicted values.

<u>Population[†]</u>	<u>Temperature</u>	<u>Reduced Time</u>	<u>Time (Relief Time Units), t c/R</u>
<u>Two dimensional runs</u>			
14491	1.01	104.3	4.4
2611	1.16	38.4	4.2
2611	0.76	76.9	6.4
2611	0.65	71.4	5.2
721	1.17	29.4	6.0
721	0.77	70.3	11.7
721	0.65	74.4	12.0
721	0.55	78.0	11.5
721	0.51	80.0	11.9
169	1.19	9.1	4.5
169	0.77	10.8	4.5
169	0.62	74.7	27.7
169	0.60	81.0	31.2
<u>Three dimensional runs</u>			
250	2.36	6.9	5.7
250	2.50	6.9	21.6

[†] including monomers

confused with the vapor. In evaluating Eq. 7.72, the surface tension was computed for the observed (rather than predicted) fragment size. Also, if the predicted fractional fragment size was larger than 1.0, it was reduced to 1.0. (Model 3 does not apply when there is no fragmentation.) This correction was only required for 22 of the 390 two dimensional fragments, and for two of the eleven three dimensional fragments; the fragments needing correction were almost always from essentially non-fragmenting runs. Finally, three fragments could not be evaluated because the temperature was above the critical point. This furnishes a reminder that the temperatures read from the results are instantaneous values rather than proper time averages, which accounts for some of the scatter in the results.

7.4.1. Comparison of the Two Dimensional Molecular Dynamics Results to the Hydrodynamic Models

The fragment sizes (in atoms) from two 2611 atom runs are shown in Fig. 7.32. The largest fragment, the average of the ten largest fragments, and the average of the largest fragments comprising 30% of the non-monomer population are shown. In each case, the raw data have been slightly adjusted (using the energy minimization model, "model 3") to uniform initial conditions (2611 non-monomer atoms, $\rho=0.6$, $c=4.0$, and $\gamma=0.32$). The only remaining variable in model 3 is the initial pressure. The slopes of the three fragment size curves are -1.03, -0.86, and -1.42, respectively; these values bracket the predicted slope of $-4/3$ from model 3 reasonably well. To illustrate the sensitivity of the fragmentation to fragment-size dependent surface tension, the prediction curve is also shown using the lower surface tensions at the actual fragment sizes; the "observed" curves would be similarly steeper when the surface tension correction (to $\gamma = 0.32$) is eliminated. Finally, the other model predictions are shown. The slopes of models 1, 2, and 4 (-2, -4, and -2, respectively) are much steeper than the molecular dynamics results.

The fragment sizes from the highest pressure run for each system size (14491, 2611, 721, and 169 atoms) are shown in Fig. 7.33. The nomenclature is identical to the previous figure. As in Fig. 7.32, the data were slightly adjusted to uniform initial conditions ($P = 1.4$, $\rho=0.6$, $c=4.0$, and $\gamma=0.32$). The only remaining variable in the models is the system size (total number of particles), N . The slopes of the middle section of the three fragment size curves are 0.75, 0.69, and 0.64, respectively. These observed values bracket the

Fig. 7.32. Observed and predicted fragment sizes (atoms) as a function of initial pressure, for two 2611 atom runs. The data and model predictions have been slightly adjusted to constant initial conditions. The three observed values for each run are for the largest fragment, the average of the ten largest fragments, and the average of the largest fragments comprising 30% of the system population (less monomers).

Fig. 7.33. Observed and predicted fragment sizes (atoms) as a function of system size, for similar heating levels. The nomenclature is identical to Fig. 7.32.

predicted slope of $2/3$ from model 3. The 169 atom data were not used to compute the slope because of minimal fragmentation. The 14491 atom fragment sizes are probably a bit low. Position snapshots and density profiles indicate that a sloshing motion was present in the system at the time the confining boundary was removed. However, if the slopes are computed using line segments between the 721 and 14491 data, the results are 0.54, 0.50, and 0.41, respectively. Thus, the molecular dynamics results indicate a possible system size dependence of the $2/3$ power (the illustrated line), but support that slope with an uncertainty of ± 0.15 . This result again is consistent with the energy minimization model (model 3). Models 1 and 2 include no system size dependence and accordingly predict very low fragment sizes for this initial condition (0.1 and 18 atoms, respectively). Model 4 predicts a much steeper slope (1.0) than found in the molecular dynamics runs.

Although the data in Figs. 7.32 and 7.33 support the energy minimization model's power law dependence of fragment size on system size and isochoric heating level (initial pressure), the magnitudes of the observed sizes (in atoms) are about ten times lower than the model 3 prediction. It is therefore suggested that the predictions of that model be reduced tenfold in applications. Macroscopic systems require extensive extrapolation; a 10 cm radius HYLIFE jet cross section contains about 2×10^{17} lithium atoms (13 more orders of magnitude in system population). If the 14491 atom run initial conditions (temperature and density) are applied to a 2×10^{17} atom system with lithium values of σ and ϵ (Table 4.6), the predicted fragment size is 2×10^{12} atoms (10^{-5} fractional size), or 0.31 mm radius

(0.10 nm radius if the factor of 10 reduction in predicted fragment population is applied). The heating level in that run was 10^{-20} J/bond, about seven times the maximum level expected in HYLIFE. The fragment radius is about 1/7th the 3-D fragment radius predicted using known lithium properties (Section 5.3.3). Because the extrapolation in system size is so large, macroscopic experiments are essential. However, the reasonable agreement between the model and microscopic (computer) experiments allows use of the model to design the experiments.

The preceding discussion of the average observed data is extended below to include individual predictions for each fragment containing ten or more atoms. The extended analysis uses surface tension evaluations at the observed fragment size to make the predictions. The prediction accuracy is examined to determine its dependence on the fragment size, and the sensitivity to errors in either the sound speed or the surface tension is discussed.

The fragment size results for all fragments with ten or more atoms in all the two dimensional runs are shown in Fig. 7.34 as a function of the temperature following isochoric heating. The observed sizes were usually somewhat smaller than the prediction. The largest fragment data point from each run is indicated by a bold symbol; these fragment sizes were closer to the prediction than the smaller fragments (Table 7.6).

The fragment size figure of merit results are cross plotted as a function of observed fragment size in Figs. 7.35 and 7.36 for the three small systems and the 14491 system, respectively. There was a definite fragment size dependence with the larger fragments being

Fig. 7.34. Ratio of the observed to the predicted fragment sizes (atoms) for all fragments containing ten or more atoms in the thirteen 2-D molecular dynamics runs. The prediction is from model 3 (Eq. 7.72).

Table 7.6. Observed and predicted fragment fractional sizes (atoms) for the largest fragment in each 2-D molecular dynamics run. As before, N_c indicates the cluster population, N_m is the number of monomers, and N is the original system population.

$N^\dagger$	Temperature After Heating	Observed N_c	$N_c / (N - N_m)$			
			Observed	Predicted Baseline	Predicted 10% γ	Predicted 50% c
14491	1.01	375	0.028	0.24	0.051	0.094
2611	1.16	136	0.056	0.14	0.030	0.056
2611	0.76	270	0.11	0.68	0.15	0.27
2611	0.65	361	0.15	1.001*	0.22	0.40
721	1.17	44	0.069	0.35	0.76	0.14
721	0.77	117	0.18	0.91	0.20	0.36
721	0.65	337	0.52	1.5*	0.33	0.61
721	0.55	593	0.90	4.1*	0.50	1.6*
721	0.51	626	0.94	16.6*	3.6*	6.6*
169	1.19	41	0.27	0.42	0.09	0.17
169	0.77	64	0.43	0.82	0.17	0.31
169	0.62	129	0.85	2.46*	0.53	0.98
169	0.50	142	0.92	23.8*	5.1*	9.4*

† including monomers

* adjusted to 1.0 for the graphs

Fig. 7.35. The ratio of the observed to the predicted fragment size (atoms), plotted as a function of the observed size, for twelve 2-D molecular dynamics fragmentation runs. The smooth curve is the locus of predicted sizes equal to the original size; the predictions have been adjusted in a few cases to prevent predictions exceeding the original size.

Fig. 7.36. The ratio of the observed to the predicted fragment size (atoms), plotted as a function of the observed size, for the 14491 atom molecular dynamics fragmentation run.

predicted the most accurately. Figure 7.35 is deceptive, however, because the five largest data points plotted were predicted to remain intact by varying margins (Table 7.6). If the non-physical predictions of fragments larger than 100% of the system size were used for these points, some of them would be considerably above the ratio = 1.0 line. Nevertheless, the larger fragments of the vigorously fragmenting systems were predicted quite well (a factor of 1.5 to 6 larger than the observed values).

The smaller fragments were not predicted very well by the model even though the surface tension was evaluated at the observed fragment size. Possible explanations for this result include the following:

- The small fragments were remnants from regions between larger fragments, and thus did not meet the energy balance criterion of model 3.

- The large local energy fluctuations in these small systems were conducive to loss of small fragments.

- The surface tension property was grossly incorrect; either due to an error in the equilibrium curves, or due to use of instantaneous temperatures rather than time averages to specify it. (This possibility was investigated by replotting Figs. 7.35 and 7.36 using values of the surface tension reduced by an order of magnitude and also by using values of the sound speed reduced by a factor of two. Although this drastic "adjustment" of properties improved the average behavior, it did not remove the characteristic fragment size dependence of the observed-to-predicted ratio; i.e. the shape of the data did not

change.)

- Vapor pressure formation was responsible for the production of small fragments (even those with more than ten atoms).

- The higher velocity divergence near the original system center would reduce the prediction by a factor of $> (0.2)^{-2} = 25$ in that region (Figs. 5.5 and 5.6). (But the total mass of small fragments was too large to be explained solely by this argument.)

At fragmentation, the fragments are definitely non-circular (e.g. Fig. 7.21). Thus, the surface to volume ratio will be higher than for a sphere (or circle), and one might speculate that the effective (instantaneous) surface tension will be higher than the equilibrium value. However, in an equilibrium drop, the instantaneous configuration is almost always non-circular, so that the "equilibrium" surface tension value includes the additional (time-averaged) surface area. Thus, the non-circular initial fragment shape probably does not force the production of a higher surface tension (and consequently, fragment size).

The ratios of the observed cluster translational temperatures to the prediction from simple planar hydrodynamics are plotted in Figs. 7.37 to 7.39, which are analagous to Figs. 7.34 to 7.36. As Fig. 7.37 shows, the fragment translational temperatures were distributed on both the high and low sides of the predictions.

The translational temperature mean appears to be at about the same level above the prediction for each fragment size (Figs. 7.38 and 7.39), i.e. fragment size was not correlated with fragment

Fig. 7.37. Ratio of the observed to the predicted fragment translational temperatures (Eq. 7.73) for all fragments containing ten or more atoms in the thirteen 2-D molecular dynamics runs.

Fig. 7.38. The ratio of the observed to the predicted fragment translational temperatures, plotted as a function of the observed size, for twelve 2-D molecular dynamics fragmentation runs.

Fig. 7.39. The ratio of the observed to the predicted fragment translational temperatures, plotted as a function of the observed size, for the 14491 atom molecular dynamics fragmentation run.

translational energy. However, the smaller fragments showed a wider temperature distribution than the large fragments. This is reasonable; if a system breaks into only a few large equal-sized fragments, those fragments must have roughly equal momenta (to not alter the initial zero momentum). Conversely, if there are a large number of small fragments, many possible combinations of wide-ranging momenta can satisfy momentum conservation. Finally, both Figs. 7.38 and 7.39 show fragments with very low energy, but no fragments with very high energy. This is also reasonable; a fragment that only marginally escapes could have almost no translational energy. Conversely, because there is only a limited amount of energy in the system, there is an upper bound on the fragment translational energy, and concentrating most of it in only one fragment is unlikely.

Because the surface tension does not enter into the fragment translational temperature prediction (Eq. 7.73), there is no sensitivity of the temperature figure of merit to a change in surface tension. The sensitivities of the translational temperature distributions to a 50% decrease in sound speed were examined by repeating the plots with the lower values of sound speed. For the 14491 atom run, the decreased sound speed improved the results, although a somewhat smaller decrease would have been better. For the other runs, decreasing the sound speed degraded the results.

The overall translational temperature observations and predictions (ignoring clusters with less than ten atoms) are listed in Table 7.7. The translational temperatures (ignoring monomer energy and mass) are shown in Fig. 7.40 as a function of system size and initial pressure. The inset shows the observed translational temperatures which properly

Table 7.7. Observed and predicted fragment translational temperatures for the largest fragment in each 2-D molecular dynamics run. As before, N_c and K_c refer to the population and translational energy of one cluster. The "Observed K/N" is the overall translational energy per atom (ignoring monomer energy and population). The "Predicted K/N" is the translational temperature (translational energy per atom) predicted by Eq. 7.73 which is independent of population.

<u>N[†]</u>	<u>Temperature After Heating</u>	<u>Observed K/N total</u>	<u>Observed K_c/N_c largest^{††}</u>	<u>K/N</u>	
				<u>Predicted Baseline</u>	<u>Predicted 50% c</u>
14491	1.01	0.35	0.33	0.10	0.41
2611	1.16	0.77	0.38	0.15	0.59
2611	0.76	0.15	0.099	0.039	0.16
2611	0.65	0.072	0.021	0.017	0.068
721	1.17	0.36	0.30	0.14	0.58
721	0.77	0.10	0.043	0.043	0.17
721	0.65	0.055	0.19	0.019	0.077
721	0.55	0.029	0.00052	0.0037	0.015
721	0.51	0.018	0.00004	0.00058	0.002
169	1.19	0.34	0.12	0.17	0.68
169	0.77	0.067	0.003	0.051	0.20
169	0.62	0.043	0.009	0.015	0.061
169	0.50	0.022	0.002	0.0008	0.003

[†] including monomers

^{††} for the largest cluster only

Fig. 7.40. Translational temperatures (scaled to the prediction of model 3) for the 13 molecular dynamics runs.

increase with heating level (initial pressure). All the values exceed $v^2/2$, where v is the jump-off velocity, (dashed line). In two dimensions, model 3 predicts

$$T_{tr} = (v^2/2) \left[1 - \frac{1}{2} \frac{N_c}{N} \right] \quad (7.74)$$

For extreme fragmentation ($N_c \rightarrow 0$), Eq. 7.74 produces the correct upper bound, but for no fragmentation Eq. 7.74 predicts 1/2 the upper bound, rather than zero. The failure at no-fragmentation is a consequence of the assumption of a homogeneous expansion in model 3.

The main portion of the figure shows the ratio of the observed to the predicted (Eq. 7.74) translational temperatures. The additional kinetic energy is from two sources: vapor pressure formation (which is limited in Fig. 7.40 by the elimination of monomers from the calculation), and fragmentation due to fluctuations (a phenomenon observed for small systems on the saturation line with no isochoric heating).

For macroscopic systems, model 3 suggests that both vapor pressure formation and fracture due to "equilibrium" fluctuations are negligible. Glenn's three dimensional (macroscopic) hydrodynamic code calculations⁴⁶ confirmed the upper bound of $v^2/2k$. The molecular dynamics calculations (Fig. 7.40) show that the discrepancy tends to increase with system size, at least for systems of a few thousand atoms or less. However, the 14491 atom result shows a decreased discrepancy (even though its initial sloshing motion would be expected to produce more translational energy than an initially quiescent system). Thus, these limited molecular dynamics results are not

inconsistent with model 3. Finally, note that the peak in the excess translational temperature is in the region of the critical nucleus size. Systems smaller than the critical size are naturally unstable, leading to fragmentation even in saturated systems.

7.4.2. Comparison of the Three Dimensional Molecular Dynamics Results to Model 3

The ratios of the observed to the predicted sizes are shown in Fig. 7.41. The high pressure run ($P = 17.9$, $T = 2.5$, $\rho = 0.99$) was predicted very well by the model (to within a factor of two). The lower pressure run ($P = 1.5$, $T = 2.4$, $\rho = 0.5$) was overpredicted by the model (by factors of 5 to 13). The cluster sizes and temperatures for both runs are listed in Table 7.8.

The ratios of the observed to the predicted translational temperatures are shown in Fig. 7.42. Here the situation was reversed; the high pressure run was overpredicted by factors of 16 to 330 while the low pressure run was predicted very well. The translational temperature data are also listed in Table 7.8.

The high pressure run had a predicted translational temperature of 1.1. The observed values for the large clusters were much lower (< 0.1); however, the non-monomer translational temperature was 0.78 while the overall translational temperature was 0.83. Thus, in this case, the fragment sizes were properly predicted, but the fragment translational energy was concentrated in the small fragments.

The low pressure run had a predicted translational temperature of 0.28. The four largest fragments had translational temperatures ranging from 0.018 to 0.48. The non-monomer translational temperature was 0.70 while the overall translational temperature was 0.80. Thus, vapor pressure formation dominated this case. The higher number of monomers in this run was further evidence that vapor pressure was dominant.

Fig. 7.41. The ratio of the observed to the predicted fragment size (atoms), plotted as a function of the observed size, for the two 3-D molecular dynamics fragmentation runs.

Table 7.8. Observed and predicted fragment sizes and translational temperatures for the largest fragments in the 3-D molecular dynamics runs. The variables are defined as before; N , N_c , and N_m indicate system, cluster, and monomer populations while Eq. 7.73 defines the translational temperature.

Fragment Temperature	Observed N_c	$N_c / (N - N_m)$		Translational Temp.	
		Observed	Predicted	Observed	Predicted
<u>$\rho = 0.495, T = 2.36, P = 1.5$</u>					
0.59	30	0.17	0.82	0.24	0.28
0.60	25	0.14	0.68	0.36	0.28
0.32	18	0.10	1.6*	0.18	0.28
0.34	14	0.078	1.2*	0.48	0.28
0.43	12	0.067	0.81	0.014	0.28
<u>$\rho = 0.991, T = 2.50, P = 17.9$</u>					
0.62	46	0.23	0.13	0.0033	1.11
0.66	29	0.14	0.10	0.02	1.11
0.57	28	0.14	0.14	0.011	1.11
0.41	17	0.083	0.14	0.051	1.11
0.76	16	0.078	0.057	0.039	1.11
0.67	11	0.054	0.063	0.067	1.11

* Adjusted to 1.0 for the graph.

Fig. 7.42. The ratio of the observed to the predicted fragment translational temperatures, plotted as a function of the observed size, for two 3-D molecular dynamics fragmentation runs.

7.5. Vapor Pressure Formation as a Competing Phenomenon

When the boundaries were released, small clusters were ejected from the surface almost immediately due to the lack of an equilibrium surface and due to the high liquid temperature. In a normal situation, these lost atoms would be replaced by vapor atoms colliding with the surface. But, in the simulation, there were no reflecting boundaries to confine (and return) the vapor atoms.

Each atom that vaporized removed $\sim 1.9\epsilon$ of potential energy from the liquid in addition to its kinetic energy (typically 0.6 to 1.3 ϵ per monomer). To conserve energy, the kinetic energy of the bulk liquid decreased to offset the increased potential energy. Consider an initial system with N liquid atoms at -1.9ϵ potential energy per atom and temperature, T . After some time, there are N_m monomers with a measurable kinetic energy, K , (and no potential energy). The remaining liquid has $N - N_m$ atoms with $\sim -1.9\epsilon$ potential energy per atom and temperature, T_1 . Assuming no change in density, the energy conservation equation is

$$\begin{aligned}
 -1.9N + N T &= -1.9(N - N_m) + K + (N - N_m)T_1 \\
 \rightarrow \Delta T_1 &= T - T_1 = \frac{1.9N_m + K}{N - N_m} - \frac{N_m}{N - N_m} T \quad . \quad (7.75)
 \end{aligned}$$

The temporal evolution of the monomers is shown in Fig. 7.43 for the 14491 atom run. The liquid cooling rate was remarkably constant. It would be expected to increase during fragmentation due to the increasing surface area, and to decrease due to the decreasing liquid temperature.

Fig. 7.43. Monomer population increase and resulting liquid cooling as a function of time for the 14491 atom run.

In Table 7.9, the monomer data from the 13 two dimensional molecular dynamics runs are shown. The times selected for the data collection are identical to the times used to evaluate fragmentation in Section 7.4.1. The last column shows the predicted liquid temperature loss based on Eq. 7.75. When the isochoric heating produced less than ~ 0.2 temperature increase, vapor pressure formation removed the added energy on the same time scale as the fragmentation. Thus, only the two dimensional simulations with $T = 0.8$ should be used to evaluate fragmentation

The monomer temperatures at the time of fragmentation for each run are listed in Table 7.9. The average liquid temperature during the monomer formation period lies somewhere between the peak listed in the second column of the table and the saturation temperature (~ 0.5). The monomer temperature exceeds both the average and the peak liquid temperatures in every case. Similar results have been found by Vicentini, Jacucci and Pandharipande⁶³ using three dimensional molecular dynamics for systems of 250 atoms.

Table 7.9. Monomer population and energy for the 13 two dimensional molecular dynamics runs. The "E/N_m" column includes both increased potential energy and monomer kinetic energy.

N	Temp.	Reduced Time	Traversal Times t c/R	N _m	$\frac{N_m}{N}$	$\frac{E}{N_m}$	Monomer Temp. kT/e	AT ₁
14491	1.01	104.3	4.4	1183	0.082	2.7	1.17	0.19
2611	1.16	38.4	4.2	200	0.077	2.9	1.43	0.17
2611	0.76	76.9	6.4	218	0.083	2.4	0.87	0.19
2611	0.65	71.4	5.2	170	0.065	2.4	0.88	0.15
721	1.17	29.4	6.0	82	0.114	2.7	1.24	0.25
721	0.77	70.3	11.7	85	0.118	2.3	0.81	0.26
721	0.65	74.4	12.0	66	0.092	2.2	0.70	0.19
721	0.55	78.0	11.5	64	0.089	2.1	0.59	0.19
721	0.51	80.0	11.9	53	0.074	2.3	0.79	0.17
169	1.19	9.1	4.5	15	0.089	2.8	1.28	0.19
169	0.77	10.8	4.5	7	0.041	2.5	1.15	0.10
169	0.62	74.7	27.7	18	0.107	2.3	0.86	0.26
169	0.60	81.0	31.2	15	0.089	2.1	0.52	0.19

Chapter Eight: Conclusions and Recommendations for Further Research

Fragmentation of free liquids in ICF reactor chambers could be the dominating factor in determining the upper bound on reactor pulse rate. Between pulses, the x-ray ablated materials must cool and recondense to allow driver beam propagation for the next pulse. The increased surface area caused by fragmentation will enhance the cooling and condensation rates.

Atomization of liquid fuels in internal combustion engines could be an analogous process to isochoric-heating-induced-fragmentation. However, atomization theory is largely empirical, and the differences in geometry make it hard to apply to the isochoric heating situation.

Early thinking about isochoric heating led to the idea that relaxation from the compressed state could rapidly move a liquid into the negative pressure region under the liquid-vapor two phase dome on a P-V diagram. If the consequent vaporization is rapid enough, the expanding vapor bubbles could drive the fragmentation process. In this work, the lithium equation of state was used to demonstrate that vaporization caused by the neutron heating uses only a minor fraction of the added heat and that fragmentation would occur due to hydrodynamic motion, even in a pure liquid that had no vaporization. In addition, it was found that a 77% expansion of the lithium was required before the rapid vaporization process of spinodal decomposition could begin, and that vapor bubble growth is slower than the hydrodynamic expansion. Therefore, it is concluded that rapid vaporization is not the driving mechanism for liquid fragmentation in ICF reactors.

An energy minimization procedure was used to determine the fragment size that would produce the least amount of non-fragment-center-of-mass energy, i.e., the sum of the surface and dilational kinetic energies. This model (the Grady-Glenn model) predicted that fragment radius, a , depended on the original system radius, R , and the amount of isochoric heating, e (in energy per unit mass units), as well as on four liquid properties: density (ρ_m), Grüneisen parameter (Γ), surface tension (γ), and sound speed (c). Use of the model predicted considerable fragmentation in the high energy density HYLIFE reactor and minimum fragmentation in low energy density reactors like Pulse*Star, EAGLE, and HIBALL.

A two-dimensional molecular dynamics model was developed to test the Grady-Glenn model at a microscopic scale for the hypothetical Lennard-Jones fluid. The two Lennard-Jones constants, σ and ϵ were chosen to represent lithium, and the required liquid properties were generated from published equation of state data and from additional molecular dynamics calculations. A two dimensional model was used because it most closely models a uniformly heated cylindrical jet, because it permits easy graphical inspection of the atomic configurations, and because it allows consideration of larger radius systems (the molecular dynamics calculations were in a size regime where the surface tension property was a function of the system radius). Molecular dynamics calculations were run using five levels of heating and four system sizes. The numerical experiments produced reasonable agreement with the Grady-Glenn model and poor agreement with three other hydrodynamic models. The power law dependence of fragment size (in atoms) on system size and heating level was correct

($N_c \sim N^{2/3} p^{-2D/3}$) where D is the number of dimensions, and the larger fragment sizes were within an order of magnitude of the predictions. The potential error in the system size dependence (from the predicted $N^{2/3}$ down to $N^{1/2}$) would produce an error of a factor of ~ 25 at the HYLIFE scale. Additional analysis of two Italian three dimensional molecular dynamics experiments also agreed with the model predictions.

For ICF reactor design, the result of this study is that the Grady-Glenn fragment radius predictions should be reduced by a factor of $10^{1/D}$. Thus, the design equation becomes

$$a = 10^{1/D} \left[\frac{D+2}{\rho_m} \gamma \left(\frac{R_c}{r_e} \right)^{2/3} \right] \quad (8.1)$$

where a indicates the radius of the larger fragments (smaller fragments are also expected). However, the excess kinetic energy generated in the simulations (due to fluctuations and vapor pressure formation) is probably correlated with the smaller than predicted fragment size. Consequently, at macroscopic sizes, the factor of $10^{1/D}$ could disappear. In either case, a prediction within a factor of ~ 2 would certainly be acceptable. For the HYLIFE inner jet conditions, Eq. 8.1 predicts a fragment radius between 1 and 2 mm, leading to a two order of magnitude increase in the liquid surface area.

There was a fair amount of uncertainty in the molecular dynamics results since the fragmentation is driven by atomic motion, and, in such small systems, fluctuations in statistical quantities among the various atoms and in time are much more significant than for

macroscopic systems. These fluctuations are expected to produce smaller fragments than predicted by the equilibrium model. It is expected that, if many more molecular dynamic runs were made using slightly different initial conditions, the ensemble results would also match the model somewhat more closely.

Although the molecular dynamics results demonstrated that the Grady-Glenn power law formulation is correct at the microscopic scale, the huge degree of extrapolation to reactor size makes it prudent to conduct macroscopic (laboratory rather than numerical) experiments before reactor construction is authorized. Several potential experiments using non-fusion sources have been proposed². These experiments include adding the heat with pulsed laser or microwave illumination, capacitor discharge through the liquid, and driving a diverging shock through the liquid with either explosives or mechanical impact. Each method appears to be capable of adding enough heat or momentum to a small system in a short enough time, but each method also has possible complications.

Laser illumination can result in non-uniform energy deposition at a very small scale, i.e., at the peaks in the diffraction pattern. In the Soviet Union, liquids illuminated with lasers have exploded, and the data indicate that the beam absorption was concentrated in very small spots which then flash vaporized⁶⁷. Capacitor discharges through liquid jets can have non-uniform heating due to the tendency of pulsed currents to travel along the outer surface of the conductor (skin effect). Further, the pulsed current generates a magnetic field that interacts with the current to produce an inward directed Lorentz force (pinch effect). Shock experiments include a constant outward

velocity and an initial pressure profile peaked at the center, as compared to isochoric heating which has zero initial velocity and either a constant or a one-surface peaked initial pressure profile.

It may be possible to simulate some of the complicating effects in molecular dynamics simulations. In any case, at least two types of experiments should be performed to facilitate separation of spurious effects from the desired results.

The molecular dynamics simulations can also be extended. One straightforward extension would be to repeat the calculations from different equilibrated configurations. Another extension would be to consider non-uniform isochoric heating. Finally, it might be possible to begin with an equilibrated surrounding vapor contained within a larger container that reflects only small clusters.

References

1. E. W. Sucov, D. A. Sink, L. Green and H. R. Howland, "EPRI Workshop on Evaluation of Engineering Opportunities in Inertial Confinement Fusion in Existing and Planned Facilities," Electric Power Research Institute Report AP-2317 (1982).
2. N. J. Hoffman, J. A. Blink, B. G. Jones, J. F. Stubbins and D. Tichenor, "Disassembly of Isochorically Heated Liquids-Final Report to EPRI", Energy Technology Engineering Center Report EPRI/DIHL (1983).
3. M. J. Monsler, J. Hovingh, D. L. Cook, T. G. Frank and G. A. Moses, "An Overview of Inertial Fusion Reactor Design," Nucl. Technol./Fusion, 1, p. 302, Sec. IX, (1982). See also Lawrence Livermore National Laboratory Laser Program Annual Reports for 1978, 1979, 1980, and 1981 (UCRL-50021-year, where year is '78, '79, '80, or 81).
4. L. A. Glenn, "ICF Reactor Chamber Cooling Following the Fusion Microexplosion," Lawrence Livermore National Laboratory Internal Memo (Aug. 10, 1978).
5. L. A. Glenn, "Dynamic Loading of the Structural Wall in a Lithium-Fall Fusion Reactor," Nuc. Eng. and Design, 54, p. 1 (1979).
6. L. A. Glenn, "Divergent Impulsive Crossflow Over Packed Columnar Arrays," Nuc. Eng. and Design, 56, p. 429 (1980).
7. L. A. Glenn, "On the Motion Following Isochoric Heating of Concentric Liquid Annuli," Lawrence Livermore National Laboratory Report UCRL-84003 (1980).

8. L. A. Glenn, "Transport Processes in an Inertial Confinement Fusion Reactor," Nuc. Eng. and Design, 64, 3, p. 375 (1981).
9. B. Badger, et al., "HIBALL-A Conceptual Heavy Ion Beam Driven Fusion Reactor Study," University of Wisconsin Report UWFD-450 (1981).
10. L. C. Pong, D. K. Sze, R. R. Peterson and G. A. Moses, "Progress on Modeling of $Pb_{83}Li_{17}$ Recondensation on INPORT Units," Fusion Power Associates Report FPA-82-5 (1982).
11. J. H. Pendergrass, T. G. Frank and L. O. Bohachevsky, "A Modified Wetted-Wall Inertial Fusion Reactor Concept," Proceedings of the 4th Topl. Mtg. Technology of Controlled Nuclear Fusion, King of Prussia, Penn., p. 1131 (1981).
12. W. O. Allen, et al, "Phase I: Engineering Test Reactor Goal Specification Final Report," Electric Power Research Institute Report EPRI-1527 (1982).
13. J. A. Blink and N. J. Hoffman, "Tritium Control and Activation in the Pulse*Star Reactor," Proceedings of the IEEE 10th Symposium on Fusion Engineering, Philadelphia, Penn. (1983).
14. E. Giffen and A. Muraszew, The Atomization of Liquid Fuels, Chapman and Hall, Ltd., London, England (1953).
15. R. D. Reitz and F. V. Bracco, "Ultra-High-Speed Filming of Atomizing Jets," Phys. Fluids, 22, 6, p. 1054 (1979).
16. R. D. Reitz and F. V. Bracco, "Mechanism of Atomization of a Liquid Jet," Phys. Fluids, 25, 10, p. 1730 (1982).
17. D. A. Young, "A Soft-Sphere Model for Liquid Metals," Lawrence Livermore National Laboratory Report UCRL-52352 (1977).

18. L. A. Glenn, "AFION Revisited: An Improved Algorithm for Numerical," Solution of Initial Value Problems in Continuum Mechanics. Part 1: The One-Dimensional Equations," Lawrence Livermore National Laboratory Report UCRL-52512 (1978).
19. W. G. Hoover, G. Stell, E. Goldmark and G. D. Degani, "Generalized van der Waals Equation of State," J. Chem. Physics, 63, 12, p. 5434 (1975).
20. G. Peterson and D. Chato, "Mathsy Manual," Lawrence Livermore National Laboratory Report UCID-18875 (1982).
21. J.A. Blink, "Lithium Equation of State," Lawrence Livermore National Laboratory Report UCID-19890 (1983).
22. J. A. Barker, D. Henderson and F.F. Abraham, "Phase Diagram of the Two-Dimensional Lennard-Jones System; Evidence for First Order Transitions", Physica, 106A, p. 226 (1981).
23. F. F. Abraham, "The Phases of Two-Dimensional Matter, Their Transitions, and Solid-State Stability: A Perspective via Computer Simulation of Simple Atomic Systems", Physics Reports, 80, 5, p. 339 (1981). This reference also contains a large bibliography of two-dimensional simulation studies.
24. D. Henderson, "Monte Carlo and Perturbation Theory Studies of the Equation of State of the Two-Dimensional Lennard-Jones Fluid," Molecular Phys., 34, 2, p. 301 (1977).
25. J. M. Phillips, L. W. Bruch and R. D. Murphy, "The Two-Dimensional Lennard-Jones System: Sublimation, Vaporization, and Melting," J. Chem. Phys., 75, 10, p. 5097 (1981).

26. F. Tsien and J. P. Valleau, "A Monte Carlo Study of the Two-Dimensional Lennard-Jones System," Molecular Phys., 27, 1, p. 177 (1974).
27. P. Fehder, "Molecular Dynamics Studies of the Microscopic Properties of Dense Fluids," J. Chem. Phys., 50, 6, p. 2617 (1969).
28. S. Toxvaerd, "The Mobile-Layer Model for Absorption," Molecular Phys., 29, 2, p. 373 (1975).
29. S. M. Thompson, K. E. Gubbins, J.P.R.B. Walton, R.A.R. Chantry and J. S. Rowlinson, "A Molecular Dynamics Study of Liquid Drops", J. Chem. Phys., 81, 1, p. 530 (1984).
30. J. H. Cahn, "Spinodal Decomposition," Transactions of the Metallurgical Society of AIME, 242, p. 166 (1968).
31. R. C. Reid, "Superheated Liquids," American Scientist, 64, p. 146 (1976).
32. J. H. Cahn, "Phase Separation by Spinodal Decomposition in Isotropic Systems," J. Chem. Phys., 42, 1, p. 93 (1965).
33. H. R. Mruzik, F. F. Abraham and G. M. Pound, "Phase Separation in Fluid Systems by Spinodal Decomposition II: A Molecular Dynamics Computer Simulation," J. Chem. Phys., 69, 8, p. 3462 (1978).
34. E. Gerum, J. Straub and U. Grigull, "Examination of the Metastable State of Surface Tension, Coexistence," Heat Transfer in Boiling, E. Hahne and U. Grigull editors, Academic Press, New York, Ch. 19 (1979).
35. J. Frenkel, Kinetic Theory of Liquids, Dover Publications Inc., New York, 2nd edition (1946).

36. W. G. Hoover, A. C. Hindmarsh and B. L. Holian, "Number Dependence of Small-Crystal Thermodynamic Properties. I," J. Chem. Phys., 57, 5, p. 1980 (1972).
37. H. M. Kottowski, "The Mechanism of Nucleation, Superheating, and Reducing Effects on the Activation Energy of Nucleation," Progress in Heat and Mass Transfer, 7, (Heat Transfer in Liquid Metals), Pergamon Press, p. 299 (1977).
38. E. N. Brodskaya and A. I. Rusanov, "Investigation of Small Systems by Molecular Dynamics Method. 2. Pressure Tensor and Surface Tension of Small Drops," Colloid Journal of the USSR, 39, 4, p. 646 (1977). See also S. I. Rusanov and E. N. Brodskaya, "The Molecular Dynamics Simulation of a Small Drop," J. of Colloid and Interface Science, 62, 3, p. 542 (1977).
39. R. E. Henry and K. Niguzaki, "Effects of System Pressure on the Bubble Growth from Highly Superheated Water Droplets", Topics in Two-Phase Heat Transfer and Flow, ASME Winter Annual Meeting, San Francisco, Cal., p. 1 (1978).
40. L. J. Briggs, "Limiting Negative Pressure of Water," J. Appl. Phys., 21, p. 721 (1950).
41. L. J. Briggs, "Maximum Superheating of Water as a Measure of Negative Pressure," J. Appl. Phys., 26, p. 1001 (1955).
42. S. J. Henderson and R. J. Speedy, "A Berthelot-Bourdon Tube Method of Studying Water Under Tension," J. Phys. E, 13, p. 778 (1980).

43. F. F. Abraham, D. E. Schreiber, M. R. Mruzik and G. M. Pound, "Phase Separation in Fluid Systems by Spinodal Decomposition: A Molecular-Dynamics Simulation," Phys. Rev. Letters, 36, 5, p. 261 (1976).
44. J. Hovingh, M. Thomson, and J. Blink, "Fluid Mechanics Considerations for Liquid Wall Inertially Confined Fusion Reactors," Proceedings of the IEEE 8th Symp. on Engineering Problems of Fusion Research, p. 2038 (1979).
45. D. E. Grady, "Local Inertial Effects in Dynamic Fragmentation," J. Appl. Phys., 53, 1, p. 322 (1982).
46. L. A. Glenn, "On the Fragmentation of Condensed Material by Isochoric Heating and Release," Lawrence Livermore National Laboratory Report UCID-19737 (1983).
47. F. A. McClintock and A. S. Argon, editors, Mechanical Behavior of Materials, Addison-Wesley Publ. Co., Reading, Mass., p. 489 (1966).
48. F. F. Abraham, W. E. Rudge, D. J. Auerbach and S. W. Koch, "Molecular-Dynamics Simulations of the Incommensurate Phase of Krypton on Graphite Using More Than 100,000 Atoms," Phys. Rev. Lett., 52, 6, p. 445 (1984).
49. W. G. Hoover, "Computer Simulation of Many-Body Dynamics", Physics Today, 37, 1, p. 44 (1984).
50. W. G. Hoover, "Nonequilibrium Molecular Dynamics," Ann. Rev. Phys. Chem., 34, p. 103 (1983).
51. F. Gibb and W. Smith, "CCP5 Literature Survey," Information Quarterly for MD & MC Simulations, 8, Daresbury Laboratory, Daresbury, Warrington, England, p. 49 (1983).

52. E. N. Brodskaya and A. I. Rusanov, "Investigation of Small Systems by Molecular Dynamics Method. 1. Energy and Molecular Structure of Small Drops," Colloid Journal of the USSR, **39**, 4, p. 561 (1977).
53. B. J. Alder and T. E. Wainwright, "Studies in Molecular Dynamics. I. General Method," J. Chem. Phys., **31**, 2, p. 459 (1959).
54. L. Verlet, "Computer 'Experiments' on Classical Fluids. 1. Thermodynamical Properties of Lennard-Jones Molecules," Phys. Rev., **159**, 1, p. 98 (1967).
55. S. M. Thompson, "Use of Neighbor Lists in Molecular Dynamics" Information Quarterly for MD & MC Simulations, **8**, p. 20, Daresbury Laboratory, Daresbury, Warrington, England (1983).
56. J. C. Slater, Introduction to Chemical Physics, McGraw-Hill Book Co., New York, p. 217 (1939)
57. C. A. Croxton and R. P. Ferrier, "Statistical Mechanical Calculation of Surface Properties of Simple Liquids: IV. Molecular Dynamics," J. Phys. C, **4**, p. 2447 (1971).
58. J. S. Rowlinson and B. Widom, Molecular Theory of Capillarity, Clarendon Press, Oxford, p. 177 (1982).
59. A. H. Falls, L. E. Scriven and H. T. Davis, "Structure and Stress in Spherical Microstructures," J. Chem. Phys., **75**, 8, p. 3986 (1981).
60. J. H. Irving and J. G. Kirkwood, "The Statistical Mechanical Theory of Transport Processes. IV. The Equations of Hydrodynamics," J. Chem. Phys., **18**, 6, p. 817 (1950).

61. A. Harasima, "Molecular Theory of Surface Tension,"
Adv. Chem. Phys., 1, p. 203 (1958).
62. S. Ono and S. Kondo, "Molecular Theory of Surface Tension in Liquids," Encyclopedia of Physics (Handbuch der Physik), edited by S. Flügge, Springer-Verlag, 10, pp. 157-161 (1960).
63. A. Vicentini, G. Jacucci, and V. R. Pandharipande, University of Illinois, in preparation for Phys. Rev. C.
64. S. W. Hoch, R. C. Desai and F. F. Abraham, "Dynamics of Phase Separation in Two-Dimensional Fluids: Spinodal Decomposition," Phys. Rev. A, 27, 4, p. 2152 (1983).
65. F. F. Abraham, "On the Thermodynamics, Structure and Phase Stability of the Nonuniform Fluid State," Physics Reports, 53, 2, p. 93 (1979).
66. F. H. Ree, "Analytic Representation of Thermodynamic Data for the Lennard Jones Fluid," J. Chem. Phys., 73, 10, p. 5401 (1980).
67. V. S. Loskutov and G. M. Strelkov, "Explosive Evaporation of Weakly Absorbing Drops Under the Action of Laser Pulses",
Publication of the Institute of Radio Engineering and Electronics, USSR Academy of Sciences, Moscow, p. 1 (1980).
Lawrence Livermore National Laboratory Translation
UCRL TRANS-11809 (1982).
68. H. Schulz, B. Kämpfer, H. W. Barz, G. Röpke and J. Bondorf, "On the Time-Development of the Liquid-Vapor Phase Transition in an Expanding Nuclear System," Phys. Letters, 147B, 1-3, p. 17 (1 Nov 1984).

Nomenclature

A	Helmholtz free energy
A^e	excess Helmholtz free energy
A_m	hexagonal-close-packed base-plane triangle area at melt
A_1-A_5	constants used in Ree's pressure equation
A_∞	Helmholtz free energy per atom in an infinite system
A_∞^*	free energy per atom in an infinite system plus the excess entropy due to surfaces
a	fragment radius
a_s	radius at which the surface tension applies
B	isentropic bulk modulus
B_m	isentropic bulk modulus at the melting point
B_T	isothermal bulk modulus
B_1-B_4, B_{10}	constants used in Ree's pressure equation
b	curvature of the parabolic potential
C	concentration (for spinodal decomposition)
C_A	concentration of phase A (for spinodal decomposition)
C_n	face centered cubic Madelung constant
C_1-C_5	constants used in Ree's pressure equation
c	sound speed
c^*	density-normalized sound speed
c_l	liquid specific heat at constant pressure
c_p	specific heat at constant pressure
c_v	specific heat at constant volume
D	number of dimensions

D_1	constant used to distinguish 2-D and 3-D results. The subscript is incremented as the constant is redefined in the derivation.
D_m	diffusion coefficient
d	interatomic spacing for a perfect crystal (at a given density)
d_0	initial interatomic spacing for a crystal
E	internal energy, internal energy per atom
E_{coh}	cohesive energy, the energy required to vaporize room temperature lithium to the critical point
e	specific energy (energy per unit mass) added suddenly
e^*	2.71828 (base for natural logarithms)
$\vec{F}, F$	interatomic force
$\vec{F}_{ij}$	force on atom i due to atom j
F_k	normal component of the intratomic force of the k 'th atom pair
F_p	function used to convert the sound speed from one density to another
f_1	constants used in Barker's pressure equation
G	Gibbs free energy per unit mass
g_j	constants used in Barker's pressure equation
H_m	enthalpy at melt
H_v	heat of vaporization
h	Planck's constant
I	moment of inertia
J	diffusional flux (for spinodal decomposition)
J_i	diffusional flux of phase i (for spinodal decomposition)

K	kinetic energy
K_c	translational kinetic energy of a given cluster
K_m	kinetic energy per unit mass (specific kinetic energy)
K_s	gradient energy coefficient (spinodal decomposition)
K_v	kinetic energy per unit volume (kinetic energy density)
k	Boltzmann's constant
L	angular momentum
$L_{1/2}$	half width of a cube
m	atomic mass
N	number of atoms
N_c	number of atoms in a given cluster
$N_i(j)$	cluster assignment for atom j
N_j	Jacob's dimensionless number
N_l	number of liquid atoms
N_m	number of monomer atoms
$N_s(S_c)$	number of clusters of size S_c
N_1, N_2	the first and second members of an atom pair (used during cluster identity determination)
n_l	number of time steps a neighbor list has been used
n_r	number of rows of atoms in a hexagonal crystal (the central atom is the first row)
P	pressure
P_c	critical pressure
P_{in}	pressure inside a liquid drop
P_l	liquid pressure
P_N	normal component of the pressure
P_{out}	pressure of the vapor outside a liquid drop

P_{sat}	pressure at the saturation line
P_T	tangential component of the pressure
P_v	equilibrium vapor pressure
P_{12}	heaviside pressure distribution
Q_e	multiplier to account for electronic effects on heat capacity
R	original liquid radius
R_B	bubble radius
R_e	equimolar radius (the system population is unchanged if the smooth gradient is replaced by a step change at R_e)
R_1	radius to the absorbing material, measured from the fusion plasma
R_s	effective radius of the surface tension force
r	unit vector normal to the test surface
$\vec{r}_i, \vec{r}_j$	interatomic separation (between atoms i and j)
r_D	interatomic spacing beyond which the parabolic potential is zero
r_C	critical nucleus size
r_h	hexagonal-close-packed lattice constant assuming perfect lattice at 500°C
r_{ij}	unit vector between atoms i and j
r_L	hexagonal-close-packed lattice constant in the base plane
r_g	neighborhood radius
r_{min}	minimum radius from the system center to the line segment (bond) between two specified atoms
r_N	nucleus radius (nucleation and growth)

r_0	bond rest length, interatomic spacing at which the potential is a minimum
r_r	cut off distance for the repulsive wall potential
r_t	interatomic spacing at which the potential is truncated
r_ρ	radial distance defining the region in which the cumulative density is calculated
r_1, r_2	random numbers used to generate an initial velocity distribution
r_2, r_3	interatomic spacing in two and three dimensions
S	entropy
S_c	cluster size
S_e	excess entropy per atom in a small solid due to the small size
s	surface energy density
T	temperature
T_c	critical temperature
T_m	melt temperature
T_{rot}	rotational temperature
T_{tr}	translational temperature
T_{th}	thermal temperature
T_l	thermal temperature at a given time after vapor pressure formation begins
t	time
t_r	relief time, time for a sound wave to traverse the radius
u_x	x coordinate of the displacement vector
u_y	y coordinate of the displacement vector
V	specific volume

V_c	specific volume at the critical point
V_j	specific volume at the spinodal (at a given temperature)
V_l	liquid specific volume
V_m	specific volume at the melting point
V_o	specific volume at room temperature
V_t	total volume
V_v	vapor specific volume
v	velocity
$\vec{v}_o, \vec{v}_0$	velocity vector or magnitude before adjustment
v_{new}	adjusted velocity (x or y component)
v_{old}	velocity x or y component before adjustment
v_s	surface velocity
v_w	wall velocity during circularization
$\vec{x}$	vector location of an atom
$\vec{x}_+$	location after a time step (next location)
$\vec{x}_0$	current location
$\vec{x}_-$	location before the previous time step (previous location)
x, x_i	x coordinate of atom i
y	fusion yield
y, y_i	y coordinate of atom i
Z_c	ratio of PV_t/NkT at the critical point
α	amplification factor (spinodal decomposition)
α_t	thermal diffusivity
α_v	volumetric coefficient of thermal expansion
β	disturbance spatial frequency (spinodal decomposition)
Γ	Grüneisen parameter

Γ_c	cumulative Grüneisen parameter from saturation to the heated state
Γ_i	Grüneisen parameter for mode i in a solid
Γ_0	Grüneisen parameter at room temperature
γ, γ_∞	surface tension in a large system (independent of system size)
γ_s	surface tension in a small system (function of system size)
γ_2, γ_3	surface tension in two and three dimensions
ΔP	pressure rise
ΔT_l	liquid temperature loss due to vapor pressure formation in a given time interval
Δt	time step
c	minimum potential energy for an interatomic potential
ϵ_{xx}	strain on the x plane in the x direction
ϵ_{xy}	strain on the x plane in the y direction
ϵ_{yy}	strain on the y plane in the y direction
η	exponent used in Young's lithium equation of state
κ	spring constant
λ	the constant that defines a vector ($\vec{r}$) from the system center to a specified point on the extended line between two atoms, $2\vec{r} = \vec{r}_i + \vec{r}_j + \lambda \vec{r}_{ij}$
λ_T	interatomic spacing at which the repulsive potential = ψ
λ_d	de Broglie wavelength
$ \lambda_{\min} $	value of $ (2\vec{r} - \vec{r}_i - \vec{r}_j)/\vec{r}_{ij} $, when the radius to the extended line between two specified atoms is minimized

μ	dimensionless constant used in the disassembly velocity profile
μ_1	chemical potential of phase 1, (spinodal decomposition)
$\lambda_{\pm}$	values of λ at the two intersections between a circular arc and the extended line between two specified atoms
v	fragment size correction factor that accounts for variable velocity divergence within the original drop
ν_1	vibration frequency 1 in a solid
E	exponent for the lithium equation of state repulsive potential
π	3.14159
ρ	atom density
$\rho_c(r)$	cumulative atom density from the center to radius r
ρ_m	mass density
ρ_y	Young's dimensionless atomic density, $N\sigma^3/\sqrt{2V}$
ρ_{lm}	mass density of the liquid
ρ^*	normalized atom density
σ	interatomic separation at which the Lennard-Jones potential is zero
τ	time for an expansion wave to travel from the surface to the center
ϕ	interatomic potential energy
ϕ_v	volume fraction of absorbing material in a reactor absorbing region
ϕ_2, ϕ_3	potential energy in two and three dimensions
ψ	repulsive potential energy at $r=\lambda$
ω, ω_1	vibration angular frequencies in a solid

Appendix A

This appendix is a draft of a journal article summarizing the study; as such, it may be read as an executive summary. It contains an independent set of figures for convenience, and it uses its own nomenclature (defined in its text). However, it cites the references from the main body of the document.

A.1. Abstract

The rapid fragmentation of two-dimensional high-pressure disks of Lennard-Jones fluid was studied using molecular dynamics. The free expansion of 169, 721, 2611, and 14491 particle systems was studied for several sound traversal times. The breakup into fragments (or clusters) can be roughly described by Grady's model, which balances the surface energy with the comoving (dilational) kinetic energy of the fragments. The model predicts that the number of fragments varies as the cube root of the system population and the $2D/3$ power of the initial pressure where D (2 or 3) is the dimensionality of the system. The molecular dynamics results confirm these predictions within about ± 0.1 and thereby rule out three other fragmentation models. The relatively high monomer temperatures and relatively uniform fragment temperatures found here correspond to temperatures found in recent three-dimensional Lennard-Jones simulations by Vicentini, Jacucci and Pandharipande.

A.2 Introduction

The expansion of a high-pressure hot fluid into a low-pressure

volume many times the original volume is a strongly nonequilibrium process. Wave propagation, fluctuations, negative pressures, surface tension, vaporization, viscosity, and heat conduction all play roles as a single fluid mass is converted to a time-dependent collection of diverging liquid and solid fragments or clusters. A complete theoretical or computational study of such a process lies well beyond our capacity. Thus, fragmentation is primarily "understood" on the basis of experimental correlations and relatively crude "theories" (models). The expansion of an isochorically heated fluid is a challenging problem involving non-equilibrium statistical mechanics, dynamics, and fluid mechanics. Three diverse fields provide sample applications which could benefit from the ability to predict fluid fragmentation. Lithium jets in Inertial Confinement Fusion reactors are heated by neutrons much more rapidly than the tens of microseconds required for pressure relief. Pressurized fluids leaving nozzles fragment¹⁶. Colliding heavy ion beams produce compressed "nuclear matter" which exhibits fragmentation and a vapor-liquid like phase transition⁶⁸.

While mean fragment size is a crude description of the fragmentation process, it is easily measured and calculated. Four hydrodynamic models have been proposed to predict the mean fragment size. Two of these models balance fragment surface forces against pressure, either (1) the increased static pressure P , or (2) the dynamic expansion pressure $(\rho v^2/2)$ where m is the atomic mass, ρ is the atom density, and v is the jump-off velocity, $P/\rho c$, with c indicating the sound speed. Two other models minimize the sum of the fragment surface and dilational energies, considering (3) the

total fragment dilational energy, or (4) the dilational energy near the fragment surfaces. These four models have markedly different dependences on the original system size and pressure.

Vaporization has also been proposed as an expansion and fragmentation mechanism. Two phase change mechanisms are "spinodal decomposition"³⁰ and "nucleation and growth". Neither mechanism suggests any dependence of mean fragment size on original system size.

Molecular dynamics provides a test of the size dependence predictions of the various theoretical models. Here, we apply molecular dynamics to a two-dimensional system because it can simulate relatively large radius systems, because it is easily diagnosed graphically, and because it best simulates the quasi-two-dimensional expansion of cylindrical jets in inertial fusion reactors.

A.3. Fragmentation Models

A.3.A. Hydrodynamic Models

The simplest model requires the surface tension (2γ or $2\pi r\gamma$ in 2- or 3-D) to balance the initial pressure, $2rP$ or $\pi r^2 P$. Thus, the "fragment" or "cluster" size, N_c (in atoms) is

$$N_c = \pi \left(\frac{D+1}{D}\right)^{D-2} \rho \left[\frac{(D-1)\gamma}{P}\right]^D \quad (A.1)$$

where the dimensionality, D , is either 2 or 3. A more realistic model accounts for the relief of the static pressure, producing a dynamic expansion pressure and replacing P in Eq. A.1 by $\rho v^2/2$, where v is the jump-off velocity,

$$N_c = \pi \left(\frac{D+1}{D}\right)^{D-2} \rho^{D+1} [2(D-1)\gamma]^D \left(\frac{S}{P}\right)^{2D} \quad (A.2)$$

An energy minimization model (proposed by Grady⁴⁵ and extended by Glenn⁴⁶ and this study) minimizes the sum of the surface energy density plus the fragment dilational energy density. The surface energy density is

$(D\gamma/r)$ where r is the fragment radius. For a homogeneous expansion, the dilational energy density is $(r\dot{p})^2/[2D(D+2)\rho]$ where $-\dot{p}/\rho = Dv/R$. Thus

$$N_c = \pi^{1/3} \left(\frac{D+1}{D}\right)^{(D-2)/3} \rho^{(D+1)/3} [(D+2)\gamma]^{D/3} \left(\frac{\epsilon}{\rho}\right)^{2D/3} N^{2/3}. \quad (A.3)$$

The inhomogeneity of the expansion can be partly considered by including the radial dependence of the velocity divergence. Then, the fragment size predicted by Eq. A.3 is reduced by one to two orders of magnitude for the innermost fragments, but most of the system mass is included in fragments within a factor of two of the size predicted by the uncorrected Eq. A.3.

If only the dilational energy in an outer shell of thickness δ is used in the energy minimization model, N_c is proportional to N ,

$$N_c = \left(\frac{2\sigma\gamma}{\delta}\right)^{D/2} \left(\frac{\epsilon}{\rho}\right)^D N. \quad (A.4)$$

If Eq. A.3 proves to be a more nearly correct model than Eq. A.4, fragmentation must be driven by collective effects, including energy in the fragment core as well as the energy at the fragment surface.

In summary, the hydrodynamic models, (1), (2), (3) and (4), predict $N_c \sim N^0 P^{-2}$, $N^0 P^{-4}$, $N^{2/3} P^{-4/3}$, and $N P^{-2}$, respectively

in two dimensions. In three dimensions, the four models predict $N_c \sim N^0 P^{-3}$, $N^0 P^{-6}$, $N^{2/3} P^{-2}$, and $N P^{-3}$.

A.3.B. Phase Change as a Fragmentation Mechanism

It is easy to see that phase change is too slow and too weak a mechanism to drive fragmentation. For example, Fig. A.1 shows the response to 800 kJ/kg of isochoric neutron heating in a 0.2 m diameter lithium jet in the HYLIFE³ ICF reactor, using Young's soft-sphere equation of state¹⁷. The sudden heating causes the liquid temperature (500°C) and pressure (essentially zero) to quickly rise to 735°C and 380 MPa with no change in density (485 kg/m³). As the relief wave moves into the jet, a nearly isentropic expansion occurs. During expansion to the saturation line (and $P_{\text{sat}} \sim 0$), the liquid temperature falls to 695°C, and the internal energy falls by ~16 kJ/kg. This energy corresponds to a jump-off velocity of about 175 m/s as the internal energy is converted to kinetic energy by the tensile wave. When the expansion continues beyond zero pressure into the two-phase liquid-vapor region, phase separation or fragmentation must eventually occur, returning the fluid to the saturated liquid and vapor lines. If the isentropic expansion could continue all the way to the isentropic spinodal (where $[\partial P / \partial V]_S$ vanishes), only 3.4 J/kg-liquid would be needed for equilibrium vaporization. This is about 4400 times less energy than the jump-off kinetic energy produced by the hydrodynamic expansion. Thus, vaporization utilizes insufficient energy to drive the hydrodynamic expansion and fragmentation.

It is unlikely that either spinodal line would even be approached in a real liquid lithium ICF reactor. At the spinode, the liquid tension is ~1560 MPa, much larger than the tensile strength of solid lithium. In an ICF reactor, the entrained gas, target debris,

Fig. A.1. P-V diagram of the heating and expansion of a lithium jet. Due to the restricted specific volume range of the diagram, the coexistence curve appears to be flat at ~ 0 pressure. The critical pressure of 114 MPa is reached at $0.011 \text{ m}^3/\text{kg}$, well to the right of the portion of the diagram shown. The isothermal and isentropic spinodal lines cross the lower right corner of the graph.

and corrosion products provide an abundance of potential nucleation sites. Vapor bubble growth (from nucleation and growth) is also ineffective from a kinetic standpoint since the growth times (milliseconds) are much longer than the liquid's hydrodynamic expansion time. Hence, it is concluded that hydrodynamic fracture is the fragmentation mechanism and that phase separation occurs later to fill the consequent voids.

A.4. Molecular Dynamics Model of Fragmentation

The well-characterized Lennard-Jones 6-12 potential was used

$$\frac{\phi(r)}{\epsilon} = 4 \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (A.5)$$

The potential was truncated at $r_t = 2.5\sigma$ to save computer time. The truncation has negligible effect on the evolution of the system, but it does allow early identification of fragment sizes. In addition, Thompson's neighbor listing procedure⁵⁵ was used to reduce computer time, at some memory expense. The largest run (14491 atoms) required a memory of 212,000 words and 6.3 Cray CPU sec for each 0.003 ps time step. In implementing Thompson's scheme, a list was constructed (for each atom) that included all atoms within some range $r_k > 2.5\sigma$. After the list was compiled, the cumulative scalar distances traveled by each atom were computed at each time step, and the maximum was compared to a test quantity, $0.95[1 - 1/(n_k + 1)](r_k - 2.5\sigma)$ where n_k is the number of time steps the list has been used. The test quantity anticipated whether or not the next step would move an atom outside the list range.

The phase diagram for two-dimensional Lennard-Jonesium was

established by Barker²² using perturbation theory for the fluid phases and a self-consistent cell model for the solid phase. Monte Carlo calculations by Abraham²³ confirmed Barker's phase boundaries. Extensive equation of state data were compiled by Henderson²⁴ using Monte Carlo calculations. These data were used to compute the pressure and sound speed in the liquid as a function of temperature at densities near $\rho^* = \rho/\rho^2 \sim 0.6$ (roughly midway between the critical and liquid triple point densities). Because no data for the surface tension were available, molecular dynamics was used to calculate the size-dependent surface tension, as discussed in Section A.5.

The initial conditions for 13 fragmentation runs are shown in Fig. A.2 and tabulated in Table A.1. The four system sizes (169, 721, 2611 and 14491 atoms) correspond to crystals in the shape of regular hexagonal crystals with 8, 16, 30 and 70 rows of particles on a side. These configurations were used to initiate the runs. (Each crystal was melted and equilibrated to approximately the desired temperature and density within a confining wall; the fragmentations runs began when the wall was removed).

Verlet's algorithm, with a time step, Δt , of ~ 0.02 in units of $(m\sigma^2/c)^{1/2}$, was used,

$$\vec{r}_+ = 2\vec{r}_0 - \vec{r}_- + \vec{F}_0(\Delta t)^2/m \quad (\text{A.6})$$

where $\vec{r}_-$, $\vec{r}_0$, and $\vec{r}_+$ are the atom locations at three successive times, and $\vec{F}_0$ is the total force from all atoms within 2.5σ . Velocities were obtained from the coordinates,

Fig. A.2. Initial conditions for the 13 molecular dynamics fragmentation runs.

Table A.1. Initial conditions and results from the two-dimensional molecular dynamics runs. The cluster populations are indicated by N_c ; N_m is the number of monomers; and N is the original system population.

State	$N^\dagger$	Initial Values				Observed Time tc/R	N_c	N_m	$N_c / (N - N_m)$		Transl. Temp.		Observed Monomer Temp K/T/c
		K/T/c	μ^2	P^2/c	$c(m/c)^{1/2}$				Observed	Predicted	Observed ^{††}	Predicted	
14491		1.01	0.61	1.02	3.7	4.4	375	1183	0.028	0.24	0.35	0.10	1.17
2611		1.16	0.62	1.38	4.1	4.2	136	200	0.056	0.14	0.77	0.15	1.43
2611		0.76	0.62	0.53	3.1	6.4	270	218	0.11	0.68	0.15	0.039	0.87
2611		0.65	0.62	0.31	2.7	5.2	361	170	0.15	1.001 [*]	0.072	0.017	0.88
721		1.17	0.61	1.31	4.0	6.0	44	82	0.069	0.35	0.36	0.14	1.24
721		0.77	0.63	0.60	3.2	11.7	117	85	0.18	0.91	0.10	0.043	0.81
721		0.65	0.65	0.40	3.2	12.0	337	66	0.515	1.5 [*]	0.035	0.019	0.70
721		0.55	0.66	0.17	2.9	11.5	593	64	0.90	4.1 [*]	0.029	0.0037	0.59
721		0.51	0.68	0.07	2.9	11.9	626	53	0.94	16.6 [*]	0.018	0.0004	0.79
169		1.19	0.65	1.75	4.6	4.5	41	15	0.27	0.42	0.34	0.17	1.28
169		0.77	0.68	0.86	4.0	4.5	64	7	0.43	0.82	0.067	0.051	1.15
169		0.62	0.68	0.41	3.5	27.7	129	18	0.85	2.46 [*]	0.043	0.015	0.86
169		0.50	0.75	0.11	3.6	31.2	142	15	0.92	23.8 [*]	0.022	0.0008	0.52

[†] including monomers

^{††} ignoring monomer energy and mass

^{*} adjusted to 1.0 for the graphs

$$\vec{v}_0 = (\vec{r}_+ - \vec{r}_-)/2\Delta t \quad . \quad (A.7)$$

The potential, translational, rotational and thermal energies and the fragment sizes were tabulated. Fragment translational temperatures were defined as the fragments' center-of-mass kinetic energies in the fixed frame of reference divided by the the product of Boltzmann's constant, k , and the corresponding fragment's size (in atoms). Fragment rotational temperatures were defined as $L^2/kN_C I$ where L is the angular momentum around the fragment center and I is the moment of inertia. Fragment thermal temperatures were given by remaining kinetic energy divided by the product of k and the corresponding fragment's size.

A.5. Results

A.5.A. Two Dimensional Surface Tension

Recently, Thompson, et. al.²⁹ published an extensive molecular dynamics study of three dimensional surface tension that used time averages of up to $t^* = t(m\sigma^2/\epsilon)^{1/2} = 1400$. To extend Thompson's study to two dimensions, a series of molecular dynamics calculations was performed on systems ranging from 70 to 700 atoms at reduced temperatures ($T^*=kT/\epsilon$) below , near, and above the triple point. Density and (Irving-Kirkwood) pressure tensor time averages were taken for up to $t^* = 1450$ in a few cases, with typical averaging periods being for $t^* = 400$ to 700. Analysis of the results indicates that the runs below the triple point did not reach equilibrium. (Low densities and negative pressures typical of the two-phase solid-vapor region were measured.) For the higher temperature runs ($T^* = kT/\epsilon$

~ 0.45), fluctuations and occasional drop fragmentation obscured the results. Only near the triple point were reasonable time averaged pressure tensor profiles obtained.

The surface tension measured at the proper radius, R_s (which is significantly different than the equimolar radius for small drops), is

$$\gamma = \int_0^{\infty} (P_N - P_T) \left(\frac{r}{R_s}\right)^{D-1} dr \quad . \quad (A.8)$$

where D is again the dimensionality (2 or 3), P_N and P_T are the normal and tangential components of the pressure tensor, and the zero of r is within the bulk of the fluid (where $P_N = P_T$). The integrand is non-zero only near the interface. The normal and tangential components are related by a force balance, leading to

$$P_N - P_T = -\left(\frac{r}{D-1}\right) \left(\frac{\partial P_N}{\partial r}\right) \quad . \quad (A.9)$$

in 2 or 3 dimensions. Finally, the Laplace equation is used to eliminate R_s ,

$$\Delta P = P_N(\text{liquid}) - P_N(\text{vapor}) = \frac{(D-1)\gamma}{R_s} \quad , \quad (A.10)$$

The result is

$$\gamma = -\left[\frac{\Delta P^{D-1}}{(D-1)^D}\right] \int_0^{\infty} \frac{\partial P_N}{\partial r} r dr \quad . \quad (A.11)$$

in 2 or 3 dimensions. The resulting surface tension at $T^*=0.35$ is plotted in Fig. A.3 as a function of $1/N_d$, where N_d is the number of liquid atoms in the drop. For interpolation, we assume that the surface tension decreases linearly with temperature to zero at the

Fig. A.3. Two dimensional surface tension at $kT/\epsilon = 0.35$ from molecular dynamics calculations.

critical point, and that it also falls to zero for a single atom system,

$$\gamma = 0.35 [1 - (N_2)^{-1/2}]^4 [1 - (\frac{T^* - 0.35}{0.21})](\epsilon/\sigma) \quad (A.12)$$

A simple scaling model based on excess energy due to missing bonds for surface atoms produced reasonable agreement between the two-dimensional data and Thompson's three-dimensional results.

A.5.B. Fragment Size as a Function of System Size and Pressure

Fragment sizes were usually tabulated after only a few sound traversal times in order to minimize the influence of vapor pressure formation (Table A.1). In cases where fragmentation was marginal, much more time elapsed before fragmentation. Examination of the atomic position plots for such cases indicates that some regions oscillated (changed overall shape) several times before fragmenting.

The fragment sizes (in atoms) from two 2611 atom runs are shown in Fig. A.4. The largest fragment, the average of the ten largest fragments, and the average of the largest fragments comprising 30% of the non-monomer population are shown. In each case, the raw data have been slightly adjusted (using the energy minimization model, "model 3") to uniform initial conditions (2611 non-monomer atoms, $\rho^* = 0.6$, $c^* = c(m/\epsilon)^{1/2} = 4.0$, and $\gamma^* = 0.32$). The only remaining variable in model 3 is the initial pressure. The slopes of the three fragment size curves are -1.03, -0.86, and -1.42, respectively; these values bracket the predicted slope of -4/3 from model 3 reasonably well. To illustrate the sensitivity of the fragmentation to

Fig. A.4. Observed and predicted fragment sizes (atoms) as a function of initial pressure, for two 2611 atom runs. The data and model predictions have been slightly adjusted to constant initial conditions. The model numbers refer to Eqs. A.1 through A.4. The three observed values for each run are for the largest fragment, the average of the ten largest fragments, and the average of the largest fragments comprising 30% of the system population (less monomers).

fragment-size dependent surface tension, the prediction curve is also shown using the lower surface tensions at the actual fragment sizes; the "observed" curves would be similarly steeper when the surface tension correction (to $\gamma^* = 0.32$) is eliminated. Finally, the other model predictions are shown. The slopes of models 1, 2, and 4 (-2, -4, and -2, respectively) are much steeper than the molecular dynamics results.

The fragment sizes from the highest pressure run for each system size (14491, 2611, 721, and 169 atoms) are shown in Fig. A.5. The nomenclature is identical to the previous figure. As in Fig. A.4, the data were slightly adjusted to uniform initial conditions ($P^* = P\sigma^2/c = 1.4$, $\rho^* = 0.6$, $c^* = 4.0$, and $\gamma^* = 0.32$). The only remaining variable in the models is the system size (total number of particles), N . The slopes of the middle section of the three fragment size curves are 0.75, 0.69, and 0.64, respectively. These observed values bracket the predicted slope of $2/3$ from model 3. The 169 atom data were not used to compute the slope because of minimal fragmentation. The 14491 atom fragment sizes are probably a bit low. Position snapshots and density profiles indicate that a sloshing motion was present in the system at the time the confining boundary was removed. However, if the slopes are computed using line segments between the 721 and 14491 data, the results are 0.54, 0.50, and 0.41, respectively. Thus, the molecular dynamics results indicate a possible system size dependence of the $2/3$ power (the illustrated line), but support that slope with an uncertainty of ± 0.15 . This result again is consistent with the energy minimization model (model 3). Models 1 and 2 include no system size dependence and accordingly

Fig. A.5. Observed and predicted fragment sizes (atoms) as a function of system size, for similar heating levels. The nomenclature is identical to Fig. A.4.

predict very low fragment sizes for this initial condition (0.1 and 18 atoms, respectively). Model 4 predicts a much steeper slope (1.0) than found in the molecular dynamics runs.

Although the data in Figs. A.4 and A.5 support the energy minimization model's power law dependence of fragment size on system size and isochoric heating level (initial pressure), the magnitudes of the observed sizes (in atoms) are about ten times lower than the model 3 prediction. We therefore suggest that the predictions of that model be reduced tenfold in applications.

A.5.C. Time Evolution of the System

As time evolved in the thirteen numerical experiments, snapshots of the atomic positions were used to visualize the fragmentation; a sample sequence is shown in Fig. A.6. Inspection of this figure indicates that the average fragment size is smallest near the system center, in agreement with model 3 when the variation of velocity divergence with radius is considered.

A more quantitative description of the fragmentation process is contained in Table A.1 and in Figs. A.7 and A.8 which show the translational and thermal temperatures and the largest cluster size as functions of time, system population and initial temperature. The abscissa of each plot, t_c/R , is the time divided by the sound traversal time. The initial temperature corresponds to the y-intercepts in Fig. A.7. To decrease the influence of vapor pressure formation on the results, both thermal and translational temperatures are based on the total number of non-monomer atoms in the system. The rotational temperature was not plotted because it was always

Fig. A.6. Snapshots of the atomic configurations at four times during the fragmentation process of a 14491 atom system ($kT/\epsilon \sim 1.0$).

$$t^* = t\sqrt{\epsilon/m/\sigma} = 13.7$$

$$t^* = 33.0$$

100σ

$$t^* = 71.4$$

$$t^* = 109.8$$

100σ

Fig. A.7. Thermal and translational temperature evolution in the fragmentation runs.

Fig. A.8. Size of the largest cluster as a function of time in the 2-D fragmentation runs. The ordinate is scaled according to model 3 to eliminate the system size dependence.

negligibly small.

The thermal temperature typically relaxes to a "post-fragmentation" level of about 0.35 to 0.4 (near the triple point) after two or three pressure relief times (R/c) (Fig. A.7). The translational temperature reaches its "post-fragmentation" value at about the same time, but this value depends on the initial temperature. For the highest initial temperature level ($T^* \sim 1.15$), the final translational temperature was ~ 0.4 , somewhat higher than the final thermal temperature. For the lower initial temperatures, the final translational temperature was 0.1 or lower. As predicted by model 3, there is an observable system size dependence for the translational temperature, with the larger systems attaining higher values. The total of the final translational and thermal temperatures was always less than the initial thermal temperature; the remaining energy was either carried as kinetic energy by monomer atoms in the vapor, or stored as potential energy in the fragments. The system potential energy increases due to bond breaking during vaporization and surface area growth (fragmentation), and decreases slightly due to the increase in bulk density caused by the lower liquid temperature.

The evolution of the largest cluster size is shown in Fig. A.8. The ordinate is scaled by $1/N^{2/3}$ to remove the system size dependence predicted by model 3. When it was widespread, fragmentation typically occurred at about two to four sound traversal times. The $T^* \sim 0.75$ runs appear to be borderline for the three smallest system sizes, with fragmentation occurring in steps over an extended period of time much longer than a few sound traversal times.

The paths followed on a T - p diagram are shown in Fig. A.9 for

Fig. A.9. Pressure-density paths followed by two fragmentation runs.

The densities were calculated in an average sense; actual local density in the fluid did not reach such low values.

two 2611 atom runs. The paths shown use spatially averaged densities up to the fragmentation point, but inspection of the position plots shows marked heterogeneity much earlier. (The definition of fragmentation used here requires a minimum fragment separation of 2.5 σ .) Internal voids which eventually become fragment surfaces appear much earlier. The internal voids decrease the "pre-fragment" density; hence, density appears to increase upon fragmentation. Temperature also decreases; as a new daughter fragment is born, its "center-of-mass translational energy" is instantaneously subtracted from the "internal" energy of its parent cluster. Most of the fragment temperatures lie along the saturated liquid phase line. Finally, although the low temperature run appeared to penetrate the unstable region under the isothermal spinodal (and may have reached the isentropic spinodal which lies below the isothermal spinodal), the regular density patterns^{64,65} characteristic of "spinodal decomposition" were not observed. This is because the fragmentation expansion is inhomogeneous. If the internal voids that precede fragmentation were not included in the density calculation, then the spinodal lines would not be reached.

A.5.D. Fragment Size Distribution

The integrated (cumulative) population distributions for three runs with similar heating levels and varying system sizes are shown in Fig. A.10. The smallest (721 atom) system had a significant portion of the population concentrated in an intermediate fragment size range (indicated by the steep portion of the curve). The larger systems' populations were peaked at relatively lower fragment sizes and

Fig. A.10. Integrated population distributions as a function of fragment size for three fragmentation runs with similar heating levels but different system sizes. The dashed lines give integrals as functions of the fractional fragment size, N_c/N , and the solid lines are normalized to the largest fragment size, i.e. the abscissa is $N_c/N_{c\max}$. The fragment data were taken just as fragment sizes became well defined.

exhibited decreasing population density with increasing fragment size. The overall effect of increasing system size was to concentrate population in smaller fractional fragment sizes; 50% of the population was in fragments smaller than 36%, 18%, and 17% of the largest fragment size for the 721, 2611, and 14491 atom systems, respectively.

A.5.E. Translational Energy of the Fragments and Monomers

The translational temperatures (ignoring monomer energy and mass) are shown in Fig. A.11 as a function of system size and initial pressure. The inset shows the observed translational temperatures which properly increase with heating level (initial pressure). All the values exceed $mv^2/2k$, where v is the jump-off velocity, (dashed line). In two dimensions, model 3 predicts

$$T_{tr} = \left(\frac{mv^2}{2k} \right) \left[1 - \frac{1}{2} \frac{N_c}{N} \right] \quad (A.13)$$

For extreme fragmentation ($N_c \rightarrow 0$), Eq. A.13 produces the correct upper bound, but for no fragmentation Eq. A.13 predicts 1/2 the upper bound, rather than zero. The failure at no-fragmentation is a consequence of the assumption of a homogeneous expansion in model 3.

The main portion of the figure shows the ratio of the observed to the predicted (Eq. A.13) translational temperatures. The additional kinetic energy is from two sources: vapor pressure formation (which is limited in Fig. A.11 by the elimination of monomers from the calculation), and fragmentation due to fluctuations (a phenomenon observed for small systems on the saturation line with no isochoric heating). It is also possible that additional kinetic energy is

Fig. A.11. Translational temperatures (scaled to the prediction of model 3) for the 13 molecular dynamics runs.

produced by the recoil of the stretched material when it fragments.

For macroscopic systems, model 3 suggests that both vapor pressure formation and fracture due to "equilibrium" fluctuations are negligible. Glenn's three dimensional (macroscopic) hydrodynamic code calculations⁴⁶ confirmed the upper bound of $\rho v^2/2k$ when no tension is allowed in the material. Our molecular dynamics calculations (Fig. A.11) show that the translational temperature tends to increase with system size, at least for systems of a few thousand atoms or less. However, the 14491 atom result shows a decreased translational temperature with increasing system size (even though its initial sloshing motion would be expected to produce more translational energy than an initially quiescent system). Thus, these limited molecular dynamics results are not inconsistent with model 3. Finally, we note that the peak in the excess translational temperature is in the region of the critical nucleus size. Systems smaller than the critical size are naturally unstable, leading to fragmentation even in saturated systems.

The monomer temperatures at the time of fragmentation for each run are listed in the last column of Table A.1. The average liquid temperature during the monomer formation period lies somewhere between the peak listed in the second column of the table and the saturation temperature (~ 0.5). The monomer temperature exceeds both the average and the peak liquid temperatures in every case. Similar results have been found by Vicentini, Jacucci and Pandharipande⁶³ using three dimensional molecular dynamics for systems of 250 atoms. Vicentini, et. al. also found that the thermal temperatures of most of the fragments are similar and essentially independent of the initial

heating level, in agreement with our results.

A.6. Conclusions

Two dimensional molecular dynamics fragmentation simulations were run using five levels of heating and four system sizes. The numerical experiments produced agreement with only one of four proposed models (the energy minimization model, model 3). The model's power law dependence of fragment size (atoms) on system size ($2/3$) and initial pressure ($-4/3$) were both supported by the data. The larger fragment sizes were about an order of magnitude smaller than the model 3 predictions. There was an unexpectedly large level of translational energy generated in these molecular dynamics runs, probably due to the combination of small system size (fluctuations) and near-critical saturation temperature (vaporization). In macroscopic systems, model 3 (with the 0.1 correction factor) predicts

$$r = \left[\frac{D+2}{\rho} \gamma \left(\frac{Rc}{\Gamma e} \right)^{2/3} \right]^{1/3} / 10^{1/D} \quad (A.14)$$

where r is the fragment radius, R is the system radius, D is the number of dimensions (2 or 3), Γ is the Grüneisen parameter, e is the added heat per unit mass, and ρ_m is the mass density. When Eq. A.14 is applied to the HY LIFE reactor initial conditions (0.1 m radius lithium jets, 800 kJ/kg added energy, 485 kg/m³ density, 1.0 Grüneisen parameter, 0.35 J/m² surface tension, and 4500 m/s sound speed, the predicted fragment radius is 2.1 mm. Thus, fragmentation will produce about two orders of magnitude increase in the surface area, making it plausible that the required pulse rate of 1.5 Hz can be achieved. The molecular dynamics fragment sizes vary as a power of

system size which could be lower than $2/3$, perhaps as low as $1/2$. Extrapolation of our results over 13 orders of magnitude in system size (to the number of atoms in a HYLIFE jet's cross section) gives a decrease in the predicted fragment radius by about a factor of 25. This deviation from model 3 is in the favorable direction from a reactor designer's point of view.

VITA

James Allen Blink was born on April 21, 1948 in Kenosha, Wisconsin. He attended elementary school in Kenosha and junior high school in Tucson, Arizona. In 1966, he graduated as valedictorian of his class at Basic High School in Henderson, Nevada. In 1970, he graduated "With Distinction" from the University of Nevada at Reno. In addition to his Bachelor of Science degree in Engineering Science, Jim was commissioned a Second Lieutenant in the United States Army Corps of Engineers. After spending the summer working as a nuclear engineer at the Nevada Test Site, Jim began his first Army assignment: attending graduate school at the Georgia Institute of Technology under the Army's "Top 5%" program. In September 1971, he graduated as a Master of Science in Nuclear Engineering. From 1976 to 1978, Jim was a military research associate in the Energy and Military Application Group of Lawrence Livermore National Laboratory's Inertial Confinement Fusion Program. During this period, he also earned his license as a Professional Engineer in the Commonwealth of Virginia. In 1979, he left the Army and rejoined LLNL as a civilian employee. In 1980, Jim enrolled in the University of California at Davis/Livermore to complete his PhD degree through the Department of Applied Science.