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Applicability Of Continuum Fracture Mechanics In Atomistic Systems

Shao-Huan Cheng
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APPLICABILITY OF CONTINUUM FRACTURE MECHANICS
IN ATOMISTIC SYSTEMS

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of

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LIST OF SYMBOLS

a	Lattice constant
C_{ij}	Elastic constants
c	Crack length
E	Energy level
$F^{\alpha\beta}$	Interatomic force between atom α and β
G_I	Energy release Rate for Mode I (opening mode)
H	Enthalpy
h	Plank's constant
K	Kinetic Energy
K_I	Stress intensity factor for Mode I (opening mode)
K^{ref}	Reference stress intensity factor
k_b	Boltzmann's constant
L	Specimen dimension
m^α	Mass of atom α
N	Number of atoms
P	Pressure
$\mathbf{p}^\alpha$	Momentum of atom α
$\mathbf{r}^\alpha$	Position of atom α

S	Entropy
T	Temperature
t_i	Traction
U	Potential (strain) energy
u_i	Displacement
V	Volume
$\mathbf{v}^\alpha$	Velocity of atom α
W_e	External Work
W_s	Separation (dissipation) Work
$\mathbf{x}^\alpha$	Position of atom α
x_c	Critical distance
γ	Surface energy
$\delta()$	Dirac delta function
ε_{cr}	Critical strain
ε_{ij}	Strain
ε_Y	Yield strain
$\mathcal{H}$	Hamiltonian
Λ	Degree of singular stress dominance (K -dominance)
$\xi()$	Heaviside step function
ρ	Density
σ_{cr}	Critical stress
σ_{ij}	Stress

σ_{th}	Theoretic strength of defect-free (perfect) specimen
σ_Y	Yield stress
ψ	Localization function
Ω	Partition function
$\langle \rangle$	Ensemble Average

LIST OF ABBREVIATIONS

BCC	Body-centered cubic
EAM	Embedded atom method
eV	Electron voltage
FCC	Face-centered cubic
FEM	Finite element method
fs	Femtosecond
LAMMPS	Large-scale atomic/molecular massively Parallel Simulator (developed by Sandia National Labs)
MD	Molecular dynamics
NaCl	Sodium Chloride
Ni	Nickel
NPT	Isothermal-isobaric ensemble
NVE	Microcanonical ensemble
NVT	Canonical ensemble
PPPM	Particle-Particle-Particle-Mesh method
ps	Picosecond
SC	Simple cubic

ABSTRACT

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By quantitating the amplitude of the unbounded stress, the continuum fracture mechanics defines the stress intensity factor K to characterize the stress and displacement fields in the vicinity of the crack tip, thereby developing the relation between the stress singularity and surface energy (energy release rate G). This G - K relation, assigning physical meaning to the stress intensity factor, makes these two fracture parameters widely used in predicting the onset of crack propagation. However, due to the discrete nature of the atomistic structures without stress singularity, there might be discrepancy between the failure prediction and the reality of nanostructured materials. Defining the local atomistic stress with convergence within one lattice ensures the near-tip stress in the discrete systems displays the detailed stress concentration. Through comparison to the equivalent continuum finite element models, although these atomistic near-tip stress distributions preserve the trend of inverse square root singularity, the corresponding fracture toughness in terms of critical stress intensity factor (or energy release rate) is size dependent (i.e., varying with the size of the singular stress zone, K -dominance zone). Consequently, the failure load predicted by constant fracture toughness deviates from what a nanostructure can sustain if the singular stress is not dominant. The two-parameter model, including the contributions from both singular and non-singular

terms, is utilized to improve the inadequacy of continuum fracture mechanics. On the other hand, since the magnitude of the atomistic near-tip stress is finite, the maximum stress criterion is valid in atomistic systems, proven by the close match between the peak stress and the theoretic strength under the failure condition. Furthermore, the surface energy determined by the overall energy balance over the crack growth within several sizes of lattice constant is shown to be size-independent, in contrast to the size-dependent results obtained by the G - K relation.

1. INTRODUCTION

Starting with Richard Feynman's famous speech entitled, "There's plenty room at the bottom" [1], the development of nanotechnology has progressed not only to capturing a single atom's location by the scanning tunneling microscope (STM) [2] or atomic force microscope (AFM) [3] but also precisely controlling the orientation of single atoms to store one bit of data within 12 atoms [4] and even to produce the smallest movie in the world [5]. If we focus on engineering materials, one of the attractive findings is the carbon nanotube due to its extremely high stiffness and strength (~ 1 TPa for Young's modulus and ~ 100 GPa for tensile strength). Since Iijima's discovery in 1991 [6], a number of publications have been devoted to carbon nanotubes' material properties [7–13], strength (failure toughness) [14–16] and further application on composite materials [17–21]. Meanwhile, many researchers also focused on the nanocomposites composed of nanoparticles, e.g., silica (SiO_2), alumina (Al_2O_3), titanium dioxide (TiO_2), etc., due to the greater reactive surface area per unit volume compared with large particles [22–25]. In light of these studies, nanotechnology has been recognized as an area of interest and concern since the beginning of this century.

As Figure 1.1 shows, based on the different levels of scales, all structures are organized hierarchically, which illustrates two directions in nanotechnology: bottom-up (structures are built from molecular components and assembled chemically) and top-

Figure 1.1 Hierarchical organization of aircraft structures.

down (devices are downsized by mechanical cutting processes). From the viewpoint of mechanical analysis, bottom-up and top-down refer to approaches based on quantum/molecular and continuum mechanics, respectively. In Figure 1.1, it is uncontested that the mechanical behavior of the airplane, the related sub-structure components and even the microstructures of which each component consists can be modeled by the continuum finite element models [26]. On the other hand, atomic/crystal structures belong to the realm of quantum/molecular mechanics. Since continuum mechanics has demonstrated its value in modeling the mechanics properties of solids and structures, it is of practical interest to realize the range of applicability for continuum

mechanics and solve problems at the atomistic scale by using knowledge accumulated within solid mechanics.

1.1 Size-Dependent Behavior of Nanostructures

Homogenizing a group of atoms as a continuum representative element is a general procedure to link the discrete systems with the macroscopic continuum variables. By either equating the potential energy of crystal structures to the strain energy of representative elements or considering the equilibrium condition once the representative element is treated as a material point, e.g., the non-local elasticity, many researchers have studied the constitutive relation [9–13, 27–29], vibration [13, 30] and buckling behavior [31, 32] of nanostructures. Among them, one of the most noticeable results is the size-dependent material properties. Sun and Zhang [28] described the plate-like nanostructure by two types of unit cells representing the atoms inside and on the surface respectively and discovered the trend of the lower Young's modulus, higher in-plane Poisson's ratio and lower out-of-plane Poisson's ratio as the thickness of the plate decreases. Chang and Gao [10] considered the potential energy from bond stretch and in-plane angle bending to derive the analytical expressions showing the diameter-dependent Young's modulus and Poisson's ratio of the single-wall carbon nanotube. Except for demonstrating the size effect on material properties, Wang et al. [12] found that the single-wall carbon nanotube exhibits orthotropic rather than isotropic symmetry when the diameter is below 1.5 nm. As also indicated in their study, the elastic moduli of a multi-wall carbon nanotube with a diameter of less than 10 nm is also size dependent. In other research not on the diameter

of nanotubes, Sundararaghavan and Waas [13] studied the influences of length on the Young's and shear moduli by using non-local elasticity.

These revised studies show the results of applying continuum mechanics on homogeneous discrete structures. Consequently, investigating the applicability of continuum mechanics to the atomistic structures with geometric discontinuity is a potential research topic. As stress concentration occurs, how to select an appropriate continuum representative element becomes a more crucial issue. Furthermore, based on continuum mechanics, the fracture parameter to predict the strength of structural materials is also treated as a material constant. Similar to the elastic moduli in nanostructures, does the fracture parameters also vary with specimen geometries? If the size-dependent fracture parameter really happens, is there any suitable way to modify the present fracture criterion? Answering these questions is one of the main topics in this dissertation. As a starting point, the next section will introduce the fracture parameter in terms of the critical stress intensity factor and energy release rate – the foundation of continuum fracture mechanics.

1.2 Continuum Fracture Mechanics

For brittle fracture, interpreted as the breaking of interatomic bonds (as opposed to the sliding of crystal planes, a phenomenon known as dislocation or ductile failure), the related failure criterion is attributed to the work of Griffith [33] and Irwin [34] in developing the concept of surface energy of creating new crack surfaces and the relation between surface energy and singular stress amplitude, respectively. In Griffith's fracture

theory, if we consider a cracked solid with the unit out-of-plane thickness, the crack propagation has to accompany the decrease of strain energy stored in the body as

$$-\Delta U = 2\gamma\Delta c \quad (1.1)$$

where ΔU is the variation of strain energy with negative sign, γ is the surface energy treated as a material constant and Δc is the crack extension. Rearranging equation (1.1), the critical energy release rate is defined as

$$G_{Ic} = -\frac{\Delta U}{\Delta c} = 2\gamma \quad (1.2)$$

According to equation (1.2), if the relation between strain energy and crack size is known, the Griffith criterion is applicable on both the discrete or continuous body, dependent on the consideration of either the finite crack or infinitesimal crack extension ($\Delta c \rightarrow dc$, $\Delta U \rightarrow dU$). Since determining the strain energy as a function of crack length may be a complicated task, Irwin proposed that the overall Griffith energy balance can be treated as the work done by the near-tip stress and displacement to remove the new crack surface (so called crack closure method). Under the opening mode (Mode I), the near-tip stresses σ_{yy} and displacement u_y in a linearly elastic solid are

$$\sigma_{yy} = \frac{K_I}{\sqrt{2\pi r}}, \quad u_y = 2\frac{K_I}{\pi E^*}\sqrt{2\pi r} \quad (1.3)$$

where r is the distance from the crack tip, E^* is the material constant dependent on plane-strain or plane-stress condition and K_I is the stress intensity factor since the normal stress approaches infinity with the singularity exponent $\lambda = -1/2$. The corresponding work done to close the crack opening is equal to the total released energy, which yields

$$G_I dc = 2 \int_0^{dc} \frac{1}{2} \sigma_{yy}(r) u_y(dc - r) dr = \frac{2K_I^2}{\pi E^*} \int_0^{dc} \sqrt{\frac{dc - r}{r}} dr = \frac{2K_I^2}{\pi E^*} \left(\frac{\pi}{2} \right) dc$$

$$\Rightarrow G_I = \frac{K_I^2}{E^*}$$
(1.4)

It is noted that the crack extension dc considered in equation (1.4) has to be infinitesimal due to the involvement of stress singularity from continuum theory. Since equation (1.4) demonstrates the equivalence between the stress intensity factor and energy release rate, Irwin redefined equation (1.2) as a failure criterion based on the critical stress intensity factor

$$K_I = K_{Ic} \quad (1.5)$$

If plastic deformation is included, similar to the William's expansion [35] in linear elasticity, the near-tip stress is defined in the following form

$$\sigma_{ij} = A \sigma_Y r^\lambda \tilde{\sigma}_{ij}(\theta) \quad (1.6)$$

where A is an unknown coefficient and σ_Y is the yield strength. Substituting equation (1.6) into the power-law hardening material

$$\frac{\varepsilon_{ij}}{\varepsilon_Y} = \alpha \left(\frac{\sigma_{ij}}{\sigma_Y} \right)^n \quad (1.7)$$

where α is a material parameter and n is the strain hardening index, the near-tip strain can be derived as

$$\varepsilon_{ij} = \alpha A^n \varepsilon_Y r^{\lambda n} \tilde{\varepsilon}_{ij}(\theta) \quad (1.8)$$

and the corresponding strain energy density is

$$w = \int \sigma_{ij} d\varepsilon_{ij} = \alpha A^{n+1} \sigma_Y \varepsilon_Y r^{\lambda(n+1)} \tilde{w}(\theta) \quad (1.9)$$

It is noteworthy that since the values of strain hardening index n in metals range from 0.1 to 0.5, equation (1.7) only concerns the plastic strain with stronger singularity and thus the elastic strain is neglected in equation (1.8). Expressing J -integral in polar-coordinate system,

$$J = r \oint \left[w \cos \theta - \sigma_{ij} n_j \frac{\partial u_i}{\partial x} \right] d\theta \quad (1.10)$$

For the path-independent J -integral, the power of r in equation (1.9) has to be -1 , that is,

$$\lambda(n+1) = -1 \Rightarrow \lambda = -\frac{1}{n+1} \quad (1.11)$$

which defines the singularity exponent as a function of the strain hardening index. Substituting the displacements u_r and u_θ (obtained by the strain-displacement relation) into equation (1.10), Hutchinson [36] and Rice and Rosengren [37] showed the unknown coefficient A as

$$A^{n+1} = \frac{J}{\alpha \sigma_Y \varepsilon_Y I_n} \quad (1.12)$$

where I_n is an integration constant. The near-tip stress and strain can be rewritten as

$$\begin{aligned} \sigma_{ij} &= \sigma_Y \left(\frac{J}{\alpha \sigma_Y \varepsilon_Y I_n r} \right)^{\frac{1}{n+1}} \tilde{\sigma}_{ij}(\theta) \\ \varepsilon_{ij} &= \alpha \varepsilon_Y \left(\frac{J}{\alpha \sigma_Y \varepsilon_Y I_n r} \right)^{\frac{n}{n+1}} \tilde{\varepsilon}_{ij}(\theta) \end{aligned} \quad (1.13)$$

where the intensity of the singular stress field is characterized by the J -integral. According to equation (1.3), (1.4) and (1.13), we can say stress singularity and infinitesimal crack extension complement each other to build the foundation of continuum fracture mechanics. However, that also brings the uncertainty of applying continuum fracture mechanics to atomistic systems where the interatomic bonds with

finite strength illustrates that stress singularity cannot exist and the nature of discreteness limits the minimum crack extension, which has to be several sizes of lattice constant.

1.3 Chapter Outlines

Following the previous sections, the main objective of this dissertation focuses on the applicability of continuum fracture mechanics in atomistic systems and further discusses the reason why the corresponding fracture parameter is size dependent. To achieve that goal, we chose the molecular dynamics (MD) simulation to collect the failure data of brittle crystals solids. A detailed background of the MD method is illustrated in Chapter 2 beginning with the introduction of statistical mechanics. According to the different types of thermodynamic conditions (ensembles, more specifically), statistical mechanics offers the guideline to define the Hamiltonian; thus, the corresponding equations of motion can be solved for all the degrees of freedom in a simulation box. Moreover, to set up the virtual experimental environment, the initial conditions and the types of interatomic functions are also included in Chapter 2.

The definitions of the local atomistic stress to observe the crack opening stress in discrete systems is addressed in Chapter 3. The local stress provides an average stress measurement within a spatial volume containing a collection of atoms. Theoretically, the smaller the averaging volume where a local stress can converge, the closer this atomistic stress definition can approach the ideal setting of the macroscopic stress. As a result, a more accurate stress concentration can be estimated for the inhomogeneous case. Two of the most-cited atomistic stress definitions are virial and Hardy's theorem. In this chapter, we indicate that once the averaging volume is periodic, the convergence of the virial and

Hardy stress can be accomplished within one single lattice, which is much smaller than what is required by other non-periodic volumes such as a sphere. In the final section, a cracked sodium chloride crystal is considered to demonstrate that the crack opening stress described by the periodic lattices preserves the detailed stress concentration near the crack tip.

Once the local virial stress with the periodic averaging volumes is adopted, we are able to overcome the barrier of the ambiguous crack-tip stress field in molecular dynamics (MD) simulations and perform direct calculations of fracture toughness. In Chapter 4, both the MD and corresponding continuum finite element method (FEM) solutions indicate that fracture toughness measured in stress intensity factor (or energy release rate) decreases with the decreasing crack length. Accordingly, fracture toughness cannot be treated as a material constant when the crack length is several nanometers. The size-dependent behavior of fracture toughness is explained in terms of the size of the singular stress zone (the K -dominance zone). It is found that as the crack length decreases, the K -dominance zone also decreases, making the singular part of the crack tip stress not capable of accounting for the full fracture driving force. As a result, the critical stress intensity factor at failure (the fracture toughness) is lowered while the remote failure stress is raised.

In Chapter 5, we further discuss the influence of geometric confinement on the size-dependent fracture toughness. Since downsizing the specimen height between two fixed layers (the dimension perpendicular to the crack line) also diminishes the size of the K -dominance zone, the corresponding critical stress intensity factor (energy release rate) decreases as the specimen height decreases, similar to the cases of various crack lengths.

In addition, to modify the present fracture criterion only composed of the stress intensity factor, we employ the two-parameter model to take the contribution of a non-singular term into account. Meanwhile, by looking at the crack opening stress distribution under failure condition, we find that the maximum stress that a unit cell can sustain is constant. This phenomenon illustrates that since stress singularity doesn't exist due to the interatomic bonds with finite strength, the maximum stress criterion is applicable in atomistic systems.

With reference to the Griffith's fracture theory, Chapter 6 emphasizes three ways to estimate the surface energy of the brittle crystal without the basis of continuum fracture mechanics (no consideration of the G - K relation as equation (1.4) shows): One is direct calculation of the potential energy difference between a perfect and split crystal; another focuses on the cracked specimen whose related released work is determined by the difference between the variations of external and internal work during crack extension (equation (1.2) plus the contribution of the external work); and the other considers the traction-separation relation whose underneath area is treated as the separation work per unit area. Different from the critical energy release rate through the G - K relation varying with the size of K -dominance zone shown in the previous chapters, we find that the critical energy release rates (the double of the surface energy) based on these three methods remain a constant regardless of the change of specimen geometries.

2. STATISTICAL MECHANICS AND MOLECULAR DYNAMICS SIMULATIONS

Statistical mechanics, illustrating the relation between the microscopic degrees of freedom (the position $\mathbf{r}$ and velocity $\mathbf{v}$ of each atom) and the macroscopic thermodynamic variables (the temperature T and pressure P of a system containing many atoms), is the theoretic foundation of molecular simulations. For Monte Carlo (MC), the microscopic configurations generated by the stochastic process have to satisfy the probability distribution from statistical mechanics [38, 39]. On the other hand, according to different thermodynamic environments, the Hamiltonian, deriving the equations of motion needed for molecular dynamics (MD), is also defined based on statistical mechanics. In this study, the connections between different research areas are illustrated in Figure 2.1. Since we use the MD simulation to model the failure process resulted from the breaking of interatomic bonds and intend to see if the solid (fracture) mechanics is able to explain these failure phenomena in discrete crystals, it is nature for us to review statistical mechanics; thus, realize the background of MD simulations.

2.1 Analytical Mechanics

Consider a system containing N atoms with the same mass m interacting via an interatomic potential $U(\mathbf{r}^1, \mathbf{r}^2, \dots, \mathbf{r}^N)$ which defines the interatomic force $\mathbf{F}^\alpha$

Figure 2.1 Connection between areas considered in this dissertation.

$$\mathbf{F}^\alpha = -\frac{\partial U}{\partial \mathbf{r}^\alpha}, \quad \alpha = 1, 2, \dots, N \quad (2.1)$$

The equations of motion of these particles are described by the Newton's second law

$$\mathbf{F}^\alpha = m\ddot{\mathbf{r}}^\alpha \quad (2.2)$$

With consideration of an isolated system, the trajectories of each atom can be estimated by solving equation (2.2). In addition, the Hamiltonian (total energy) $\mathcal{H}$ of the whole system is the sum of kinetic energy K and potential energy U

$$\mathcal{H}(\mathbf{r}^1, \mathbf{r}^2, \dots, \mathbf{r}^N, \dot{\mathbf{r}}^1, \dot{\mathbf{r}}^2, \dots, \dot{\mathbf{r}}^N) = K + U \quad (2.3)$$

By the Lagrangian equation of motion

$$\frac{d}{dt} \left(\frac{\partial K}{\partial \dot{\mathbf{r}}^\alpha} \right) + \frac{\partial U}{\partial \mathbf{r}^\alpha} = 0 \quad (2.4)$$

,the kinetic energy K

$$K = \frac{1}{2} \sum_{\alpha} m(\dot{\mathbf{r}}^\alpha)^2 \quad (2.5)$$

and the interatomic forces in equation (2.1), we can derive the same equations of motion as equation (2.2). This shows that the (dynamic) equilibrium condition of each particle can be treated as the conservation of energy. Defining the generalized coordinates as momentum of each atom $\mathbf{p}^\alpha$, the total energy becomes a functional denoted as $\mathcal{H}(\mathbf{r}^1, \mathbf{r}^2, \dots, \mathbf{r}^N, \mathbf{p}^1, \mathbf{p}^2, \dots, \mathbf{p}^N)$ and kinetic energy is rewritten as

$$K = \sum_{\alpha} \frac{(\mathbf{p}^\alpha)^2}{2m} \quad (2.6)$$

The Lagrangian equation of motion in equation (2.4) gives us

$$\dot{\mathbf{p}}^\alpha = -\frac{\partial \mathcal{H}}{\partial \mathbf{r}^\alpha} \quad (2.7)$$

Consider the conversation of total energy, that is

$$\frac{d\mathcal{H}}{dt} = \sum_{\alpha} \frac{\partial \mathcal{H}}{\partial \mathbf{r}^\alpha} \dot{\mathbf{r}}^\alpha + \frac{\partial \mathcal{H}}{\partial \mathbf{p}^\alpha} \dot{\mathbf{p}}^\alpha = \sum_{\alpha} \frac{\partial \mathcal{H}}{\partial \mathbf{r}^\alpha} \dot{\mathbf{r}}^\alpha - \frac{\partial \mathcal{H}}{\partial \mathbf{p}^\alpha} \frac{\partial \mathcal{H}}{\partial \mathbf{r}^\alpha} = 0 \quad (2.8)$$

which implies the relation

$$\dot{\mathbf{r}}^\alpha = -\frac{\partial \mathcal{H}}{\partial \mathbf{p}^\alpha} \quad (2.9)$$

Equation (2.7) and (2.9) are known as Hamilton's equation of motion [40, 41]. Compared with the Lagrangian equation of motion in equation (2.4) as a set of $3N$ second order-differential equations, the Hamilton's equation constitute an equivalent set of $6N$ first order-differential equations.

2.1.1 Numerical Integration Algorithms

For a system containing a large number of atoms, solving equation (2.2) numerically becomes the only feasible process. One of most popular algorithms used in MD

simulation is the velocity Verlet integration scheme since it is more convenient to satisfy the initial condition, i.e., $\mathbf{r}(-\Delta t)$ and $\mathbf{v}(-\Delta t)$ are not involved. The positions and velocities of atoms after a time step Δt are calculated as

$$\begin{aligned}
 \mathbf{r}^\alpha(t + \Delta t) &= \mathbf{r}^\alpha(t) + \dot{\mathbf{r}}^\alpha(t) \Delta t + \ddot{\mathbf{r}}^\alpha(t) \frac{\Delta t^2}{2} \\
 \dot{\mathbf{r}}^\alpha\left(t + \frac{\Delta t}{2}\right) &= \dot{\mathbf{r}}^\alpha(t) + \ddot{\mathbf{r}}^\alpha(t) \frac{\Delta t}{2} \\
 \dot{\mathbf{r}}^\alpha(t + \Delta t) &= \dot{\mathbf{r}}^\alpha\left(t + \frac{\Delta t}{2}\right) + \ddot{\mathbf{r}}^\alpha(t + \Delta t) \frac{\Delta t}{2} \\
 m\ddot{\mathbf{r}}^\alpha(t + \Delta t) &= -\frac{\partial U(\mathbf{r}^\alpha(t + \Delta t))}{\partial \mathbf{r}^\alpha(t + \Delta t)}
 \end{aligned} \tag{2.10}$$

With knowing the positions, velocities and accelerations at time t , the positions at $t + \Delta t$ can be calculated by the first equation of (2.10). Subsequently, accelerations at t and $t + \Delta t$ corresponding to the first derivative of the potential function are used to estimate the velocities from t to $t + \Delta t/2$ and from $t + \Delta t/2$ to $t + \Delta t$, respectively.

2.2 Microcanonical Ensemble

If the energy level of an isolated system is denoted as E , the number of microstates which allows the energy of a system maintains at level E is expressed as

$$\Omega_{\text{NVE}} = \frac{1}{N!h^{3N}} \int d\mathbf{r}^1 d\mathbf{r}^2 \cdots d\mathbf{r}^N d\mathbf{p}^1 d\mathbf{p}^2 \cdots d\mathbf{p}^N \delta(\mathcal{H}(\mathbf{r}, \mathbf{p}) - E) \tag{2.11}$$

where δ is the Dirac delta function, factor $N!$ comes from the indistinguishable atoms (for example, it is still the same state if two atoms switch their position) and h is Planck's constant to let Ω_{NVE} be dimensionless. The Heisenberg's uncertainty principal in quantum

mechanics states the volume (error) of measuring the position and momentum of any particle simultaneously is

$$d\mathbf{r}^\alpha d\mathbf{p}^\alpha = h^3 \quad (2.12)$$

Ω_{NVE} is also called as microcanonical partition function representing the sum of all possible events. According to the Boltzmann relation, entropy S is related with how many allowable microstates in a system, which yields

$$S = k_b \ln \Omega_{\text{NVE}} \quad (2.13)$$

(k_b is the Boltzmann's constant) and the thermodynamic variables (for example, we control how much external work done and heat added in an isolated system)

$$\begin{aligned} dE &= TdS - PdV \\ \Rightarrow dS &= \frac{1}{T}dE + \frac{P}{T}dV \\ \Rightarrow \frac{\partial S}{\partial E} &= \frac{1}{T}, \quad \frac{\partial S}{\partial V} = \frac{P}{T} \end{aligned} \quad (2.14)$$

,we obtain the relations describing the macroscopic observables (temperature T , pressure P) and the microstates

$$\begin{aligned} \frac{1}{k_b T} &= \frac{\partial \ln \Omega_{\text{NVE}}}{\partial E}, \text{ while } V \text{ is fixed} \\ \frac{P}{k_b T} &= \frac{\partial \ln \Omega_{\text{NVE}}}{\partial V}, \text{ while } E \text{ is fixed} \end{aligned} \quad (2.15)$$

Besides, any observables can be estimated by the ensemble average

$$\begin{aligned} \langle a \rangle_{\text{NVE}} &= \frac{1}{\Omega_{\text{NVE}}} \frac{1}{N! h^{3N}} \int d^N \mathbf{r} d^N \mathbf{p} a(\mathbf{r}, \mathbf{p}) \delta(\mathcal{H}(\mathbf{r}, \mathbf{p}) - E) \\ &= \frac{\int d^N \mathbf{r} d^N \mathbf{p} a(\mathbf{r}, \mathbf{p}) \delta(\mathcal{H}(\mathbf{r}, \mathbf{p}) - E)}{\int d^N \mathbf{r} d^N \mathbf{p} \delta(\mathcal{H}(\mathbf{r}, \mathbf{p}) - E)} \end{aligned} \quad (2.16)$$

following the definition of the expected value – a sum of the possible values times the corresponding probabilities. Let us take a look at the average kinetic energy of any atom at equilibrium. According to equation (2.16),

$$\langle K^\alpha \rangle = \left\langle \frac{p_i^\alpha p_i^\alpha}{2m} \right\rangle = \left\langle \frac{p_i^\alpha}{2} \frac{\partial \mathcal{H}}{\partial p_i^\alpha} \right\rangle = \frac{1}{2} \frac{\int d^N \mathbf{r} d^N \mathbf{p} \left[p_i^\alpha \frac{\partial \mathcal{H}}{\partial p_i^\alpha} \delta(\mathcal{H}(\mathbf{r}, \mathbf{p}) - E) \right]}{\int d^N \mathbf{r} d^N \mathbf{p} \delta(\mathcal{H}(\mathbf{r}, \mathbf{p}) - E)} \quad (2.17)$$

Following the derivative of Heaviside step function ξ as the Dirac delta function δ , the partition function Ω_{NVE} is written as

$$\begin{aligned} \Omega_{\text{NVE}} &= \frac{1}{N! h^{3N}} \int d^N \mathbf{r} d^N \mathbf{p} \delta(\mathcal{H}(\mathbf{r}, \mathbf{p}) - E) \\ &= -\frac{1}{N! h^{3N}} \int d^N \mathbf{r} d^N \mathbf{p} \frac{\partial}{\partial E} \xi(\mathcal{H}(\mathbf{r}, \mathbf{p}) - E) \end{aligned} \quad (2.18)$$

The numerator in equation (2.17) is rewritten as

$$\begin{aligned} &\int d^N \mathbf{r} d^N \mathbf{p} \left[p_i^\alpha \frac{\partial \mathcal{H}(\mathbf{r}, \mathbf{p})}{\partial p_i^\alpha} \delta(\mathcal{H}(\mathbf{r}, \mathbf{p}) - E) \right] \\ &= -\int d^N \mathbf{r} d^N \mathbf{p} \frac{\partial}{\partial E} \left[p_i^\alpha \frac{\partial \mathcal{H}(\mathbf{r}, \mathbf{p})}{\partial p_i^\alpha} \xi(\mathcal{H}(\mathbf{r}, \mathbf{p}) - E) \right] \\ &= -\int_{\mathcal{H} > E} d^N \mathbf{r} d^N \mathbf{p} \frac{\partial}{\partial E} \left[p_i^\alpha \frac{\partial (\mathcal{H}(\mathbf{r}, \mathbf{p}) - E)}{\partial p_i^\alpha} \right] \\ &= -\int_{\mathcal{H} > E} d^N \mathbf{r} d^N \mathbf{p} \frac{\partial}{\partial E} \left[\frac{\partial}{\partial p_i^\alpha} p_i^\alpha (\mathcal{H}(\mathbf{r}, \mathbf{p}) - E) - 3 (\mathcal{H}(\mathbf{r}, \mathbf{p}) - E) \right] \end{aligned} \quad (2.19)$$

The first term is equal to zero because of $\mathcal{H}(\mathbf{r}, \mathbf{p}) = E$ at the limit of $\mathbf{p}^\alpha$. The factor of 3 comes from

$$\frac{\partial p_i^\alpha}{\partial p_i^\alpha} = \delta_{ii} = 3 \quad (2.20)$$

The remained terms becomes

$$-3 \int_{\mathcal{H} > E} d^N \mathbf{r} d^N \mathbf{p} = -3 \int d^N \mathbf{r} d^N \mathbf{p} \xi (\mathcal{H}(\mathbf{r}, \mathbf{p}) - E) \quad (2.21)$$

Substitute equations (2.18) and (2.21) into (2.17) gives

$$\begin{aligned} \langle K^\alpha \rangle &= \frac{3}{2} \frac{\int d^N \mathbf{r} d^N \mathbf{p} \xi (\mathcal{H}(\mathbf{r}, \mathbf{p}) - E)}{\int d^N \mathbf{r} d^N \mathbf{p} \frac{\partial}{\partial E} \xi (\mathcal{H}(\mathbf{r}, \mathbf{p}) - E)} \\ &= \frac{3}{2} \left(\ln \int d^N \mathbf{r} d^N \mathbf{p} \frac{\partial}{\partial E} \xi (\mathcal{H}(\mathbf{r}, \mathbf{p}) - E) \right)^{-1} \\ &= \frac{3}{2} \left(\frac{\partial}{\partial E} \ln \int d^N \mathbf{r} d^N \mathbf{p} \delta (\mathcal{H}(\mathbf{r}, \mathbf{p}) - E) \right)^{-1} \quad \text{for } N \rightarrow \infty \\ &= \frac{3}{2} \left(\frac{\partial S}{\partial E} \right) = \frac{3k_b T}{2} \end{aligned} \quad (2.22)$$

through equation (2.15). Sum the average kinetic energy of each atom, which leads to

$$\langle K \rangle = \sum_{\alpha} \langle K^\alpha \rangle = \frac{3Nk_b T}{2} \quad (2.23)$$

representing the well-known relation between the total average kinetic energy and the temperature.

2.2.1 Ergodicity

At current stage, it seems that these derivations do not directly relate with the implement of MD simulations since the equations of motion has been known as equation (2.2), which can be solved by the numerical integration algorithm as shown in equation (2.10). However, even though we have realized the positions and velocities of every atom at any given time, how can we relate these microstates with the behavior of the entire system? For example, with knowing the velocity of each atom, is it possible to estimate

the average kinetic energy shown in equation (2.23)? Ergodicity, hypothesizing the system has been through all possible microstates in an infinite time, provides the foundation to show the equivalence between the ensemble average and the time average of any observables, which leads to

$$\langle a \rangle = \frac{\int d^N \mathbf{r} d^N \mathbf{p} a(\mathbf{r}, \mathbf{p}) \delta(\mathcal{H}(\mathbf{r}, \mathbf{p}) - E)}{\int d^N \mathbf{r} d^N \mathbf{p} \delta(\mathcal{H}(\mathbf{r}, \mathbf{p}) - E)} = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau a(t) dt \quad (2.24)$$

For examples, if τ is equal to $N_{\Delta t} \Delta t$ (τ is taken as a large enough number compared with the time step Δt), the average total kinetic energy is

$$\langle K \rangle = \frac{1}{N_{\Delta t}} \sum_{n_{\Delta t}=1}^{N_{\Delta t}} \sum_{\alpha} \frac{1}{2} m (\dot{\mathbf{r}}^{\alpha}(n_{\Delta t}))^2 \quad (2.25)$$

Combining equations (2.23) and (2.25) shows the way to control the temperature by adjusting the velocities of atoms. This will be the topic of the next section discussing how to derive the equations of motion if we choose to control the temperature T rather than the energy E of a system.

2.3 Canonical Ensemble

As the previous section demonstrates, in the microcanonical ensemble, an isolated system is characterized by the number of atoms N , volume V and total energy E . However, from the viewpoint of experiments, it would more practical to control the temperature T rather than the energy E . Therefore, in the canonical ensemble with controlled variables as N , V , and T , the system is assumed to contact with an infinite

Figure 2.2 A system with a fixed volume touching with the heat reservoir.

thermal reservoir. As Figure 2.2 shows, the system with Hamiltonian $\mathcal{H}_1$ and heat reservoir with Hamiltonian $\mathcal{H}_2$ is isolated, which leads to

$$\Omega_{\text{NVT}} = \frac{1}{N!h^{3N}} \int d^{N_1}\mathbf{r}_1 d^{N_1}\mathbf{p}_1 d^{N_2}\mathbf{r}_2 d^{N_2}\mathbf{p}_2 \delta(\mathcal{H}_1(\mathbf{r}_1, \mathbf{p}_1) + \mathcal{H}_2(\mathbf{r}_2, \mathbf{p}_2) - E) \quad (2.26)$$

based on equation (2.11). Let us look at the integration over $\mathbf{r}_2$ and $\mathbf{p}_2$ first and take the nature logarithm for the application of the Boltzmann relation in (2.13),

$$\begin{aligned} & \ln \int d^{N_2}\mathbf{r}_2 d^{N_2}\mathbf{p}_2 \delta(\mathcal{H}_1(\mathbf{r}_1, \mathbf{p}_1) + \mathcal{H}_2(\mathbf{r}_2, \mathbf{p}_2) - E) \\ &= \ln \int d^{N_2}\mathbf{r}_2 d^{N_2}\mathbf{p}_2 \delta(\mathcal{H}_2(\mathbf{r}_2, \mathbf{p}_2) - E) \\ & \quad - \mathcal{H}_1 \frac{\partial}{\partial E} \ln \int d^{N_2}\mathbf{r}_2 d^{N_2}\mathbf{p}_2 \delta(\mathcal{H}_2(\mathbf{r}_2, \mathbf{p}_2) - E) \end{aligned} \quad (2.27)$$

through the Taylor expansion about $\mathcal{H}_1 = 0$ ($\mathcal{H}_2 \gg \mathcal{H}_1$) and the relations

$$\frac{\partial}{\partial \mathcal{H}_1} \delta(\mathcal{H}_1(\mathbf{r}_1, \mathbf{p}_1) - E) = -\frac{\partial}{\partial E} \delta(\mathcal{H}_1(\mathbf{r}_1, \mathbf{p}_1) - E) \quad (2.28)$$

Defining

$$\begin{aligned}
S_2 &= k_b \ln \int d^{N_2} \mathbf{r}_2 d^{N_2} \mathbf{p}_2 \delta(\mathcal{H}_2(\mathbf{r}_2, \mathbf{p}_2) - E) \\
&\Rightarrow \frac{\partial \ln \int d^{N_2} \mathbf{r}_2 d^{N_2} \mathbf{p}_2 \delta(\mathcal{H}_2(\mathbf{r}_2, \mathbf{p}_2) - E)}{\partial E} = \frac{1}{k_b T}
\end{aligned} \tag{2.29}$$

based on equation (2.15), equation (2.27) becomes

$$\int d^{N_2} \mathbf{r}_2 d^{N_2} \mathbf{p}_2 \delta(\mathcal{H}_1(\mathbf{r}_1, \mathbf{p}_1) + \mathcal{H}_2(\mathbf{r}_2, \mathbf{p}_2) - E) = e^{\frac{S_2}{k_b} - \frac{\mathcal{H}_1}{k_b T}} \tag{2.30}$$

Substituting equation (2.30) into (2.26) and neglecting the constant term in equation (2.30), we obtain the canonical partition function as

$$\Omega_{\text{NVT}} = \frac{1}{N! h^{3N}} \int d^N \mathbf{r} d^N \mathbf{p} e^{-\frac{\mathcal{H}}{k_b T}} \tag{2.31}$$

where the subscript “1” is taken away. Like the Boltzmann relation in (2.13), the relation between the allowable microstates and the thermodynamic variables is

$$A = k_b T \ln \Omega_{\text{NVT}} \tag{2.32}$$

where $A = E - TS$ is the Helmholtz free energy. Moreover, the ensemble average can be represented as

$$\begin{aligned}
\langle a \rangle &= \frac{1}{\Omega_{\text{NVT}}} \frac{1}{N! h^{3N}} \int d^N \mathbf{r} d^N \mathbf{p} a(\mathbf{r}, \mathbf{p}) e^{-\mathcal{H}/k_b T} \\
&= \frac{\int d^N \mathbf{r} d^N \mathbf{p} a(\mathbf{r}, \mathbf{p}) e^{-\mathcal{H}/k_b T}}{\int d^N \mathbf{r} d^N \mathbf{p} e^{-\mathcal{H}/k_b T}}
\end{aligned} \tag{2.33}$$

Following the microcanonical ensemble in equation (2.23), let us take a look at the average kinetic energy of atom α in the canonical ensemble

$$\langle K^\alpha \rangle = \left\langle \frac{p_i^\alpha p_i^\alpha}{2m} \right\rangle = \left\langle \frac{p_i^\alpha}{2} \frac{\partial \mathcal{H}}{\partial p_i^\alpha} \right\rangle = \frac{1}{2} \frac{\int d^N \mathbf{r} d^N \mathbf{p} p_i^\alpha \frac{\partial \mathcal{H}}{\partial p_i^\alpha} e^{-\mathcal{H}/k_b T}}{\int d^N \mathbf{r} d^N \mathbf{p} e^{-\mathcal{H}/k_b T}} \quad (2.34)$$

By the relation,

$$\begin{aligned} \frac{\partial}{\partial p_i^\alpha} e^{-\mathcal{H}/k_b T} &= \frac{\partial}{\partial \mathcal{H}} e^{-\mathcal{H}/k_b T} \frac{\partial \mathcal{H}}{\partial p_i^\alpha} = -\frac{1}{k_b T} e^{-\mathcal{H}/k_b T} \frac{\partial \mathcal{H}}{\partial p_i^\alpha} \\ \Rightarrow \frac{\partial \mathcal{H}}{\partial p_i^\alpha} e^{-\mathcal{H}/k_b T} &= -k_b T \frac{\partial}{\partial p_i^\alpha} e^{-\mathcal{H}/k_b T} \end{aligned} \quad (2.35)$$

,we can get

$$\begin{aligned} \langle K^\alpha \rangle &= \frac{1}{2} \frac{-k_b T \left[\int d^N \mathbf{r} d^N \mathbf{p} \frac{\partial}{\partial p_i^\alpha} p_i^\alpha e^{-\mathcal{H}/k_b T} - \int d^N \mathbf{r} d^N \mathbf{p} e^{-\mathcal{H}/k_b T} \frac{\partial p_i^\alpha}{\partial p_i^\alpha} \right]}{\int d^N \mathbf{r} d^N \mathbf{p} e^{-\mathcal{H}/k_b T}} \\ &= \frac{1}{2} \frac{-k_b T \left[\int d^N \mathbf{r} d^{N-1} \mathbf{p} p_i^\alpha e^{-\mathcal{H}/k_b T} \Big|_{-\infty}^{\infty} - 3 \int d^N \mathbf{r} d^N \mathbf{p} e^{-\mathcal{H}/k_b T} \right]}{\int d^N \mathbf{r} d^N \mathbf{p} e^{-\mathcal{H}/k_b T}} \end{aligned} \quad (2.36)$$

The first term is equal to zero since the Hamiltonian is the function of $(\mathbf{p}^\alpha)^2$. Thus,

$$\langle K^\alpha \rangle = \frac{3k_b T}{2} \frac{\int d^N \mathbf{r} d^N \mathbf{p} e^{-\mathcal{H}/k_b T}}{\int d^N \mathbf{r} d^N \mathbf{p} e^{-\mathcal{H}/k_b T}} = \frac{3}{2} k_b T \quad (2.37)$$

The average kinetic energy of the entire system is

$$\langle K \rangle = \sum_{\alpha} \langle K^\alpha \rangle = \frac{3Nk_b T}{2} \quad (2.38)$$

which means both the microcanonical and canonical ensembles have the same relation describing the average kinetic energy and the temperature (see equation (2.23)). That will be shown to be a significant step to derive the equations of motion in the following section.

2.3.1 Molecular Dynamics in the Canonical Ensemble: Equations of Motion

Deriving the equations of motion to sample the canonical distribution (reproduction of the canonical partition function as equation (2.31) shows) is the main task to develop the MD technique. Nose [42] proposed the extended phase space method to modify the Hamiltonian by the addition of the artificial variable s , playing the role as a time-scaling parameter, which yields

$$\begin{aligned} d\tilde{t} &= s dt \\ \Rightarrow \dot{\mathbf{r}}^\alpha &= s \dot{\mathbf{r}}^\alpha, \ddot{\mathbf{r}}^\alpha = \frac{ds \dot{\mathbf{r}}^\alpha}{dt} = \frac{ds \dot{\mathbf{r}}^\alpha}{d\tilde{t}} \frac{d\tilde{t}}{dt} = s \ddot{\mathbf{r}}^\alpha + s^2 \ddot{\mathbf{r}}^\alpha \end{aligned} \quad (2.39)$$

The kinetic energy becomes

$$\begin{aligned} K &= \frac{1}{2} \sum_{\alpha} m (\dot{\mathbf{r}}^\alpha)^2 = \frac{1}{2} \sum_{\alpha} m s^2 (\dot{\mathbf{r}}^\alpha)^2 \\ \Rightarrow \tilde{\mathbf{p}}^\alpha &= \frac{\partial K}{\partial \dot{\mathbf{r}}^\alpha} = m s^2 \dot{\mathbf{r}}^\alpha, K = \sum_{\alpha} \frac{(\tilde{\mathbf{p}}^\alpha)^2}{2m s^2} \end{aligned} \quad (2.40)$$

the kinetic and potential energy corresponding to s are chosen to be

$$K_s = \frac{1}{2} Q \dot{s}^2 \Rightarrow \tilde{p}_s = \frac{\partial K_s}{\partial \dot{s}} = Q \dot{s}, K_s = \frac{\tilde{p}_s^2}{2Q} \quad (2.41)$$

$$U_s = g k_b T_o \ln s$$

where T_o is the prescribed temperature and Q is the associated “mass” (with actual unit as energy $\times$ time²), which controls the strength of coupling between the heat reservoir (the lower Q means the system temperature can be adjusted more easily but with larger fluctuation and vice versa, similar to the relation between the mass and force). The Hamiltonian $\mathcal{H}_N$ is defined as

$$\mathcal{H}_N = \sum_{\alpha} \frac{(\tilde{\mathbf{p}}^\alpha)^2}{2m s^2} + U + \frac{\tilde{p}_s^2}{2Q} + g k_b T_o \ln s \quad (2.42)$$

Substitute equation (2.42) into the microcanonical partition function without the prefactor since the extended phase space is treated as an isolated system

$$\Omega = \int d^N \mathbf{r} d^N \tilde{\mathbf{p}} ds d\tilde{p}_s^2 \delta \left(\sum_{\alpha} \frac{(\tilde{\mathbf{p}}^{\alpha})^2}{2m s^2} + U + \frac{\tilde{p}_s^2}{2Q} + g k_b T_o \ln s - E \right) \quad (2.43)$$

Based on

$$\tilde{\mathbf{p}}^{\alpha} = m s^2 \dot{\mathbf{r}}^{\alpha} = m s \dot{\mathbf{r}}^{\alpha} = s \mathbf{p}^{\alpha} \quad (2.44)$$

we can get

$$\begin{aligned} \Omega &= \int d^N \mathbf{r} d^N \mathbf{p} ds d\tilde{p}_s s^{3N} \delta \left(\sum_{\alpha} \frac{(\mathbf{p}^{\alpha})^2}{2m} + U + \frac{\tilde{p}_s^2}{2Q} + g k_b T_o \ln s - E \right) \\ &= \int d^N \mathbf{r} d^N \mathbf{p} ds d\tilde{p}_s s^{3N} \delta \left(\mathcal{H}(\mathbf{r}, \mathbf{p}) + \frac{\tilde{p}_s^2}{2Q} + g k_b T_o \ln s - E \right) \\ &= \frac{1}{g k_b T_o} \int d^N \mathbf{r} d^N \mathbf{p} d\tilde{p}_s e^{(3N+1)(E - \mathcal{H}(\mathbf{r}, \mathbf{p}) - \tilde{p}_s^2/2Q)/g k_b T_o} \\ &= \frac{e^{E/KT} \sqrt{2\pi Q k_b T_o}}{(3N+1)k_b T_o} \int d^N \mathbf{r} d^N \mathbf{p} e^{-\mathcal{H}(\mathbf{r}, \mathbf{p})/k_b T_o} \quad \text{for } g = 3N + 1 \end{aligned} \quad (2.45)$$

with the use of the relations

$$\delta(f(s)) = \frac{\delta(s - s_o)}{f'(s_o)}, \quad \int_{-\infty}^{\infty} e^{-\tilde{p}_s^2/2Q k_b T_o} d\tilde{p}_s = \sqrt{2\pi Q k_b T_o} \quad (2.46)$$

where

$$\begin{aligned} f(s) &= \mathcal{H}(\mathbf{r}, \mathbf{p}) + \frac{\tilde{p}_s^2}{2Q} + g k_b T_o \ln s - E \\ \Rightarrow s_o &= e^{(E - \mathcal{H}(\mathbf{r}, \mathbf{p}) - \tilde{p}_s^2/2Q)/g k_b T_o} \end{aligned} \quad (2.47)$$

$$\frac{1}{f'(s_o)} = \frac{1}{g k_b T_o} e^{(E - \mathcal{H}(\mathbf{r}, \mathbf{p}) - \tilde{p}_s^2/2Q)/g k_b T_o}$$

It is noteworthy that equation (2.45) yields the canonical partition function (having the same function form as the canonical partition function as equation (2.31) shows). Thus, we confirm that the equations of motion derived from the Hamiltonian in equation (2.42) generate the canonical distribution if the ergodic hypothesis is concerned (see Section 2.2.1). Substituting equations (2.40) and (2.41) into the Lagrangian equation of motion

$$\begin{aligned}\ddot{\mathbf{r}}^\alpha &= \frac{\mathbf{F}^\alpha}{ms^2} - \frac{2\dot{s}\dot{\mathbf{r}}^\alpha}{s} \\ \ddot{s} &= \frac{1}{Qs} \sum_\alpha ms^2(\dot{\mathbf{r}}^\alpha)^2 - gk_bT_o\end{aligned}\tag{2.48}$$

and then transforming these equations back to the original time scale by equation (2.39)

$$\ddot{s} = s^2\ddot{\tilde{s}} + s(\dot{\tilde{s}})^2, \quad g = 3N + 1 \approx 3N, \quad \eta_T = \frac{\dot{s}}{s}\tag{2.49}$$

we obtain

$$\begin{aligned}\ddot{\mathbf{r}}^\alpha &= \frac{\mathbf{F}^\alpha}{m} - \eta_T \dot{\mathbf{r}}^\alpha \\ \dot{\eta}_T &= \frac{1}{Q} \sum_\alpha m(\dot{\mathbf{r}}^\alpha)^2 - 3Nk_bT_o = \frac{3Nk_bT_o}{Q} \left(\frac{\sum_\alpha m(\dot{\mathbf{r}}^\alpha)^2}{3Nk_bT_o} - 1 \right) \\ &= \frac{1}{\tau_T^2} \left(\frac{T}{T_o} - 1 \right)\end{aligned}\tag{2.50}$$

through the relations between the kinetic energy and temperature in equation (2.38)

$$\langle K \rangle = \sum_\alpha \frac{1}{2} m(\dot{\mathbf{r}}^\alpha)^2 = \frac{3Nk_bT}{2}\tag{2.51}$$

and

$$Q = 3Nk_bT_o\tau_T^2\tag{2.52}$$

Note that τ_t is in the unit of time whose value is suggested around 100 timesteps in LAMMPS [43].

Figure 2.3 A system with a variable volume touching with the heat reservoir.

2.4 Isobaric Ensemble

In some circumstances, e.g., piston in the combustion chamber, controlling the pressure P instead of the volume V is a more suitable way to model a system. As Figure 2.3 shows, the system connected with an infinite heat reservoir and simultaneously allowed to change its volume by moving a piston is described by the isothermal-isobaric ensemble. The whole system including the total Hamiltonian $\mathcal{H}_1 + \mathcal{H}_2$ and external work PV can be treated as an isolated system whose partition function is defined as

$$\Omega_{\text{NPT}} = \frac{1}{N!h^{3N}V_o} \int_0^\infty dV \int d^{N_1}\mathbf{r}_1 d^{N_1}\mathbf{p}_1 d^{N_2}\mathbf{r}_2 d^{N_2}\mathbf{p}_2 \delta(\mathcal{H}_1(\mathbf{r}_1, \mathbf{p}_1) + \mathcal{H}_2(\mathbf{r}_2, \mathbf{p}_2) + PV - H) \quad (2.53)$$

where H is enthalpy ($H = E + PV$ for energy conservation) and V_o is a reference volume to make equation (2.53) dimensionless. Following the same procedures in the canonical ensemble from equations (2.27) to (2.31) gives us a partition function only composed of the microstates of the target system (the subscript “1” is removed)

$$\Omega_{\text{NPT}} = \frac{1}{N!h^{3N}V_o} \int_0^\infty dV \int d^N \mathbf{r} d^N \mathbf{p} e^{-\frac{\mathcal{H}+PV}{k_b T}} \quad (2.54)$$

2.4.1 Molecular Dynamics in the Isobaric Ensemble: Equations of Motion

To develop the MD technique with the capability of controlling pressure, the extended phase space method proposed by Anderson [44] includes the volume as the additional variable in Hamiltonian to reproduce the isobaric-isenthalpic ensemble (without the thermal bath). Parrinello and Rahman [45] extended Anderson's method to allow the anisotropic size change corresponding to six stress components. In Anderson's method, a new variable $\mathbf{s}^\alpha$ is introduced by rescaling the position of each atom $\mathbf{r}^\alpha$ with the cubic root of volume V

$$\begin{aligned} \mathbf{s}^\alpha &= V^{-1/3} \mathbf{r}^\alpha \\ \Rightarrow \dot{\mathbf{r}}^\alpha &= V^{1/3} \dot{\mathbf{s}}^\alpha + \frac{1}{3} V^{-2/3} \dot{V} \mathbf{s}^\alpha \end{aligned} \quad (2.55)$$

The kinetic and potential energy become

$$\begin{aligned} K &= \frac{1}{2} \sum_\alpha m (V^{1/3} \dot{\mathbf{s}}^\alpha)^2 \Rightarrow \mathbf{p}_s^\alpha = \frac{\partial K}{\partial \dot{\mathbf{s}}^\alpha} = m V^{2/3} \dot{\mathbf{s}}^\alpha, K = \sum_\alpha \frac{(\mathbf{p}_s^\alpha)^2}{2m V^{2/3}} \\ U(\mathbf{r}^1, \mathbf{r}^2, \dots, \mathbf{r}^N) &= U(V^{1/3} \mathbf{s}^1, V^{1/3} \mathbf{s}^2, \dots, V^{1/3} \mathbf{s}^N) \end{aligned} \quad (2.56)$$

It is noted that for simplicity, the kinetic energy in the Anderson's original paper does not follow the real kinetic energy with consideration of the velocity in equation (2.55). The kinetic and potential energy corresponding to V are chosen to be

$$\begin{aligned} K_V &= \frac{1}{2} W \dot{V}^2 \Rightarrow p_V = \frac{\partial K_V}{\partial \dot{V}^\alpha} = W \dot{V}^\alpha, K_V = \frac{p_V^2}{2W} \\ U_V &= P_o V \end{aligned} \quad (2.57)$$

where P_o is the prescribed pressure and W is the associated “mass”. The Hamiltonian $\mathcal{H}_A$ is defined as

$$\mathcal{H}_A = \sum_{\alpha} \frac{(\mathbf{p}_s^{\alpha})^2}{2mV^{2/3}} + U(V^{1/3}\mathbf{s}^1, V^{1/3}\mathbf{s}^2, \dots, V^{1/3}\mathbf{s}^N) + \frac{p_V^2}{2W} + P_o V \quad (2.58)$$

It can be shown that this Hamiltonian produce the isobaric-isenthalpic partition function approximately [39]. Substituting equations (2.56) and (2.57) into the Lagrangian equation of motion and transforming back to the real coordinates by equation (2.55), we obtain

$$\begin{aligned} \ddot{\mathbf{r}}^{\alpha} &= \frac{\mathbf{F}^{\alpha}}{m} - \frac{1}{3} \frac{\dot{V}}{V} \dot{\mathbf{r}}^{\alpha} \\ \ddot{V} &= \frac{1}{W} \left[\frac{1}{3V} \sum_{\alpha} m(\dot{\mathbf{r}}^{\alpha})^2 + \mathbf{F}^{\alpha} \mathbf{r}^{\alpha} \right] - P_o \\ &= \frac{1}{3Nk_bT_o\tau_P^2} (P - P_o) \end{aligned} \quad (2.59)$$

where W has the same form of Q in the Nose-Hoover thermostats (see equation (2.51))

$$W = 3Nk_bT_o\tau_P^2 \quad (2.60)$$

(The value of τ_P is suggested as 1000 timesteps in LAMMPS [43]) and the pressure P inside the system is

$$P = \frac{1}{3V} \sum_{\alpha} m(\dot{\mathbf{r}}^{\alpha})^2 + \mathbf{F}^{\alpha} \mathbf{r}^{\alpha} \quad (2.61)$$

following the virial stress definition in the next chapter.

Due to the difficulty of fully satisfying the isothermal-isobaric partition function, different versions of Hamiltonians with the extended phase space (or equations of motion) have been proposed to approximately approach the partition function in equation (2.54), based on the fundamental work of equation (2.59) under the isobaric-isenthalpic

ensemble. Here shows the result as the combination of equations (2.50) and (2.59).

Redefine the variable η_P as

$$\eta_P = \frac{1}{3} \frac{\dot{V}}{V} \quad (2.62)$$

the equations of motion under the isothermal-isobaric ensemble are given below [46]

$$\begin{aligned} \ddot{\mathbf{r}}^\alpha &= \frac{\mathbf{F}^\alpha}{m} - (\eta_P + \eta_T) \dot{\mathbf{r}}^\alpha \\ \dot{\eta}_T &= \frac{3Nk_b}{Q}(T - T_o) + \frac{1}{Q}(W\eta_P^2 - k_b T_o) \\ \dot{\eta}_P &= \frac{3V}{W}(P - P_o) - \eta_T \eta_P \end{aligned} \quad (2.63)$$

Compared with the equations only composed of Nose-Hoover thermostat or Anderson barostat, two extra terms appear to describe the coupling effect between temperature and pressure.

2.5 Initial Positions and Velocities

Dependent on the type of crystal structures and related lattice constant, the initial configuration of crystalline nanostructures can be built by repeating the periodic unit cell along the x , y and z direction. For three types of cubic symmetry, i.e., simple cubic (SC), body-centered cubic (BCC) and face-centered cubic (FCC), the smallest repeat vectors are

$$\text{SC : } \mathbf{R} = n_x \mathbf{e}_1 + n_y \mathbf{e}_2 + n_z \mathbf{e}_3 \quad (2.64)$$

$$\text{BCC : } \begin{cases} \mathbf{R} = n_x \mathbf{e}_1 + n_y \mathbf{e}_2 + n_z \mathbf{e}_3 \\ \mathbf{R} = (n_x + \frac{1}{2}) \mathbf{e}_1 + (n_y + \frac{1}{2}) \mathbf{e}_2 + (n_z + \frac{1}{2}) \mathbf{e}_3 \end{cases} \quad (2.65)$$

$$\text{FCC : } \begin{cases} \mathbf{R} = n_x \mathbf{e}_1 + n_y \mathbf{e}_2 + n_z \mathbf{e}_3 \\ \mathbf{R} = (n_x + \frac{1}{2}) \mathbf{e}_1 + (n_y + \frac{1}{2}) \mathbf{e}_2 + n_z \mathbf{e}_3 \\ \mathbf{R} = (n_x + \frac{1}{2}) \mathbf{e}_1 + n_y \mathbf{e}_2 + (n_z + \frac{1}{2}) \mathbf{e}_3 \\ \mathbf{R} = n_x \mathbf{e}_1 + (n_y + \frac{1}{2}) \mathbf{e}_2 + (n_z + \frac{1}{2}) \mathbf{e}_3 \end{cases} \quad (2.66)$$

where $\mathbf{e}_1$, $\mathbf{e}_2$ and $\mathbf{e}_3$ are the lattice constant times the unit vectors along the x , y and z direction, n_x , n_y and n_z are the integers dependent on the specimen size.

After setting up the initial atomistic positions, the initial velocities are directly related with the prescribed temperature T_o according to the canonical ensemble in equation (2.31). Thus, the velocity distribution is expressed as

$$f(\mathbf{v}^\alpha) = \frac{e^{-\frac{m(\mathbf{v}^\alpha)^2}{2k_b T_o}}}{\int_{-\infty}^{\infty} d^N \mathbf{v} e^{-\frac{m(\mathbf{v}^\alpha)^2}{2k_b T_o}}} = \sqrt{\frac{m}{2\pi k_b T_o}} e^{-\frac{m(\mathbf{v}^\alpha)^2}{2k_b T_o}} \quad (2.67)$$

With consideration of random numbers, the velocity of each atom is assigned to satisfy the distribution of equation (2.67) [39, 41]. Once the initial conditions are specified, the algorithm such as velocity Verlet in equation (2.10) is ready to perform MD simulations by integrating the equations of motion corresponding to different ensembles.

2.6 Interatomic Potentials

In the previous sections, we keep seeing the potential energy U involving into the Hamiltonian but never discuss its exact form. In solids, the interatomic potential is directly related with the material constants since it describes how strain energy stored in the crystal structures. Besides, the rupture of interatomic bonds is usually considered as the initiation point of material failure. From the viewpoint of quantum mechanics, the

interatomic interaction should be a solution of Schrodinger's equation for interacting electrons, which corresponds to the first principles or ab initio theory. However, the numerical calculations based on quantum mechanics are computationally expensive and thus only cover hundreds of atoms. In the context of discussing the applicability of continuum mechanics in atomistic systems, such small specimens increase the uncertainty in that we need a more extensive crystal structure as a reference to study the size effect. The alternative way is to employ the interatomic potentials described in a relatively simple functional form. The related parameters are usually fitted by experimental or ab initio simulation data.

Corresponding to the types of bonds, i.e., covalent, ionic or metallic, numerous interatomic potentials have been proposed for various kinds of materials. In this study, the interactions in the ionic crystal are described by the Buckingham potential [47] with an electrostatic contribution

$$U^\alpha = \frac{1}{2} \sum_{\alpha \neq \beta} \left[4k_e \frac{q_1 q_2}{r^{\alpha\beta}} + B \exp \left(-\frac{r^{\alpha\beta}}{\rho_o} \right) - \frac{D}{(r^{\alpha\beta})^6} \right] \quad (2.68)$$

Table 2.1 Potential parameters for NaCl.

Interactions	B (eV)	ρ_o (Å)	D (eV Å ⁶)
Na ⁺ – Na ⁺	7895.4	0.1709	29.06
Na ⁺ – Cl ⁻	2314.7	0.2903	0.00
Cl ⁻ – Cl ⁻	1227.2	0.3214	29.06

$$q_{\text{Na}^+} = +0.988; q_{\text{Cl}^-} = -0.988$$

where $r^{\alpha\beta}$ is the interatomic distance, k_e is the Coulomb constant, q_1 and q_2 are the ionic charges, B , ρ_o , and D are potential parameters. The involvement of the electrostatic

force means the long-range solver, either the Ewald summation [48] or Particle-Particle-Particle-Mesh (PPPM) [49], is necessary. For sodium Chloride (NaCl), the relevant values are listed in Table 2.1 [50]. It is noted that there is no force equilibrium point (the minimum in the potential energy) for the pairs of $\text{Na}^+ - \text{Na}^+$ and $\text{Cl}^- - \text{Cl}^-$.

The concept of total potential energy as the sum of each pair interaction brings us great convenience but also leads to great challenge especially for metal. One of well-known evidences is that producing the equal value for the elastic constants $C_{12} = C_{44}$ is inevitable for the pair potential. By contrast, the ratio of C_{12} and C_{44} is close to 2 in the FCC metal. The main reason comes from the lack of capability for the pair potential to reflect the local environment around an atom, i.e., bulk or surface. Thus, the embedded atom method (EAM) is introduced by Daw and Baskes [51, 52] with an extra term to describe how much energy is needed to embed an atom into the electronic cloud

$$U^\alpha = F^\alpha \left(\sum_{\alpha \neq \beta} \rho_e(r^{\alpha\beta}) \right) + \frac{1}{2} \sum_{\alpha \neq \beta} \Phi^\alpha(r^{\alpha\beta}) \quad (2.69)$$

where Φ is the pair interaction and ρ_e is the electron density, depending on the local environment around atom α . As a result, EAM potential is capable of reproducing a more realistic isotropic elastic behavior of metal ($C_{12} \neq C_{44}$) than the simple pair potentials.

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3. CALCULATION OF LOCAL STRESS IN MOLECULAR MODELS

The continuum theory has demonstrated its value in modeling the mechanics properties of solids and structures. However, as the dimension is downsized to the atomistic scale, continuum stress and atomistic stress may not match each other due to the discrete nature of the atomistic structure. It brings up a question about how we can interpret results from molecular simulations in terms of continuum mechanics. One possible solution to this problem is homogenizing a group of atoms as a material point, similar to the micromechanics in composites materials [53]. Since this method has not been standardized, the stress value may depend on the choice of homogenization technique used. This issue becomes even more pronounced when the size of geometric discontinuity is also reduced to the nanometer range. In order to connect a phenomenon at nanoscale to the macroscopic continuum variable, there is a need to develop a physically reasonable homogenization technique for obtaining the local stress information in atomistic systems.

In addition, the local atomistic stress definition is emphasized due to the emergence of multiscale modeling. Several different methods (quasicontinuum [54], bridging scale method [55], bridging domain [56], etc.) have been proposed to extend the length and time scale of molecular simulations. A comprehensive review about multiscale modeling techniques can be found in the work of Miller and Tadmor [57]. Since these multiscale

modeling methods involve two or more levels of simulation techniques such as molecular dynamics (MD) and continuum finite element method (FEM), it is of practical interest to understand how to define the concept of stress in atomistic systems and ensure a smooth communication between two different scale domains.

The development of stress definitions can be traced back to the 19th century. Clausius [58] and Maxwell [59] developed the virial theorem to measure the internal stress of a fixed volume containing the interacted atoms at high temperature ($T > 0\text{K}$). Cheung and Yip [60] revised the virial theorem to calculate the momentum flux and force across an area and claimed their definition can present the correct stress distribution near the free surface. Zhou [61] pointed out the virial stress including the kinetic contribution is not equivalent to Cauchy stress in continuum. However, Subramaniyan and Sun [62] performed the thermal stress analysis to demonstrate that both kinetic and potential parts in the virial theorem are essential to interpret the virial stress as Cauchy stress in MD simulations.

Irving and Kirkwood [63] considered mass, momentum and energy conservations in terms of the statistical ensemble to derive alternative stress formalism. To simplify a series expansion of Dirac delta functions in Irving and Kirkwood's work, Hardy [64] and Murdoch [65] proposed the localization function to represent the probability density distribution. As a result, the discrete variables such as the atomistic mass, velocity, and total energy per atom, can be mapped into the continuous fields as density, momentum and energy density, respectively. The other related works can be referred to Lutsko [66] and Cormier et al. [67]. Drawing on the concept of localization function, Ulz and Moran

[68] utilized the Gaussian mixture modeling to measure the similarity of atoms and decide if atoms belong to the same space-averaging volume.

Recently, with the focus on perfect crystals under uniform loading, Zimmerman et al. [69], Branicio and Srolovitz [70], and Admal and Tadmor [71] studied the size of a sphere that is necessary for the local virial or Hardy stress to converge to the continuum stress. If the single-atom crystal is considered, the convergent radii of the virial and Hardy stresses cross 4 and 2 times the size of lattice constant, respectively [69, 71]. As for the multi-atom crystal, the advantage of the Hardy's definition diminishes and both stress definitions require a radius of 5 times the size of lattice constant to achieve convergence [70]. The main purpose of this chapter is to demonstrate if the spatial averaging volume is periodic, the convergence of the virial and Hardy stress can be accomplished within one single lattice distance. To demonstrate the superiority of the periodic averaging volume, we consider a central crack embedded in sodium chloride crystal. With comparison to continuum finite element solutions, the crack opening stress from a series of periodic lattices captures more detailed stress concentration than what is presented by other non-periodic averaging volumes.

3.1 Definition of Stresses in Atomistic Systems

3.1.1 Virial Stress

For a fixed volume V containing N interacting atoms, the equation of motion of each atom inside is given by

$$\sum_{\alpha \neq \beta} F_i^{\alpha\beta} + b_i^\alpha = m^\alpha \ddot{v}_i^\alpha \quad (3.1)$$

where $i, j = 1, 2, 3$ indicate the x, y or z direction, $\mathbf{F}^{\alpha\beta}$ is the interaction of atom α due to atom β , $\mathbf{b}^\alpha$ is the external force outside the volume, m^α and $\mathbf{v}^\alpha$ are the mass and the velocity of atom α , respectively. The summation of the tensor product between equation (3.1) and $(\mathbf{x}^\alpha - \mathbf{x}^o)$, where $\mathbf{x}^\alpha$ is the atomistic position and $\mathbf{x}^o$ is an arbitrary fixed point in space, can be expressed as

$$\sum_{\alpha} \sum_{\alpha \neq \beta} (x_j^\alpha - x_j^o) F_i^{\alpha\beta} + \sum_{\alpha} (x_j^\alpha - x_j^o) b_i^\alpha = \sum_{\alpha} (x_j^\alpha - x_j^o) m^\alpha \dot{v}_i^\alpha \quad (3.2)$$

Through the Newton's third law

$$F_i^{\alpha\beta} = -F_i^{\beta\alpha} \quad (3.3)$$

and the integration by parts

$$\sum_{\alpha} (x_j^\alpha - x_j^o) m^\alpha \dot{v}_i^\alpha = \frac{d}{dt} \sum_{\alpha} (x_j^\alpha - x_j^o) m^\alpha v_i^\alpha - \sum_{\alpha} m^\alpha v_i^\alpha v_j^\alpha \quad (3.4)$$

Equation (3.2) can be rearranged as

$$\begin{aligned} \sum_{\alpha} (x_j^\alpha - x_j^o) b_i^\alpha &= -\frac{1}{2} \sum_{\alpha} \sum_{\alpha \neq \beta} (x_j^\alpha - x_j^\beta) F_i^{\alpha\beta} - \sum_{\alpha} m^\alpha v_i^\alpha v_j^\alpha \\ &\quad + \frac{d}{dt} \sum_{\alpha} (x_j^\alpha - x_j^o) m^\alpha v_i^\alpha \end{aligned} \quad (3.5)$$

The time average is necessary to make equation (3.5) be observed macroscopically (see the ergodic hypothesis in Section 2.2.1). Hence, the last term in equation (3.5) can be eliminated if the duration of time average is taken sufficiently long [72].

Meanwhile, in the continuum viewpoint, the moment produced by the traction $\mathbf{t}$ with respect to the distance between a fixed point $\mathbf{x}^o$ and a material position $\mathbf{x}$ is

$$\int (x_j - x_j^o) t_i ds = \int (x_j - x_j^o) \sigma_{ik} n_k ds \quad (3.6)$$

Through the divergence theorem,

$$\int (x_j - x_j^o) \sigma_{ik} n_k ds = \int \frac{\partial}{\partial x_k} (x_j - x_j^o) \sigma_{ik} dV = \int \sigma_{ij} + x_j \frac{\partial \sigma_{ik}}{\partial x_k} dV \quad (3.7)$$

The last term is cancelled out because of the equilibrium condition. Equation (3.7) is rewritten as

$$\int (x_j - x_j^o) \sigma_{ik} n_k ds = \sigma_{ij} V \quad (3.8)$$

Assuming the external force terms in the discrete and continuum viewpoints, i.e., equation (3.5) and (3.8), are equivalent, we can define the virial stress

$$\sigma_{ij} = -\frac{1}{V} \sum_{\alpha} \left(m^{\alpha} v_i^{\alpha} v_j^{\alpha} + \frac{1}{2} \sum_{\alpha \neq \beta} (x_j^{\alpha} - x_j^{\beta}) F_i^{\alpha\beta} \right) \quad (3.9)$$

As equation (3.9) indicates, the information of calculating the virial stress, e.g., the atomistic velocity and the interaction force between pairs of atoms, is already known through the numerical integration in MD simulations (see the velocity Verlet integration algorithm in Section 2.1.1). This straightforward implementation makes the virial theorem the most widely used atomistic stress definition. It is noted that equation (3.9) is derived with V as the total volume of a simulation box. In order to deal with the stress concentration resulting from the crystal imperfection, the local virial stress is calculated based on the average over a small group of atoms inside the box.

3.1.2 Hardy Stress

Introducing a localization function ψ , Hardy [64] transformed the discrete atomistic mass m^{α} , atomistic velocity $\mathbf{v}^{\alpha}$ and total energy of an atom (potential energy U^{α} + kinetic energy K^{α}) into the continuous density ρ , momentum $\mathbf{p}$ and energy density E fields at a material point $\mathbf{x}$

$$\rho(\mathbf{x}, t) = \sum_{\alpha} m^{\alpha} \psi(r^{\alpha}) \quad (3.10)$$

$$p_i(\mathbf{x}, t) = \sum_{\alpha} m^{\alpha} v_i^{\alpha} \psi(r^{\alpha}) \quad (3.11)$$

$$E(\mathbf{x}, t) = \sum_{\alpha} \left[\frac{1}{2} M^{\alpha} (v_i^{\alpha} v_i^{\alpha})^2 + U^{\alpha} \right] \psi(r^{\alpha}) \quad (3.12)$$

where $r^{\alpha} = |\mathbf{x}^{\alpha} - \mathbf{x}|$ is the distance between atom position $\mathbf{x}^{\alpha}$ and material point $\mathbf{x}$. The localization function has the following properties:

1. ψ has the unit of inverse volume as equation (3.10) implies.
2. ψ is a normalized function, such that $\int \psi dV = 1$.
3. ψ is peaked at the material point $\mathbf{x}$ and decays smoothly to zero along the boundary of localization volume R .

Figure 3.1 shows the two kinds of localization functions considered in this chapter (material point $\mathbf{x}$ is located at origin). One is step function remaining constant within the localization volume. Another is the 3rd order polynomial

$$\frac{\psi(r^{\alpha})}{\psi|_{r^{\alpha}=0}} = 1 - 3\left(\frac{r^{\alpha}}{R}\right)^2 + 2\left(\frac{r^{\alpha}}{R}\right)^3 \quad (3.13)$$

It is noted that equation of (3.13) and its first derivatives are equal to zero along $r_{\alpha} = R$.

On the basis of equation (3.10) and (3.11), the material velocity is defined as

$$v_i(\mathbf{x}, t) = \frac{\sum_{\alpha} m^{\alpha} v_i^{\alpha} \psi(r^{\alpha})}{\sum_{\alpha} m^{\alpha} \psi(r^{\alpha})} \quad (3.14)$$

Substituting equations (3.10-12) and (3.14) into the relations of mass, momentum and energy conservation

Figure 3.1 Localization function ψ .

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial x_j}(\rho v_j) \quad (3.15)$$

$$\frac{\partial \sigma_{ij}}{\partial x_j} = \frac{\partial p_i}{\partial t} + \frac{\partial}{\partial x_j}(\rho v_i v_j) \quad (3.16)$$

$$\frac{\partial}{\partial x_j}(\sigma_{ij} v_i) = \frac{\partial E}{\partial t} + \frac{\partial}{\partial x_j}(E v_j) + \frac{\partial q_j}{\partial x_j} \quad (3.17)$$

where q_j is the heat flux, the Hardy stress at a material point $\mathbf{x}$ is expressed as

$$\sigma_{ij} = - \sum_{\alpha} \left(m^{\alpha} (v_i^{\alpha} - v_i)(v_j^{\alpha} - v_j) \psi + \frac{1}{2} \sum_{\alpha \neq \beta} (x_j^{\alpha} - x_j^{\beta}) F_i^{\alpha\beta} B^{\alpha\beta} \right) \quad (3.18)$$

Equation (3.18) has been shown to be valid for the multi-body potentials [73]. The relative velocity between the atomistic velocity $\mathbf{v}^{\alpha}$ and material velocity $\mathbf{v}$ is considered in the kinetic term and $B^{\alpha\beta}$ represents the weight of the bond length between atom α and atom β as

$$B^{\alpha\beta} = \int_0^1 \psi [\lambda(\mathbf{x}^{\alpha} - \mathbf{x}^{\beta}) + \mathbf{x}^{\beta} - \mathbf{x}] d\lambda \quad (3.19)$$

where $r^{\alpha\beta}$ is the interatomic distance and r^β represents the distance between atom β and material point. Hardy [64] also provided the expression for the heat flux $\mathbf{q}$.

3.2 Molecular Models

In the present study, we consider two crystals: sodium chloride (NaCl) and Nickel (Ni) described by the pair potential in equation (2.68) [50] and EAM potential in equation (2.69) [52], respectively. Both NaCl and Ni crystals are arranged in the cubic orientations with $x = [100]$, $y = [010]$ and $z = [001]$. The MD simulations are performed using the package LAMMPS [74] with a time step of 1 fs. Under the periodic boundary condition applied in both x and z directions, the MD model is initially equilibrated for 20 ps under isobaric-isothermal (NPT) ensemble followed by canonical (NVT) ensemble for 20 ps. Subsequently, the two outmost layers along the y direction are shifted oppositely to produce pure tensile loading under canonical (NVT) ensemble. After each displacement increment, the whole system is equilibrated by fixing the positions of the outmost layers for 20 ps, followed by data averaging for another 20 ps.

3.3 Local Stress Calculation in Perfect Crystals

For a perfect crystal subjected to uniform loadings, three kinds of stress definitions including local atomistic stress (either in virial or Hardy's theorem), global stress (the whole volume-averaged virial stress) and continuum stress, are supposed to be identical. Therefore, this homogeneous case provides a reference point for determining the size of the averaging volume necessary for the local atomistic stress to match the continuum stress. Here, we compare the results of spherical and cubic volumes to realize how the

different shaped volumes influence the convergence of the virial and Hardy stresses.

With consideration of the engineering strain defined as

$$\varepsilon_{yy} = \frac{u_y}{L_o} \quad (3.20)$$

where u_y is the applied displacement and L_o is the height after initial relaxation, we present the results under $\varepsilon_{yy} = 0.01$. Both NaCl and Ni crystal consist of 50 unit cells in the x , y and z direction. After initial relaxation, the lattice constants of NaCl and Ni at 1 Kelvin are determined as $a = 2.786 \text{ \AA}$ and $3.517 \text{ \AA}$, respectively.

3.3.1 Sodium Chloride

Focusing on the spherical volume of radius R , i.e., $V = \frac{4}{3}\pi R^3$, Figure 3.2 shows with the increasing radius R (normalized by the lattice constant of NaCl), the local stress σ_{yy} calculated either by the virial or Hardy's theorem initially oscillates drastically and then approaches the continuum (global) stress. The local virial stress needs to have a volume of radius at least larger than 5 times the size of lattice constant to reach the converged value. On the other hand, the Hardy stress shows the dependence on the choice of localization functions due to the different results from two types of localization functions. The convergence of the step function is very slow and the fluctuation is still noticeable at $R = 10a$. Meanwhile, the 3rd order polynomial enables the Hardy stress to converge once $R > 3a$. This verifies the statement in the previous studies [69, 71] that the Hardy stress with the high order localization functions performs a quicker convergence than the local virial stress.

Figure 3.2 Local stress averaged within the spherical volume of increasing radius R in NaCl subjected to $\varepsilon_{yy} = 0.01$.

Figure 3.3 Local stress averaged within the cylindrical volume of increasing radius R in NaCl subjected to $\varepsilon_{yy} = 0.01$.

In addition to the spherical volume, the results based on the cylindrical volume with $V = \pi R^2 \times (\text{specimen size in the } z\text{-direction})$ are shown in Figure 3.3. Following the conclusion made for the spherical volumes, the convergent radius of the Hardy stress with the 3rd order polynomial ($R > 3a$) is less than what is required by the local virial stress ($R > 5a$). Through the comparison between Figure 3.2 and Figure 3.3, even though the cylindrical volume contains more atoms than the sphere volume under the same radius, the cylindrical volume doesn't have an obvious advantage in convergence process for both virial and Hardy stress.

Theoretically, the smaller averaging volume where a local stress can converge, the closer this atomistic stress definition can approach the ideal setting of the macroscopic stress. As a result, the more accurate stress concentration can be estimated for the inhomogeneous case. To deal with this demand, we start looking for the averaging volume other than sphere and cylinder. Regarding the crystal structure of NaCl, a simple symmetric cubic lattice where the sodium and chloride ions are arranged alternatively in three-dimensional space, we assert a cubic volume could be a more suitable candidate than a sphere. By varying the half-length R of a cube with volume $V = (2R)^3$, although the fluctuation of the local virial stress in Figure 3.4 is larger than that in Figure 3.2 or Figure 3.3, the local virial stress can get to exact value if the dimension of the cubic volume $R = 1a, 2a, 3a, \dots$ is selected. It is noted that all these cubic volumes that make the local virial stress converge are periodic in NaCl crystal. We also find the Hardy stress under the step function leads to the same phenomenon as the local virial stress at $R = 1a, 2a, 3a, \dots$. Thus, under the periodic averaging volume, both the local virial and Hardy

stress can achieve convergence within one lattice, which is much smaller than what is required by the spherical volume.

Figure 3.4 Local stress averaged within the cubic volume of increasing R in NaCl subjected to $\varepsilon_{yy} = 0.01$.

In an attempt to apply the periodic averaging volume on other kinds of crystals, the periodicity of lattices can be set up by dividing an atom depending on its position in a volume. If we take a cubic volume shown as red lines in Figure 3.5 ($R = 0.5a$), all the eight atoms in this volume are located at corners so each atom only occupies one-eighth portion in the viewpoint of periodicity. Once R is enlarged to $1.5a$ (blue square in Figure 3.5), the periodic volume consists of 8 atom inside the volume (entire portion), 24 atoms located on the surface (half portion), 24 atoms along the intersection between two planes (quarter portion) and 8 corner atoms (one-eighth portion). Thus, the virial stress definition of equation (3.9) can be rewritten as

$$\sigma_{ij} = -\frac{1}{V} \sum_{\alpha} w^{\alpha} \left(m^{\alpha} v_i^{\alpha} v_j^{\alpha} + \frac{1}{2} \sum_{\alpha \neq \beta} (x_j^{\alpha} - x_j^{\beta}) F_i^{\alpha\beta} \right) \quad (3.21)$$

where w^{α} representing the portion of an atom α occupying in the periodic volume with $V = (2R)^3$. In Figure 3.4, the consistence between the results of equation (3.21) and the continuum (global) stress verifies the convergence can be accomplished within the minimum periodic volume of $R = 0.5a$.

Figure 3.5 Periodic volume to calculate the local stress in NaCl crystals.

3.3.2 Nickel

Focusing on the Nickel atoms grouped together in FCC crystals, the comparisons between the local virial and Hardy stress over the spherical and cylindrical volumes are demonstrated in Figure 3.6 and Figure 3.7, respectively. The superiority of the Hardy stress in the single-atom system is even more prominent than in the multi-component atomistic system since the convergent radii (under sphere, $R = 2a$ for the 3rd order polynomial and $R = 4a$ for the step function; $R = 1a$ for the cylindrical volume with the

Figure 3.6 Local stress averaged within the spherical volume of increasing radius R in Nickel subjected to $\varepsilon_{yy} = 0.01$.

Figure 3.7 Local stress averaged within the cylindrical volume of increasing radius R in Nickel subjected to $\varepsilon_{yy} = 0.01$.

Figure 3.8 Local stress averaged within the cubic volume of increasing R in Nickel subjected to $\varepsilon_{yy} = 0.01$.

3rd order polynomial) are smaller than those of the corresponding localization functions in NaCl crystals (see Figure 3.2 and Figure 3.3).

Because a FCC crystal is not arranged in simple cubic lattices, Figure 3.8 shows the local virial stress and Hardy stress averaged with the cubic volume cannot get to exact value at $R = 1a, 2a, 3a, \dots$. Even though the normal stress varies regularly with the increase of the half-length R , a periodic volume in the FCC crystal is unlikely to be found by simply taking a cubic volume. Therefore, counting the portion of an atom provides an alternative way to define the periodic volume in FCC. As Figure 3.9 shows, the periodic volume of $R = 0.5a$ (red square) consists of six atoms on the surface (half portion) and the other eight atoms at corners (one-eighth portion). The next periodic volume is located at $R = 1a$, which consists of 14 whole atoms, 24 atoms in half and 24 atoms in quarter. Substituting those portions into equation (3.21), the corresponding local virial

stress with the increasing periodic volume is shown as the green dots in Figure 3.8, which verifies that the local virial stress can be convergent even when the minimum periodic volume is selected.

Figure 3.9 Periodic volume to calculate the local virial stress in Nickel crystals.

3.4 Local Stress Calculation in Cracked Crystals

One of purposes of developing the local atomistic stress is to study the stress concentration in atomistic systems. In this section, the non-uniform stress distribution is induced by embedding a crack in the NaCl crystal. As the 30p-type model in Chapter 4, a central crack along the xz plane is created by artificially cutting 30 interaction pairs. The specimen size is $417.9 \times 560.0 \times 27.9 \text{ \AA}^3$ containing 150, 200 and 10 lattices in the x , y and z directions, respectively. Following the procedure of applying displacement loading in the last section and defining the engineering strain by equation (3.20), the global stress versus engineering strain curves of a perfect crystal and a cracked specimen are

demonstrated in Figure 3.10. The global stress of the perfect crystal is equivalent to the uniform continuum stress and thus the theoretic strength of NaCl is determined as $\sigma_{th} = 3.43$ GPa. As for the cracked specimen, since the continuum stress is non-uniform, the global stress only provides the information of an entire cracked specimen, which indicates the failure condition is at $\varepsilon_{cr} = 0.020638$ corresponding to the maximum global stress.

Figure 3.10 Stress-strain curves of a perfect NaCl crystal and the cracked specimen.

To describe the crack opening stress by the local atomistic stress definitions, the blot dots in Figure 3.11(a) (the midpoints of each unit cell along the crack line) represent the centers of averaging volumes or the material points in the Hardy's definition. In addition, Figure 3.11(a) shows that the initial crack tip is assumed to be at the location of the first $\text{Na}^+ - \text{Cl}^-$ pair without removing the interaction (the detailed description can be found in

Section 4.2) and the unit cells are numbered according to their positions from the initial crack tip.

Figure 3.11 Crack tip position and atomistic snapshot at (a) the initial state, the numbered unit cells according to their position from the initial crack tip; (b) the failure condition of $\epsilon_{cr} = 0.020638$ where the second unit cell has the peak normal stress and crack tip position is moved forward a lattice constant.

Since Figure 3.4 illustrates keeping periodicity of averaging volume improves the convergence process of the local atomistic stress for both the virial and Handy definition, the crack opening stress around the crack tip is calculated by the square-shaped volume shown in Figure 3.12 with volume $V = 5.57 \times 5.57 \times 27.86 \text{ \AA}^3$ ($2a \times 2a \times 10a$).

Although this square-shaped volume spans over the entire thickness, it still maintains the periodicity in space. In contrast, the cylindrical volume of axis lying along the z direction is treated as the non-periodic volume. There are two radii considered in the cylindrical volume, $8.36 \text{ \AA}$ ($3a$) and $13.93 \text{ \AA}$ ($5a$) which correspond to the convergence radius of the Hardy and local virial stress in Figure 3.3, respectively.

Figure 3.12 Square-shaped volume for calculating crack opening stress.

While the global stress of the cracked specimen reaches the maximum (the failure condition $\varepsilon_{cr} = 0.020638$ in Figure 3.10), Figure 3.13(a) (with numbers to mark the positions of unit cells in Figure 3.11) shows the crack opening stress distributions based on the virial theorem. The result of the square-shaped volume shows the unit cell that gives rise to the maximum normal stress is the second unit cell ahead of the initial crack tip and this maximum value is close to the theoretic strength $\sigma_{th} = 3.43 \text{ GPa}$ of perfect NaCl crystals. This provides the evidence that the strength, which a unit cell can sustain, is equivalent to the theoretic strength of the perfect crystal. Since the unit cell with the

Figure 3.13 Crack opening stress calculated by the (a) virial theorem and (b) Hardy's definition; the numbers (1 to 6) used to mark the position of unit cells in Figure 3.11.

maximum normal stress, under the failure condition, has been moved from the first unit cell to the second one, the crack tip no longer stays at the initial position but moves forward a lattice constant as shown in Figure 3.11(b). Additionally, Figure 3.11(b) shows the distance from the present crack tip to the center of each unit cell along the crack line, which is employed as the horizontal axis in Figure 3.13.

Based on the secant moduli and the crack length = 91.94 Å (initial crack length plus two sizes of lattice constant), the FEM solution (the detailed procedure to build the equivalent FEM model is referred to Section 4.3) subjected to the critical strain $\varepsilon_{cr} = 0.020638$ is presented as the black line in Figure 3.13. The virial stress averaged over the square-shaped volume closely matches with the FEM solution except the unit cell closest to the crack tip (the second unit cell) where the stress approaches infinity according to the continuum fracture mechanics. As for the cylindrical volume with the radius 8.36 Å ($3a$) where the local virial stress doesn't converges (see Figure 3.3), the corresponding crack opening virial stress deviates significantly from other distributions. Once the radius of the cylinder is increased to 13.93 Å ($5a$), even though the performance of the virial stress is improved (the consistence with the FEM solution for the distance from the present crack tip larger than $16a$), the near-tip stress distribution doesn't match with the FEM solution or the local stress averaged over the square-shaped volume.

As for the Hardy's definition, the crack opening stress distributions calculated by either the combination of the square-shaped volume with step function or cylindrical volume with 3rd order polynomial are shown in Figure 3.13(b). With comparison to the continuum FEM solution, the Hardy stress with the square-shaped volume and step function demonstrates the same accuracy as the local virial stress averaged over the same

volume in Figure 3.13(a) except the lower peak stress. Such lower value of the maximum stress indicates when the extremely large stress gradient happens in a unit cell, the local virial stress leads to the more precise result than the Hardy stress based on the step function.

The result from the cylindrical volume with radius $8.36 \text{ \AA}$ ($3a$) in Figure 3.13(b) is better fitted into the FEM solution than the corresponding virial stress since the Hardy stress reaches the converged value for $R > 3a$. It is important to note that the Hardy stress, averaged over the cylindrical volume with radius $13.93 \text{ \AA}$ ($5a$) where both stress definitions converge (see Figure 3.3), still performs better than the virial stress due to the high order localization functions to decrease the contribution from the high stress level near the near-tip region.

In addition to the comparison between atomistic and continuum models, the value of the maximum stress is typically the most representative parameter used for failure prediction [75] and is directly related to the stress concentration factor. The decrease of stress concentration is characterized as the flaw-tolerance in nanostructure [76]. In Figure 3.13, the value of maximum local stress is dependent on the shape and size of averaging volumes. Since the size of the square-shaped volume is smaller than those of cylindrical volumes, both virial and Hardy stress with the periodic volumes demonstrate the higher degree of stress concentration than what is presented by non-periodic volumes. With the increase of the cylindrical volumes, the stress concentration decreases even further and the lattice with the maximum stress moves away from the crack tip. Considering the best agreement with the FEM solution and the highest stress concentration (the maximum stress close to the theoretical strength), the local virial stress based on the square-shaped

volume is the appropriate way to present the characteristic brittle fracture process in NaCl crystals.

3.5 Conclusions

Under the spherical or cylindrical (non-periodic) averaging volume, the Hardy's definition with the 3rd order localization function not only performs a quicker convergence and lower stress fluctuation with the increasing volume size but also provides a more accurate near-tip stress distribution than the corresponding virial theorem. However, the spherical or cylindrical radius with which the Hardy stress converges still spans the size of several lattice constants. In this paper, we demonstrate that, if both the local virial stress and Hardy stress are averaged over a periodic volume, the convergence can be accomplished within one single lattice. Furthermore, we employ a cracked NaCl crystal to demonstrate that the crack opening stress distributions, determined respectively by the virial and Hardy stress with periodic volumes, are consistent with the continuum FEM solution. Although the stress singularity doesn't exist in local atomistic stress, the corresponding virial near-tip stress shows that the maximum stress that a unit cell can sustain is nearly equal to the theoretic strength of perfect NaCl crystals. It is also noted that since the non-periodic volume needs a larger size to converge, it loses the resolution to reflect the actual degree of stress concentration at the crack tip.

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4. SIZE-DEPENDENT FRACTURE TOUGHNESS AND FLAW-TOLERANCE OF NANOSCALE STRUCTURES

Drawing on stress singularity at a crack tip, linear elastic fracture mechanics (LEFM) proposes fracture toughness, the critical stress intensity factor K_{Ic} or energy release rate G_{Ic} , to determine whether a brittle solid loses its load-carrying capability by crack propagation. If there is a central crack in an infinite plate subjected to remote uniform tension, the critical remote stress σ_{cr} as a function of crack length $2c$ can be estimated by

$$\sigma_{cr} = \frac{K_{Ic}}{\sqrt{\pi c}} \text{ or } \sqrt{\frac{2E^*\gamma}{\pi c}} \quad (4.1)$$

where E^* is the material constant dependent on plane-strain or plane-stress condition, and γ is surface energy, i.e., $G_{Ic} = 2\gamma$. On the basis of fracture toughness as a material constant, once the crack length $2c$ is downsized to approach zero, the critical stress σ_{cr} according to equation (4.1) could exceed the theoretic strength σ_{th} of a perfect solid. Since this is not physically acceptable, we can calculate the critical crack length as

$$c_{cr} = \frac{K_{Ic}^2}{\pi\sigma_{th}^2} \text{ or } \frac{2E^*\gamma}{\pi\sigma_{th}^2} \quad (4.2)$$

below which the strength of nanoscale structures is given by the theoretic strength but not by fracture toughness.

This flaw-tolerance behavior of cracked nanostructures first appears in the study of Gao et al. [77] for mineral plates in bones, followed by Buehler et al. [76]. Such concept

has been used by many researchers in an attempt to explain their observations from simulations or experiments[78–82]. Among them, Meyers et al. [80] used scanning electron microscope (SEM) and atomic force microscopy (AFM) to observe the diameter of holes in organic layers and the asperities/bridges spacing are around 50 nm. By substituting the rough values of $K_{Ic} = 1 \text{ MPa}\sqrt{\text{m}}$ and $\sigma_{th} = 3.3 \text{ GPa}$ into equation (4.2), they estimated the critical crack length $2c_{cr} = 56 \text{ nm}$, which satisfies the experimental value above and explains why the abalone nacre is strong. Jang and Greer [81] also drew on the similar relation as equation (4.1) and concluded that once the diameter of metallic glass nanopillars is below 100 nm, not only the tensile strength is improved but the failure mechanism transits from brittle to ductile.

The revised studies show that the flaw-tolerance concept is commonly used to address the superiority of nanoscaled structures. However, the validity of LEFM and especially fracture toughness as a constant from nanoscale to macroscale has not been carefully examined. Even though some researchers [83–87] tried to compare the atomistic simulation results with the classic Griffith theory of fracture, their studies do not demonstrate the existence of inverse square root singular stress field at the atomistic level. Therefore, we believe that the most important step is to examine the crack-tip stress field in molecular dynamics (MD) simulations. There have been a few studies focusing on near-tip stress distributions either by use of the virial or Hardy stress definition [88–92]. Yet none of these results is detailed enough in directly measuring the stress intensity factor, not to mention the comparison with continuum solutions.

In order to describe the near-tip stress field at the atomistic scale, Adnan and Sun [93] employed the continuum finite element method (FEM) based on the failure condition

obtained from MD simulations. In the following sections, by considering the average of the virial stress in each unit cell as shown in Chapter 3, it can be further demonstrated the existence of not only the trend of inverse square root singularity in atomistic systems but also a complete crack-opening stress distribution that can be used to determine the critical stress intensity factor. Through the comparison with continuum FEM solutions, the same trend of fracture toughness against different crack lengths illustrate that fracture toughness measured in terms of K_{Ic} or G_{Ic} , decreases with the decreasing crack length, indicating that the remote failure stress predicted by equation (4.1) with constant K_{Ic} or G_{Ic} is not valid below certain crack length.

4.1 Molecular Models

Sodium Chloride (NaCl) is selected owing to its brittleness [93]. The corresponding interatomic potential can be found in equation (2.68) and Table 2.1. The MD environment is under a time step of 1 fs and temperature of 1 Kelvin. Such low temperature is selected because we focus on the comparison of the near-tip stress between MD and FEM solutions. Additionally, reducing the relaxation time by this low temperature is another concern. We arrange the NaCl crystal in the cubic orientations with $x = [100]$, $y = [010]$ and $z = [001]$ and apply the periodic boundary conditions in both x and z directions. To get the initial stress-free state at the prescribed temperature (1 Kelvin), the MD model is equilibrated for 20 ps under isobaric-isothermal (NPT) ensemble with target pressure P equal to 0 Pa, which is followed by canonical (NVT) ensemble for 20 ps. Subsequently, the whole system is subjected to pure tensile loading by moving two outmost layers along the y direction with the incremental displacement

Δu_y . After being subjected to displacement loading, the whole system is relaxed by fixing the positions of the outmost layers for 2 ps. The data are recorded for 2 ps and the next increment is applied later.

4.1.1 Perfect NaCl Crystals

The lattice constant at 1 Kelvin is determined as $a = 2.786 \text{ \AA}$ after the initial relaxation. The material properties are calculated by the stress-strain curve of a perfect NaCl crystal shown in Figure 4.1. Since the interatomic potential in equation (2.68) is not in harmonic form, the material properties are not constant but decreasing with the increasing applied strain. By taking the secant line from the origin in the stress-

Figure 4.1 Stress-strain curve of a perfect NaCl crystal and the secant lines to determine the material constants.

Table 4.1 Secant moduli under various applied strain ($C_{12} = C_{44}$).

ε_{yy}	C_{11} (GPa)	C_{12} (GPa)
0.01	56.053	12.494
0.02	52.925	12.619
0.03	49.931	12.538
0.04	47.096	12.396
0.05	44.377	12.255
0.06	41.899	12.096

strain curve, three material constants (C_{11} and $C_{12} = C_{44}$ for pair potentials) at different applied strains are listed in Table 4.1. Also indicated by Figure 4.1, the virial stress at failure is obtained as $\sigma_{th} = 3.43$ GPa. This can be regarded as the theoretic strength of NaCl.

Figure 4.2 Model geometries with a central crack initiated by removing bonds.

Table 4.2 Specimen sizes of various models.

Type	L_x (Å)	L_y (Å)	L_z (Å)
2p ~ 60p	417.9	560.0	27.86
90p	585.1	782.9	27.86

4.1.2 Central Cracked Specimens

Figure 4.2 shows the specimen geometries with a central crack along the xz plane. We consider six models with different crack lengths by artificially cutting 2, 6, 18, 30, 60 and 90 interaction pairs, which are denoted as 2p, 6p, 18p, 30p, 60p and 90p models, respectively. These artificially cutting bonds with different lengths are embedded into two specimen sizes listed in Table 4.2. For the 2p, 6p, 18p, 30p, 60p models, the specimen size is $417.9 \times 560.0 \times 27.9 \text{ \AA}^3$ containing 150, 200 and 10 lattices in the x , y and z directions, respectively. As for the 90p model, a larger size with $585.1 \times 783.4 \times 27.9 \text{ \AA}^3$ is employed to minimize the boundary effect. In the following two sections, the 30p-type model is taken as an example to realize how the crack tip is defined in the NaCl crystal and the crack opening stress evolves with the increasing applied strain.

Figure 4.3 Crack opening stress of the 30p-type model under $\varepsilon_{yy} = 0.01$.

Figure 4.4 Crack tip position of the 30-type model at (a) the initial state (b) $\epsilon_{yy} = 0.020638$.

4.2 Initial Crack Tip Position

Since the crack tip, where the radius of curvature approaches zero, is a vague concept in discrete systems, the starting point of connecting continuum fracture mechanics with the failure process happening in discrete crystals is defining the crack tip position. Through the comparison between the MD and FEM simulations, the near-tip stress under $\epsilon_{yy} = 0.01$ is demonstrated in Figure 4.3, where the crack tip of the FEM model is assumed at the location of the first $\text{Na}^+ - \text{Cl}^-$ pair without removing the interaction. Such small strain ($\epsilon_{yy} = 0.01$) is taken because the NaCl crystal can be directly modeled as a linear elastic solid without consideration of nonlinear effect from interatomic potentials. As we can see from Figure 4.3, the coincident distributions of MD and FEM results, except for the near-tip region, provides the evidence that the assumption of the initial crack tip position at the location of the first un-removed interatomic pair is reasonable. Such setting is also considered for other models with different crack lengths shown in

Figure 4.2. To better explain how the crack grows with the increasing applied strain, the unit cells are numbered according to their positions from the initial crack tip shown in Figure 4.4(a).

4.3 Evolution of Crack Opening Stress during Failure process

For all the specimens considered in this paper, the displacement increment $\Delta u_y = 0.05 \text{ \AA}$ is applied within 1 ps before the local stress of the first unit cell reaches the maximum. To detail the specific moment when each unit cell reaches the maximum local stress state, the displacement increment is adjusted to $\Delta u_y = 0.0005 \text{ \AA}$ within 0.1 ps when approaching the final failure point. Based on the engineering strain defined as $\varepsilon_{yy} = u_y / L_o$ where u_y is the applied displacement and L_o is the height after initial relaxation, Figure 4.5(a) demonstrates the stress-strain curve to confirm the occurrence of brittle failure in a NaCl crystal. Note that the normal stress in Figure 4.5(a) is the whole volume-averaged virial stress (global stress), which provides the information of an entire cracked body rather than the remote stress state.

Using the local virial stress averaged over the square-shaped volume in Figure 3.12, the crack opening stresses corresponding to different applied strains are plotted in Figure 4.5(b). It is noted that $\varepsilon_{yy} = 0.018391 \sim 0.020685$ represent the applied strains where each unit cell ahead of the initial crack tip reaches the maximum normal stress. Since the crack propagates in the same plane by breaking the interatomic bonds incrementally, the normal stress of a unit cell increases until it reaches the maximum value and subsequently the value decreases as the applied strain is increased further. Thus, instead of demonstrating stress singularity, the atomistic near-tip stress distributions in Figure 4.5(b)

Figure 4.5 Various types of normal stress distributions illustrating the failure process of the 30p-type model: (a) stress-strain curve with bolt dots marking the applied strain levels where each near-tip unit cell reaches the maximum opening; (b) crack opening stress evolution corresponding $\epsilon_{yy} = 0.018391 \sim 0.020685$ representing when each unit cell ahead of the initial crack tip reaches the maximum opening stress.

show the maximum stress, which a unit cell can sustain, is finite and these maximum values are close to the theoretic strength $\sigma_{th} = 3.43$ GPa of perfect NaCl crystals except for $\varepsilon_{yy} = 0.018391$ corresponding to the maximum local stress state of the first unit cell.

To realize the influence of the maximum local stress on the global behavior of the cracked crystal, we mark the applied strains at which each near-tip unit cell achieves the maximum local stress as bold dots in Figure 4.5(a). The final failure point is determined when the normal stress of the second unit cell (not the first unit cell) reaches the maximum, namely $\varepsilon_{cr} = 0.020638$. Meanwhile, note that, except for the first unit cell, the maximum stress value of each unit cell in Figure 4.5(b) is equal to 3.37 GPa which is close to the theoretic strength $\sigma_{th} = 3.43$ GPa of perfect NaCl crystals. From the different behavior of the first unit cell, we believe that the artificial cutting-bond to create the initial crack surfaces affects the natural characteristic of the initial crack tip.

Despite the absence of crack tip singular stress in atomistic systems, it is of interest to compare the crack opening stress calculated by the local virial stress with the FEM solution that contains stress singularity. In order to do this, we need to redefine the crack tip position to deal with the situation when the crack starts propagating. Here, the crack tip is assumed to follow the unit cell with the maximum normal stress. As illustrated by Figure 4.4(b), it indicates that when the second unit cell attains the maximum stress (at $\varepsilon_{yy} = 0.020638$), the crack tip propagates forward a lattice constant. Given this setting, we multiply the crack opening stress distribution in Figure 4.5(b) by $(2\pi x)^{0.5}$ where x is the distance from the present crack tip, to extract stress intensity factor. These results are plotted as the solid lines in Figure 4.6.

Figure 4.6 Distributions of the crack opening stress $\sigma_{yy}(2\pi x)^{0.5}$ of the 30-type model using the same colors as Figure 4.5(b) to represent different applied strain levels; solid lines with dots and dash lines are MD and FEM solutions, respectively.

Furthermore, the corresponding 2-D plane-strain orthotropic solid with the secant moduli listed in Table 4.1 is modeled by FEM. To maintain the equivalence with the MD model, we need to ensure that the boundaries along the transverse directions are periodic, and that the magnitude of applied displacement is identical to that in the MD model. In Figure 4.6, the FEM results are shown in dashed lines with the same colors as MD solutions to mark the applied strain levels. Before crack propagation ($\epsilon_{yy} = 0.01$ and 0.018391), the MD result near the crack tip does not follow what is observed from FEM, which confirms that the artificial cutting-bond influences the stress around the original crack tip. Once the crack moves ahead to new positions, the crack opening stresses obtained from MD follow the trend of inverse square root singularity.

In Figure 4.6, it is noted that, with the increasing applied strains and updated crack tip positions, $\sigma_{yy}(2\pi x)^{0.5}$ distributions of MD simulations ($\epsilon_{yy} = 0.020638 \sim 0.020685$)

approach a saturated state which agrees with the distribution of the continuum FEM result for $\varepsilon_{yy} = 0.020638$. Since the failure initiation point is identified as $\varepsilon_{cr} = 0.020638$, this saturated $\sigma_{yy}(2\pi x)^{0.5}$ distribution at the crack tip projects a stress intensity factor at failure.

4.4 Size-Dependent Fracture Toughness and Failure Prediction

We now consider the 2p, 6p, 18p, 30p, 60p and 90p models. All these models except for the 2p model show the failure condition to be when the second unit cell ahead of the initial crack tip reaches the maximum normal stress and thus the crack length at failure is equivalent to the initial value plus two sizes of lattice constant, as listed in Table 4.3. The stress-strain curve of the 2p-type model shows its failure condition depends on the maximum normal stress of the first unit cell ahead of the initial crack tip. As a result, the crack length at failure of the 2p-type model is identical to the initial crack length.

Table 4.3 Crack lengths and failure strains of various models.

Type	Initial Crack Length (Å)	Crack Length at Failure (Å)	ε_{cr}
2p	8.358	8.358	0.057471
6p	19.50	25.07	0.039621
18p	52.93	58.51	0.025311
30p	86.37	91.94	0.020638
60p	169.95	175.52	0.017007
90p	253.53	259.10	0.014158

Based on the critical failure strains ε_{cr} listed in Table 4.3, we calculate the corresponding remote critical stress σ_{cr} by averaging the local virial stress within the layer of unit cells underneath the fixed layer (where the displacement is applied) in MD simulations. For the equivalent FEM models there is a necessity to consider the influence

Figure 4.7 Material constant C_{11} and C_{12} dependence on applied strain; the dash lines mark the critical strains ϵ_{cr} against different models.

Figure 4.8 Comparison of critical remote stress σ_{cr} against crack length.

of the nonlinearity in the stress-strain relations. Figure 4.7 indicates that the secant moduli decrease as the applied strain increases. In this figure, the dash lines mark the failure strains of the six models. Substituting the secant moduli in the FEM models for the corresponding applied strain, we obtain the reaction traction (the remote stress at failure) σ_{cr} . Figure 4.8 shows that the MD and FEM results agree with each other.

Also, under the consideration of ε_{cr} , we demonstrate the critical $\sigma_{yy}(2\pi x)^{0.5}$ distributions through local virial stress calculation in Figure 4.9(a). The critical stress intensity factor is determined by the following relation

$$K_I = \lim_{x \rightarrow 0} \sigma_{yy} \sqrt{2\pi x} \quad (4.3)$$

Here, in the process of projecting stress intensity factors using equation (4.3), we neglect the data next to the crack tip due to their deviation resulting from the nonlinearity in the potentials. The value of critical stress intensity factors K_{Ic} corresponding to different crack lengths can be found in Table 4.4 and the enlarged diagram of Figure 4.9(a). They clearly show that K_{Ic} values thus obtained are somewhat proportional to crack length except for models with large crack lengths. In addition, the secant moduli are used to calculate the corresponding FEM results. The FEM solutions are represented as the dash lines with the same colors as the MD solutions in Figure 4.9(b) where we can see that the MD and FEM results match well with each other except for the data points very close to the crack tip.

From the results in Figure 4.9(a), it is seen that K_{Ic} approaches a constant value only for crack lengths larger than $100\text{\AA}$. Thus, K_{Ic} (and G_{Ic}) cannot be considered as a constant. Consequently, the use of equation (4.1) to predict the failure stress of a cracked

Figure 4.9 Estimation of fracture toughness for six different models: (a) $\sigma_{yy}(2\pi x)^{0.5}$ distributions under critical strain ε_{cr} with an enlarged plot showing the determination of critical stress intensity factor K_{Ic} ; (b) comparison of $\sigma_{yy}(2\pi x)^{0.5}$ distributions; solid lines with dots and dash lines are MD and FEM solutions, respectively.

Table 4.4 Fracture toughness from MD or FEM.

Type	K_{Ic} (MD) (Pa√m)	G_{Ic} (MD) (N/m)	G_{Ic} (FEM) (N/m)
2p	9.1191×10^4	0.2257	0.2093
6p	11.5458×10^4	0.3358	0.3327
18p	12.2817×10^4	0.3587	0.3503
30p	12.5955×10^4	0.3689	0.3621
60p	12.9643×10^4	0.3864	0.3797
90p	12.8886×10^4	0.3778	0.3764

material at nanoscale may not be valid. As an example, the failure stress can be predicted by the general form of equation (4.1) as

$$\sigma_{cr} = \frac{1}{F(2c/L_x)} \frac{K_{Ic}}{\sqrt{\pi c}} \quad (4.4)$$

where

$$F\left(\frac{2c}{L_x}\right) = 1 + 0.128 \left(\frac{2c}{L_x}\right) - 0.288 \left(\frac{2c}{L_x}\right)^2 + 1.525 \left(\frac{2c}{L_x}\right)^3 \quad (4.5)$$

is the empirical expression accounting the ratio between dimensions and crack length [94]. By using the critical stress intensity factor $K_{Ic} = 12.8886 \times 10^4$ Pa√m of the 90p-type model, the predicted failure stresses for different crack lengths are shown in Figure 4.8. It is evident that the predictions based on constant K_{Ic} deviate significantly from the MD or FEM results for crack lengths smaller than 100 Å. This says that equation (4.4) cannot be used to predict failure stress for crack lengths smaller than 100 Å for NaCl.

Zhang et al. [95] had recently performed MD simulations to investigate the uniaxial tensile fracture behaviors of the nanocrystalline graphene with a central hole. They claimed while the radius of a hole is smaller than the critical crack length $c_{cr} = 20$ Å with the substitution of $2\gamma = 8$ N/m and $\sigma_{th} = 26.86$ GPa into equation (4.2), the deviation of MD results from the Griffith's prediction proves the flaw tolerance of nanostructures.

However, according to our present research, the size-dependent fracture toughness is the main reason for the discrepancy between the actual failure stress and fracture mechanics prediction. Figure 4.8 highlights even though the crack length of the 2p-type model is smaller than the critical crack length c_{cr} of NaCl as $9 \text{ \AA}$, its actual failure stress calculated by MD is much lower than the theoretic strength σ_{th} . Thus, the flaw tolerance doesn't occur even in the case with the smallest crack length.

The critical energy release rate G_{Ic} of MD simulation is determined by the G - K relation in continuum fracture mechanics expressed as [96]

$$G_I = \frac{K_I^2}{E^*}, E^* = 2(C_{11} + C_{12}) \sqrt{\frac{C_{44}(C_{11} - C_{12})}{C_{11}(C_{11} + C_{12} + 2C_{44})}} \quad (4.6)$$

where C_{11} , C_{12} and C_{44} are the secant material constants, which can be found in Figure 4.7. As for the FEM model, we follow the procedure used in MD simulation to estimate the energy release rate by the G - K relation with the projection of the FEM solutions in Figure 4.9(b). Figure 4.10 indicates that values of G_{Ic} obtained by continuum FEM and MD simulations decrease as the crack length decreases. It is important to note that as the crack length exceeds $100 \text{ \AA}$, the critical energy release rate G_{Ic} approaches a constant.

In view of the well-matched $\sigma_{yy}(2\pi x)^{0.5}$ distributions in Figure 4.9(b) and the same G_{Ic} trend of MD and FEM results in Figure 4.10, we can say the behavior of size-dependent fracture toughness is not originated from model types, i.e., atomistic vs. continuum. Different from the quantized fracture mechanics [97] illustrating that the size-dependent fracture toughness is resulted from the curvature of an atomistic blunt crack due to the lattice discreteness [98], we regard the main reason as the use of stress

intensity factor (or equivalently the energy release rate) to measure fracture toughness. This is discussed in the following section.

Figure 4.10 Critical energy release rate G_{Ic} against the crack length.

4.5 K-Dominance Zone and Two-Parameter Model Prediction

The size-dependent fracture toughness for cracks shorter than 100 Å raises the concern about the applicability of K_{Ic} and G_{Ic} as fracture criteria. Recently, Sun and Qian [99] have encountered a similar problem using LEFM to characterize fracture toughness of brittle PMMA. They concluded that, if the singular stress is not dominant near the crack tip, K_{Ic} or G_{Ic} alone cannot fully capture the fracture driving force and a second parameter describing the nonsingular stress must be included. Dividing the crack opening stress σ_{yy} into the singular and non-singular parts, we can express the degree of singular stress dominance (K -dominance) as

Figure 4.11 Degree of K -dominance as a function of the distance from the crack tip; the mark $\Lambda = 90\%$ illustrates that the size of K -dominance zone decreases as the crack length decreases.

$$\Lambda = \frac{\sigma_{yy}^{\text{singular}}}{\sigma_{yy}^{\text{singular}} + \sigma_{yy}^{\text{non-singular}}} \quad (4.7)$$

where

$$\sigma_{yy}^{\text{singular}} = \frac{K_I}{\sqrt{2\pi x}}$$

is the singular part of the near tip opening stress. According to specimen dimensions and final crack lengths, Figure 4.11 shows the degree of K -dominance as a function of the crack size and distance from the crack tip for the six MD models considered earlier.

As we can see from Figure 4.11, the degree of K -dominance starts from 1 at the crack tip and decreases as the distance from the crack tip increases. If we focus on the region where $\Lambda = 90\%$, the size of K -dominance zone decreases as the crack length decreases. Consequently, with the decrease of K -dominance zone size, the singular stress represented by the stress intensity factor alone may not be sufficient to represent the

fracture driving force in the fracture process zone. As a result, the value of K_{Ic} (or G_{Ic}) tends to be lower (see Table 4.4) but the corresponding remote failure stress becomes higher (see Figure 4.8). In contrast, for the cases with large K -dominance zone, i.e., crack lengths are greater than 100 Å in this study, G_{Ic} approaches the constant value (theoretic value of surface energy) and the Griffith fracture theory ($G_{Ic} = 2\gamma$) becomes valid.

The decreasing K -dominance zone with the decreasing crack length, as Figure 4.11 shows, indicates that the singular stress alone cannot represent the full fracture driving force. As a result, the contribution of the non-singular stress must be taken into account to modify the present failure criterion which consists of only the stress intensity factor. Following the procedures established by Sun and Qian [99], we employ the William's expansion of the near-tip stress and consider only one non-singular term as

$$\sigma_{yy}\sqrt{2\pi x} = K_{Ic} + \lambda_0 x \quad (4.8)$$

where K_{Ic} is the critical stress intensity factor in Table 4.4, and λ_0 is the first dominant non-singular term obtained from the slope of a projecting line in the enlarged plot of Figure 4.9(a). Rearranging equation (4.8), we have

$$\frac{\sigma_{yy}\sqrt{2\pi x}}{K_{Ic}} = 1 + \mu x \quad (4.9)$$

where $\mu = \lambda_0/K_{Ic}$ is a function of crack length to represent the ratio between the non-singular and singular terms. Dividing the $\sigma_{yy}(2\pi x)^{0.5}$ in Figure 4.9(a) by the critical stress intensity factor listed in Table 4.4, the non-singular term μ as a function of different crack lengths is shown in Figure 4.12. It can be found that the distributions of $\sigma_{yy}(2\pi x)^{0.5} / K_{Ic}$ for the 60p and 90-type model are almost identical, which represents the crack

Figure 4.12 $\sigma_{yy}(2\pi x)^{0.5} / K_{Ic}$ distributions against different crack length.

length effect on the fracture toughness vanishes when the crack length gets to a certain value.

From equation (4.9), if there is a critical distance x_c to be determined from MD results, we can define the reference stress intensity factor K^{ref} as

$$K^{ref} = \sigma_{yy} \sqrt{2\pi x_c} \quad (4.10)$$

Along with the reference stress intensity factor K^{ref} and the critical distance x_c as material constants, the apparent stress intensity factor can be explicitly given by

$$K_{Ic} = \frac{K^{ref}}{1 + \mu x_c} \quad (4.11)$$

Equation (4.11) indicates that the reference fracture toughness K^{ref} is the K_{Ic} corresponding to $\mu = 0$. In Figure 4.13, $K^{ref} = 13.0551 \times 10 \text{ Pa}\sqrt{\text{m}}$ with $\mu = 0$ is obtained by fitting K_{Ic} as a function of μ . Subsequently, $x_c = 3.048 \text{ \AA}$ is determined by the least square solution of the MD results for six different crack lengths. In the form of

Figure 4.13 Curve-fitting the relation between the apparent fracture toughness K_{IC} and non-singular term μ to estimate the reference fracture toughness K^{ref} .

Figure 4.14 Critical remote stress σ_{cr} predicted by the two-parameter model.

equation (4.11), the failure load for a cracked material is given by the apparent stress intensity factor K_{Ic} which depends on the reference fracture toughness K^{ref} and μ . The comparison of the failure loads with the use of the apparent fracture toughness K_{Ic} calculated from equation (4.11) is shown in Figure 4.14. It is evident that the two-parameter model is accurate in predicting the failure load.

4.6 Conclusions

By adopting the local virial stress, we demonstrated that the opening stress distribution ahead of a crack in NaCl obtained by MD simulations can match that in the corresponding continuum model. Through the comparison with continuum FEM models, the MD calculated crack tip opening stress was used to determine fracture toughness. It was found that fracture toughness measured in stress intensity factor (or energy release rate) cannot be a material constant when the crack length is shorter than 100 Å. Once the size of K -dominance zone is large such as in cases where the crack lengths are longer than 100 Å, fracture toughness approaches the theoretic value of surface energy and Griffith fracture theory ($G_{Ic} = 2\gamma$) becomes valid. This size-dependent behavior is the result of the continuum fracture mechanics which is developed based on continuum models that adopt singular crack tip stress field represented by the stress intensity factor. In the case where the singular stress is not dominant in a reasonably large zone, the two-parameter model that accounts for the contribution of both singular and non-singular stress terms can predict the failure load more accurately.

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5. FRACTURE TOUGHNESS VARIATION INDUCED BY GEOMETRIC CONFINEMENT

Fiber in composite materials exemplifies how reducing structure dimension improves the mechanical properties of load-bearing solids. In addition to diminishing the probability of defect formation, decreasing the specimen size also increases the critical failure load from the viewpoint of continuum fracture mechanics. With consideration of a central crack in a plate subjected to the constant uniform tensile strain, while the specimen height (the dimension perpendicular to the crack line) is decreasing and other dimensions remain the values much larger than the crack length, Figure 5.1 shows a decreasing trend of stress intensity factors. As a result, if fracture toughness in terms critical stress intensity factor is treated as a material constant, the predicted failure load is supposed to increase with the decreasing specimen height.

However, as the dimension is downsized to the atomistic scale at which the continuum mechanics seems to be inapplicable, two questions may arise: (1) if the K -field (the singular stress term) exists and (2) if fracture toughness in terms of stress intensity factor K_{Ic} or energy release rate G_{Ic} is sufficient to represent the full fracture driving force. Many researchers have used molecular simulations to study the fracture mechanism of nanostructures. Although the invalidity of the classic Griffith theory, the predicted critical failure higher than the theoretic strength of the perfect crystals, is explained as the flaw-tolerance behavior of nanostructures [76, 77, 95], these two

Figure 5.1 Effect of reducing specimen heights on stress intensity factor.

questions are not yet fully answered.

In an attempt to solve the first question, whether K -field exists in the molecular model, we employ the local virial stress averaged over a periodic volume. In Chapter 3, it has been shown that once the averaging volume is periodic, the convergence of the local virial stress can be accomplished within one single lattice and therefore this atomistic near-tip stress preserves the detailed stress concentration near the crack tip. By the comparison of FEM solutions containing stress singularity, we are able to figure out if the crack opening stress in discrete models keeps the trend of stress singularity.

As for the second question, whether fracture toughness in terms of single parameter (K_{Ic} or G_{Ic}) is sufficient to represent the full fracture driving force, a number of previous studies have discussed the variation of single fracture parameter at the macroscopic scale, especially when the effect of geometric constrain on the crack becomes severe. For the

ductile material like metal, the size and the related shape of plastic zone are used to explain the size-dependent fracture toughness [100, 101]. More recently, Sun and Qian [99] and Kumar et al. [102], characterizing the fracture toughness of brittle PMMA, concluded if the singular stress is not dominant near the crack tip (determined by the size of K -dominance zone), K_{Ic} or G_{Ic} alone cannot fully capture the fracture driving force. These researchers also developed a two-parameter fracture criterion to include the contribution of the nonsingular stress.

Inspired by their research, the present study in this chapter, based on the cracked sodium chloride (NaCl) crystals with different specimen sizes, not only demonstrates that the trend of inverse square root singularity exists in the atomistic near-tip stress but also verifies that the result of Sun and Qian's work in continuum can be further applied on the nanostructure. These results provide the answers for the applicability of continuum fracture mechanics at nanoscale – employing the fracture toughness drawing on stress singularity to predict the failure of nanostructures has to include the contribution from non-singular term. On the other hand, different from the unbounded stress at crack tips in continuum, since the maximum stress that a unit cell can sustain is finite and close to the theoretic strength, the application of the maximum tensile stress criterion is also feasible.

5.1 Molecular Models

Along the xz plane, a central crack created by removing 30 interaction pairs (initial crack length $2c = 86.37 \text{ \AA}$) is embedded into the sodium chloride (NaCl) crystals in the cubic orientations with $x = [100]$, $y = [010]$ and $z = [001]$. The interatomic potential is described in equation (2.68) and the related parameters are listed in Table 2.1. In the

present study, while the width ($L_x = 417.9 \text{ \AA}$) and thickness ($L_z = 27.86 \text{ \AA}$) of the cracked specimens are kept constant, the height (L_y) is reduced to increase the geometric constraining effect.

Figure 5.2 Model geometries with different heights.

Figure 5.2 shows the specimen geometries with different specimen heights (the distance between two fixed layers marked as yellow) varied from $19.50 \text{ \AA}$ to $838.6 \text{ \AA}$. At the prescribed temperature of 1 Kelvin (the lattice constant $a = 2.786 \text{ \AA}$), the molecular model is initially relaxed under isobaric-isothermal (NPT) ensemble for 20 ps to reach the initial stress-free state. Subsequently, under canonical (NVT) ensemble to maintain the constant environment temperature and fix the width and thickness of the simulation

box, pure tensile loading is applied by moving the two fixed layers along the y direction. To ensure the same strain rate for all specimens, the displacement increments are adjusted from $\Delta u_y = 0.00175 \text{ \AA}$ for $L_y = 19.50 \text{ \AA}$ to $\Delta u_y = 0.075 \text{ \AA}$ for $L_y = 838.6 \text{ \AA}$. After each loading increment, the whole system is relaxed by fixing the positions of the outmost layers, followed by data averaging.

5.2 Global and Local Stress Analysis

To realize how the different specimen height influences the mechanical properties of cracked models, we analyze the global and local virial stresses from two specimens with $L_y = 52.93 \text{ \AA}$ and $560.0 \text{ \AA}$. The global stress is calculated by equation (3.9) with V taken as the total volume of a simulation box. The unit cells surrounded by a square-shaped volume ($V = 5.57 \times 5.57 \times 27.86 \text{ \AA}^3$, see Figure 3.12) are used to average the crack opening stress.

5.2.1 Atomistic Stress

By defining the engineering strain $\varepsilon_{yy} = u_y/L_o$ where u_y is the applied displacement and L_o is the height after initial relaxation, the curves of the global stress against the applied strain level based on the samples with $L_y = 52.93 \text{ \AA}$ and $560.0 \text{ \AA}$ are plotted in Figure 5.3(a) and Figure 5.4(a), respectively. It can be found that the rapid drop after failure in Figure 5.4(a) demonstrates the occurrence of the typical brittle failure. On the other hand, once the specimen height is decreased, Figure 5.3(a) shows the zigzag distribution near the final failure.

Figure 5.3 (a) global stress versus applied strain for the specimen with $L_y = 52.93 \text{ \AA}$ (bolt dots mark the applied strain levels where each near-tip unit cell reaches the maximum opening stress); (b) crack opening stress evolution corresponding $\varepsilon_{yy} = 0.036902 \sim 0.053538$ representing the strains at which each unit cell ahead of the initial crack tip reaches the maximum opening stress.

Figure 5.4 (a) global stress versus applied strain for the specimen with $L_y = 560.0 \text{ \AA}$ (bolt dots mark the applied strain levels where each near-tip unit cell reaches the maximum opening stress); (b) crack opening stress evolution corresponding $\varepsilon_{yy} = 0.018391 \sim 0.020685$ representing the strains at which each unit cell ahead of the initial crack tip reaches the maximum opening stress.

Furthermore, the crack opening stress distributions based on two values of L_y are shown in Figure 5.3(b) and Figure 5.4(b). Like the setting in the previous chapter, all the unit cells are numbered according to their positions from the initial crack tip located at the first $\text{Na}^+ - \text{Cl}^-$ pair without removing the interaction (see Figure 4.4). With the increasing applied strain, the local stress of a unit cell approaches the maximum value that a unit cell can sustain. After passing the maximum local stress, the unit cell loses the load-carrying capability, which can be illustrated by the decreasing stress value as the applied strain increases further. Figure 5.3(b) and Figure 5.4(b) show the crack opening stress distributions corresponding to the applied strains while the first six unit cells reach the maximum local-stress state and all the values of the maximum local stress in each unit cell are close to the theoretic strength $\sigma_{th} = 3.43$ of perfect NaCl crystals except for the first one. This is the consequence resulted from the artificially cutting bond shown in the previous chapter.

We further mark the applied strains at which the local stress of each unit cell achieves the maximum value as the bolt dots in Figure 5.3(a) and Figure 5.4(a). For the large specimen ($L_y = 560.0 \text{ \AA}$), the applied strain where the second unit cell gets to the maximum local-stress state is equivalent to the maximum global stress that a cracked body can sustain. Therefore, it is reasonable to set the failure condition for the specimen with $L_y = 560.0 \text{ \AA}$ as $\varepsilon_{cr} = 0.020638$.

With regard to the small specimen ($L_y = 52.93 \text{ \AA}$), each zigzag in Figure 5.3(a) (the drop of the global stress) corresponds to the maximum local stress state of each unit cell. However, different from the aforementioned large specimen, the applied strain, at which

the second unit cell achieve the maximum local stress state, doesn't cause the catastrophic failure. We employ the failure condition as the applied strain causing the maximum global stress. In this case, the failure condition is set to be $\varepsilon_{cr} = 0.053538$ corresponding to the maximum local stress state of the sixth unit cell.

5.2.2 Continuum Finite Element Solutions

To check if the atomistic near-tip stress keeps the properties of the inverse square root stress singularity, the two-dimensional plane strain FEM model is built to compare the local atomistic stress. To maintain the equivalence between the MD and FEM model, in addition to the periodic boundary condition in the transverse direction and the identical magnitude of applied displacement, one consideration is that the secant moduli in Table 4.1 used to deal with the nonlinearity of the potential function. Another consideration is that the crack tip position follows the unit cell with the maximum local stress based on the observation in Figure 5.3(b) and Figure 5.4(b).

In this section, we still employ the $\sigma_{yy}(2\pi x)^{0.5}$ distributions, where σ_{yy} is the crack opening stress distribution and x is the distance from the present crack tip, to emphasize the trend of inverse square root stress singularity. With respect to two different specimen heights, Figure 5.5 and Figure 5.6 show the $\sigma_{yy}(2\pi x)^{0.5}$ distributions under the applied strains causing the maximum local stress state of each unit cell. It is noted that the solid and dash lines in Figure 5.5 and Figure 5.6 represent the MD and FEM solutions, respectively.

If the crack tip remains at the initial position (the results of $\varepsilon_{yy} = 0.01$ and $\varepsilon_{yy} = 0.036902$ for $L_y = 52.93 \text{ \AA}$ or $\varepsilon_{yy} = 0.01$ and $\varepsilon_{yy} = 0.018391$ for $L_y = 560.0 \text{ \AA}$), the

Figure 5.5 Crack opening stress $\sigma_{yy}(2\pi x)^{0.5}$ distributions of $L_y = 52.93 \text{ \AA}$.

Figure 5.6 Crack opening stress $\sigma_{yy}(2\pi x)^{0.5}$ distributions of $L_y = 560.0 \text{ \AA}$.

divergence between the local atomistic stress and the continuum Cauchy stress comes from the artificial cutting-bond, which is also the reason why the maximum stress that the first unit cell can sustain is lower than those of other unit cells. Once the crack starts moving to a new position, the influence from the artificial cutting-bond becomes minor and the distributions of discrete and continuum models coincide with each other. Under the failure condition ($\varepsilon_{yy} = 0.053538$ for $L_y = 52.93 \text{ \AA}$ and $\varepsilon_{yy} = 0.020638$ for $L_y = 560.0 \text{ \AA}$), we can further verify that the local near-tip stress in NaCl crystals follows the trend of inverse square root singularity.

Table 5.1 Failure strains and crack lengths of specimens with various sizes.

Size L_y ($\text{\AA}$)	ε_{cr}	Initial Crack Length ($\text{\AA}$)	Crack Length at Failure ($\text{\AA}$)
19.50	0.089351	86.37	97.51
52.93	0.053538	86.37	114.23
86.37	0.039733	86.37	108.66
169.9	0.027501	86.37	97.51
560.0	0.020638	86.37	91.94
838.6	0.019662	86.37	91.94

5.3 Apparent Fracture Toughness Dependent on Specimen Geometries

Table 5.1 lists the failure strains of all specimens shown in Figure 5.2. It is noteworthy that the failure strain increases as the specimen height decreases. To determine the crack tip, the stress-strain curves of $L_y = 86.37 \text{ \AA}$ and $L_y = 169.9 \text{ \AA}$ are demonstrated in Figure 5.7 and Figure 5.8, which indicate that the failure conditions (the strains causing the maximum global stress) of two specimens are related with the maximum local stress state of the fifth and third unit cell, respectively. This provides the information to determine the crack tip position at failure, as listed in Table 5.1.

Figure 5.7 Stress-strain curve of the specimen with $L_y = 86.37 \text{ \AA}$ (bolt dots mark the applied strain levels where each near-tip unit cell reaches the maximum opening stress).

Figure 5.8 Stress-strain curve of the specimen with $L_y = 169.9 \text{ \AA}$ (bolt dots mark the applied strain levels where each near-tip unit cell reaches the maximum opening stress).

Under the failure condition, the $\sigma_{yy}(2\pi x)^{0.5}$ distributions of various specimen sizes are shown in Figure 5.9(a). Through the projection lines, we can estimate the critical stress intensity factor K_{Ic} as listed in Table 5.2. Both Figure 5.9(a) and Table 5.2 clearly show that the values of K_{Ic} are not constant but dependent on the specimen sizes. It is noted that the $\sigma_{yy}(2\pi x)^{0.5}$ distributions of $L_y = 560.0 \text{ \AA}$ and $L_y = 838.6 \text{ \AA}$ approach a limit curve, which reflects the coincident K_{Ic} in Table 5.2 and a saturated size of K -dominance zone discussed in the following section.

Table 5.2 Variation of fracture toughness induced by size effect.

Size L_y ($\text{\AA}$)	K_{Ic} (MD) ($\text{Pa}\sqrt{\text{m}}$)	G_{Ic} (MD) (N/m)	G_{Ic} (FEM) (N/m)
19.50	8.8490×10^4	0.2566	0.2803
52.93	11.3487×10^4	0.3414	0.3327
86.37	11.8328×10^4	0.3499	0.3399
169.9	12.1412×10^4	0.3528	0.3465
560.0	12.5955×10^4	0.3689	0.3637
838.6	12.6729×10^4	0.3706	0.3675

Additionally, the coincident distributions between MD and FEM in Figure 5.9(b) not only demonstrate that the atomistic near-tip stress follows the trend of inverse square root singularity but verify the behavior of the size-dependent K_{Ic} also occurs in the FEM solutions. We further use the G - K relation in equation (4.6) to calculate the critical energy release rate G_{Ic} . Based on the secant moduli, both MD and FEM results in Figure 5.10 show the critical energy release rate G_{Ic} decreases as the geometric confinement increases. When the specimen size is larger than $L_y = 500 \text{ \AA}$, the approach of G_{Ic} toward a constant value illustrates the Griffith fracture theory is validated.

Figure 5.9 Estimation of fracture toughness against different sizes (a) $\sigma_{yy}(2\pi x)^{0.5}$ distributions under critical strain ε_{cr} with projection lines to determine the critical stress intensity factor K_{Ic} ; (b) comparison of $\sigma_{yy}(2\pi x)^{0.5}$ distributions; solid lines with dots and dash lines are MD and FEM solutions, respectively.

Figure 5.10 Size-dependent critical energy release rate G_{Ic} .

5.4 Two-Parameter Model and Maximum Stress Criterion

The size of the K -dominance zone explains why fracture toughness is dependent on the specimen heights. Based on equation (4.7), the degree of K -dominance varying with the specimen size is shown in Figure 5.11, which indicates that the size of K -dominance zone for $\Lambda = 90\%$ decreases as specimen size decreases. It is also noteworthy that the same tendency of the Λ curves for $L_y = 560.0 \text{ Å}$ and $L_y = 838.6 \text{ Å}$ results in the same $\sigma_{yy}(2\pi x)^{0.5}$ distributions in Figure 5.9 and a constant fracture toughness in Table 5.2.

Following the two-parameter model in Section 4.5, the apparent fracture toughness can be predicted by the two-parameter model

$$K_{Ic} = \frac{K^{ref}}{1 + \mu x_c} \quad (5.1)$$

Figure 5.11 Degree of K -dominance as a function of the distance from the crack tip; the mark $\Delta = 90\%$ illustrates that the size of K -dominance zone decreases as the crack length decreases.

Figure 5.12 Comparison between two-parameter prediction and simulation results.

Figure 5.13 Atomistic near-tip stress σ_{yy} at the failure conditions of (a) varying crack lengths and (b) varying specimen heights.

with $K^{ref} = 13.0551 \times 10^4 \text{ Pa}\sqrt{\text{m}}$ and $x_c = 3.048 \text{ \AA}$. With consideration of the non-singular term μ as the ratio between the slope of the projection lines in Figure 5.9(a) and the apparent stress intensity factor in Table 5.2, the comparison between the two-parameter model prediction and the simulation results is shown in Figure 5.12, which illustrates the reference fracture toughness K^{ref} and the critical distance x_c fitted by the data of varying crack lengths well predict the simulation data of varying specimen heights. This provides the evidence to verify the assumption of the two parameters K^{ref} and x_c as material constants.

Furthermore, under the failure conditions of different crack lengths and specimen heights listed in Table 4.3 and Table 5.1, the atomistic near-tip stress distributions at failure are demonstrated in Figure 5.13. Although the degree of stress concentration decreases with the decreasing crack length or specimen, the flaw-tolerance doesn't occur even in the case with the smallest crack length or specimen. With reference to the previous study [103], the nonlinear softening behavior of NaCl shown in Figure 4.1 makes the NaCl less likely to lead to flaw tolerance, compared with nonlinear stiffening material. Meanwhile, it is also noteworthy in Figure 5.13 that no matter how the crack length and specimen height changes, the maximum normal stress values are independent of specimen geometries and always close to the theoretic strength $\sigma_{th} = 3.43 \text{ GPa}$. Thus, instead of considering the K -field, it is nature to use the maximum stress as the fracture criterion in molecular models. On the other hand, once the continuum fracture mechanics is considered, the contribution of the non-singular term has to be taken into account.

5.5 Conclusions

Considering the periodicity of averaging unit cells for local virial stress calculation, we demonstrate how to employ the complete near-tip stress distribution in MD simulations to directly measure the relevant fracture toughness. This has been proven as a significant step for verifying the trend of inverse square root singularity through the comparison with continuum FEM models. The corresponding size-dependent fracture toughness in terms of critical stress intensity factor K_{Ic} or energy release rate G_{Ic} illustrates that fracture toughness cannot be a material constant especially when the specimen size is very small. By contrast, once the specimen height is large enough ($> 500 \text{ \AA}$ in this study) and the size of K -dominance is saturated, the fracture toughness approaches the constant value and thereby Griffith fracture theory becomes valid. In the end of this chapter, the consistence between the simulation data and the prediction of the two-parameter model verifies the two parameters K^{ref} and x_c are material constants. On the other hand, under the failure conditions, the constant peak stress values in the near-tip stress distributions illustrate the applicability of the maximum stress criterion.

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6. DETERMINATION OF ENERGY RELEASE RATE UNDER FINITE CRACK EXTENSION

Griffith fracture theory introduces the surface energy to balance the difference between the variations of external and internal work during crack extension. Since determining all the energy variations for a propagating crack is regarded as a complicated process, continuum fracture mechanics proposes that the overall Griffith energy balance can be treated as the work done by the near-tip stress and displacement to remove the new crack surface (known as crack closure method). This, based on the infinitesimal crack extension and stress singularity, leads to the well-known G - K relation, which illustrates the equivalence between the energy release rate (surface energy) and the stress intensity factor (the amplitude of the singular stress).

While the dimension is downsized to the atomistic scale, the two conditions mentioned above (the vanishingly small crack extension and unbounded stress at crack tip) may no longer be valid due to the discrete nature of atomistic systems. Nevertheless, many researchers still employed the continuum fracture theories to calculate the dissipation energy rate during rapid crack propagation in brittle crystals [104–106] or to predict the failure load obtained by molecular simulations. These previous studies provided many insightful results, e.g., the zone of hyperelasticity related to the maximum crack velocity [107] and the flaw-tolerance of nanostructures [108–110]. But there is a need to check the applicability of the Griffith fracture theory by actually

measuring the changes of external and internal works while a crack tip moves to a new position.

In this chapter, we consider three different methods to estimate the surface energy of sodium chloride. One is direct calculation of the potential energy difference between a perfect and split crystal. Another is the separation work resulted from the crack extension, which is determined by how much external work done minus the change of internal energy stored in a body. The other is the area underneath the traction-separation relation, which is treated as the work of separation per unit area on the basis of the J -integral. The crack extension of all these three methods is not an extremely small value (the size of several lattice constants) compared with specimen dimensions, thereby providing the constant critical energy release rate no matter how the specimen dimension changes. This result is different from the critical energy release rate through the G - K relation, which varies with the size of K -dominance zone shown in the previous chapters.

6.1 Surface Energy by Splitting a Perfect Crystal

Calculating the energy difference between a perfect crystal and the model with extra free surfaces is the straightforward way to estimate the surface energy γ (energy per unit area) defined as the work of creating free surfaces by breaking the atomistic bonds. Consider a perfect NaCl crystal consisting of 150, 200 and 10 lattices in the x , y and z directions ($417.9 \times 560.0 \times 27.9 \text{ \AA}^3$). Two additional free surfaces (along the xz plane) can be created by splitting a perfect crystal into two identical pieces.

Figure 6.1 Kinetic and potential energy variations of a perfect crystal and split model after initial relaxation.

After initial relaxation, the time variations of the kinetic and potential energies are depicted in Figure 6.1. The contribution of kinetic energy can be neglected since the environmental temperature is kept at 1 Kelvin. Such low temperature also allows us not to estimate entropy in the Gibbs free energy (at zero pressure), which has been employed by many researchers to measure the surface energy at high temperatures [111–113]. Consequently, the surface energy is only the difference between two potential energy levels, i.e.,

$$\gamma = \frac{U^{split} - U^{perfect}}{2A} = \frac{(-120.326 + 120.356) \times 10^4}{2(417.9 \times 27.9)} \frac{1.60218 \times 10^{-19} \text{ J}}{10^{-20} \text{ m}} \quad (6.1)$$

$$= 0.2062 \text{ N/m}$$

According to the Griffith fracture theory, the critical energy release rate of NaCl is $G_{Ic} = 2\gamma = 0.4124 \text{ N/m}$ at 1 Kelvin, which is higher than the result in the Zeggeren and

Benson's work [114] ($2\gamma = 0.374 \text{ N/m}$) and the saturated energy release rate in Figure 4.10 and Figure 5.10. In the following sections, we introduce the procedures of measuring the actual released energy during crack propagation.

6.2 Energy Variation during Crack Extension

Focusing on the models with various specimen sizes (L_y) in Figure 5.2, we take the case with $L_y = 86.37 \text{ \AA}$ as an example to illustrate how to calculate the energy variation during crack propagation. As we can see from Figure 6.2, each drop in the global stress represents that one unit cell along the crack line (numbered as shown in Figure 4.4) reaches the maximum normal stress state. Based on the discussion in the previous chapter, if the crack tip position is assumed to follow the location of the unit cell with the maximum local stress, the zigzag distributions in Figure 6.2(a) represent a steady crack propagation process compared with the catastrophic failure at large L_y (see Figure 5.4 for $L_y = 560.0 \text{ \AA}$). This leads us to estimate the static energy release rate. To confirm that the kinetic energy is negligible, Figure 6.3 shows that the kinetic energy remains at a constant level while the potential energy increases to reflect external work done.

6.2.1 Griffith Energy Balance with External Work

As Figure 6.2(b) indicates, from the applied strain $\varepsilon_{yy} = 0.029605$ to 0.035059 , the crack tip moves forward by one lattice constant. After $\varepsilon_{yy} = 0.038088$, the interval for the crack tip movement becomes the size of two lattice constants and is even enlarged to

Figure 6.2 (a) global stress versus applied strain for the specimen with $L_y = 86.37$ Å (dash lines mark the applied strain levels where each near-tip unit cell reaches the maximum opening stress); (b) crack opening stress evolution corresponding $\varepsilon_{yy} = 0.029605 \sim 0.043542$ representing the strains at which each unit cell ahead of the initial crack tip reaches the maximum opening stress.

Figure 6.3 Kinetic and potential energy of the specimen with $L_y = 86.37 \text{ \AA}$ during crack propagation (dash lines mark the applied strain levels where each near-tip unit cell reaches the maximum opening stress).

three lattice constants at $\varepsilon_{yy} = 0.042849 \sim 0.043542$.

Since the crack extension is a finite distance, the overall Griffith energy balance (neglect of the kinetic energy) has to include the contribution of external work during crack growth, i.e.,

$$\Delta W_e = \Delta U + \Delta W_s \quad (6.2)$$

where ΔW_e is the work done by external forces, ΔU is the increment of strain energy, and ΔW_s is the separation work. In the Griffith theory of fracture, the separation work can be further expressed in terms of the critical energy release rate G_{Ic}

$$\Delta W_s = 2G_{Ic}\Delta c \quad (6.3)$$

where Δc is the crack tip extension according to Figure 6.2(b) and the factor of 2 means two crack tips in this study. Thus, the corresponding critical energy release rate G_{Ic} is

$$G_{Ic} = \frac{\Delta W_e - \Delta U}{2\Delta c} \quad (6.4)$$

By calculating the reaction traction t_y as the average of the local virial stress within the unit cell underneath the fixed layer (where the uniform displacement is applied), the amount of external work within a certain loading step i is

$$\Delta W_e^i = t_y^i \Delta u_y A \quad (6.5)$$

where the displacement increment $\Delta u_y = 0.075 \text{ \AA}$ for the specimen with $L_y = 86.37 \text{ \AA}$ and $A = L_x \times L_z$ is cross-sectional area. Meanwhile, the stored strain energy ΔU^i is directly provided by the MD and FEM simulations.

6.2.2 Variation of External Work and Strain Energy during Crack Propagation

Since the characteristic of the first unit cell is influenced by the artificially cutting-bond (as Figure 6.2(b) shows, except for the first unit cell, the maximum stress which a unit cell can sustain is close to the theoretic strength $\sigma_{th} = 3.43$), the applied strain ($\varepsilon_{yy} = 0.035059$), at which the local stress of the second unit cell is maximum, is selected as the reference state to accumulate the total external work and strain energy. While $\varepsilon_{yy} \geq 0.035059$, Figure 6.4(a) shows the average reaction traction t_y as a function of applied strains. Both the average reaction traction in Figure 6.4(a) and the global stress in Figure 6.2(a) demonstrate the similar zigzag distributions but they represent different physical meanings: one is the state of stress along a boundary and another provides the information of an entire cracked body.

Figure 6.4 For $L_y = 86.37 \text{ \AA}$, (a) the average reaction traction t_y ; (b) the external work and strain energy accumulated from $\epsilon_{yy} = 0.035059$ corresponding to the maximum local stress state of the second unit cell.

Substituting the results of Figure 6.4(a) into equation (6.5) and summing up the external work of each loading step, the total external work after $\varepsilon_{yy} \geq 0.035059$ is shown as the red line in Figure 6.4(b). Meanwhile, the strain energy stored inside the body is calculated by three methods: one is the potential energy difference obtained by the MD simulation and the other two are the results of the FEM model with and without consideration of crack extension. For the equivalent FEM model, the secant moduli are considered to deal with the nonlinearity of NaCl crystals (see the stress-strain curve in Figure 4.1).

In Figure 6.4(b), the distribution of strain energy by the FEM model without extending the crack size is close to those of external work and strain energy obtained by MD simulation. Theoretically, if there is no crack extension, the work done by the external forces must equal the increase of strain energy based on the conservation of energy. However, since the present crack tip has propagated to a new position (due to the shift of the unit cell with the maximum normal stress), the similarity between the external work and the strain energy obtained by MD simulation provides the evidence that the potential energy in the MD simulation includes the contribution of surface energy. On the other hand, based on the significant difference between the external work and the strain energy from the FEM model of updating crack tip position, the critical energy release rate from $\varepsilon_{yy} = 0.035039$ to 0.036963 is calculated as

$$G_{Ic} = \frac{\Delta W_e - \Delta U}{2\Delta c} = \frac{16.2371 - 12.2054}{2(2.786 \times 27.86)} \frac{1.60218 \times 10^{-19} \text{ J}}{10^{-20} \text{ m}} = 0.4161 \text{ N/m} \quad (6.6)$$

The other results during the different applied strain levels (marked as the vertical dash lines in Figure 6.4) are listed in Table 6.1. It can be found that all the values of G_{Ic} in Table 6.1 are close to the value of 2γ from equation (6.1).

Table 6.1 Variation of external work (ΔW_e) and strain energy (ΔU) to calculate the released energy per unit area (G_{Ic}).

Strain Interval, ε_{yy}	Δc (a)	ΔW_e (eV)	ΔU (eV)	G_{Ic} (N/m)
0.035059 ~ 0.036963	1	16.2371	12.2054	0.4161
0.036963 ~ 0.038088	1	9.5502	5.7662	0.3905
0.038088 ~ 0.039733	2	15.1309	6.7323	0.4334
0.039733 ~ 0.041032	2	11.2981	3.5325	0.4007
0.041032 ~ 0.041984	2	8.1670	0.0234	0.4202
0.041984 ~ 0.042849	2	7.2394	-0.4177	0.3951
0.042849 ~ 0.043542	3	5.5585	-6.5287	0.4158

6.2.3 Energy Release Rate of Various Specimen Sizes

If the various specimen heights ($L_y = 30.65, 52.93$ and 169.9 Å) are considered, following the result of $L_y = 86.37$ Å, Figure 6.5–6.7 (b) show, with the increasing applied strain, the external work is approximately equal to the difference of potential energy (strain energy) in MD simulations. Thus, instead of using the variation of the strain energy from MD simulations, the critical energy release rate defined by equation (6.4) is calculated by the difference between the external work and strain energy calculated by the FEM model with consideration of updating crack tip position, which is determined by the location of a unit cell with the maximum normal stress shown in Figure 6.5–6.7 (a). Figure 6.8 highlights the critical energy release rates based on the energy balance are independent of the specimen sizes and close to the value of 2γ from equation (6.1) while the results of the G - K relation decreases as the specimen height L_y

Figure 6.5 For $L_y = 30.65 \text{ \AA}$, (a) the crack opening stress evolution corresponding $\varepsilon_{yy} = 0.065438 \sim 0.080061$ representing the strains at which each unit cell ahead of the initial crack tip reaches the maximum opening stress; (b) the external work and strain energy accumulated from $\varepsilon_{yy} = 0.065438$ corresponding to the maximum local stress state of the second unit cell (dash lines mark the applied strain levels where each near-tip unit cell reaches the maximum opening stress).

Figure 6.6 For $L_y = 52.93 \text{ \AA}$, (a) the crack opening stress evolution corresponding $\varepsilon_{yy} = 0.045010 \sim 0.056916$ representing the strains at which each unit cell ahead of the initial crack tip reaches the maximum opening stress; (b) the external work and strain energy accumulated from $\varepsilon_{yy} = 0.045010$ corresponding to the maximum local stress state of the second unit cell (dash lines mark the applied strain levels where each near-tip unit cell reaches the maximum opening stress).

Figure 6.7 For $L_y = 169.9 \text{ \AA}$, (a) the crack opening stress evolution corresponding $\varepsilon_{yy} = 0.026708 \sim 0.028823$ representing the strains at which each unit cell ahead of the initial crack tip reaches the maximum opening stress; (b) the external work and strain energy accumulated from $\varepsilon_{yy} = 0.026708$ corresponding to the maximum local stress state of the second unit cell (dash lines mark the applied strain levels where each near-tip unit cell reaches the maximum opening stress).

Figure 6.8 Comparison of critical energy release rates versus different specimen sizes.

decreases, corresponding to the diminishing size of K -dominance zone with the decreasing L_y . It is also noted that for large L_y (the case of $L_y = 169.9 \text{ Å}$), the discrepancy between the continuum and $2\gamma = 0.4124 \text{ N/m}$ from equation (6.1) may have resulted from the size of crack length, which also affects the size of K -dominance zone as shown in Chapter 4.

6.3 Atomistic Traction-Separation Relation

Instead of employing stress singularity as the fracture parameter, the realistic fracture process can be described by two cohesive surfaces, which are held together by a traction-separation law. Since the experimental measurement has been regarded as a difficult task [115], many studies focusing on the macroscopic scale [116–118] only used a phenomenological traction-separation law consisting of a predefined shape and certain specified parameters, e.g., the maximum cohesive traction and cohesive energy density

etc. According to the original idea of cohesive zone as the model to represent the interatomic bond-breaking, the molecular simulation gives us insights into how the fracture process develops at the atomistic level and distinctly estimates the traction-separation law.

There have been a few studies focusing on the extraction of traction-separation law through molecular simulations [119–122]. Yamakov et al. [119] studied the intergranular fracture in aluminum and observed that the brittle bond-breaking and the ductile failure (dislocation emission and crack-blunting) occur respectively at two crack tips of a central crack. As a result, two types of traction-separation laws were derived to describe both fracture mechanisms. Developing a fictitious potential function to keep two dissimilar materials across the crack with the same lattice constant but different elastic moduli, Zhou et al. [86] investigated the traction-separation laws for interfacial crack problems. Later, Lloyd et al. [120] considered the continuum finite element model embedded with the atomistic cohesive relation developed by Zhou et al. [86] and verified both MD and FEM simulations have the well-matched stress and displacement distributions. Krull and Yuan [121] used single-crystal aluminum and compared their atomistic traction-separation relation with the existing form proposed by Needleman [123].

With reference to these previous studies, we can say that the averaging volume to calculate the local stress is not small compared with lattice constants. The reason may come from the fluctuation of local atomistic stress due to the non-periodic averaging volume. According to Figure 3.13, a larger averaging volume diminishes the stress concentration near the crack tip. Since the convergence of local atomistic stress can be accomplished within one single lattice if the periodicity of averaging volumes is

concerned, in this section, we consider the periodic averaging volume to improve the accuracy of atomistic traction-separation relation.

Figure 6.9 Definitions of (a) local stress and (b) local displacement of a unit cell to determine the atomistic traction-separation relation.

6.3.1 Material and Method

We consider five models with different crack lengths, i.e., 6p, 18p, 30p, 60p and 90p shown in Figure 4.2, to determine the cohesive relation. Following the coordinate setting as the cubic orientations of the NaCl crystal ($x = [100]$, $y = [010]$ and $z = [001]$), the Mode I loading is applied by moving the outmost layer along the y direction. Figure 6.9 shows that the crack opening stress is calculated by the local virial stress with volume $V = 5.57 \times 5.57 \times 27.86 \text{ \AA}^3$, same as Figure 3.12. Meanwhile, dividing a unit cell into the upper (denoted as “+”) and lower (denoted as “-”) parts along the crack line provide the information for the crack opening displacement defined as

Figure 6.10 Among different location of unit cells, the traction-separation laws measured by the models with different crack lengths.

$$u_y^{cell} = \frac{1}{n_z} \sum_{i=1}^{n_z} \left[\frac{1}{2} \sum_{j=1}^2 (u_{iy}^{j+} - u_{iy}^{j-}) \right] \quad (6.7)$$

where $n_z = 10$ is the number of layers along the thickness (z) direction. It is noted that the stress and displacement are recorded at every 0.2 ps within the time-averaging of 2 ps.

6.3.2 Cohesive Relations of Various Crack Lengths

Among different locations of unit cells numbered in Figure 4.4(a), demonstrates the traction-separation relations measured by the models with different crack lengths. Similar to the cohesive model used at the macroscopic scale, the atomistic local stress initially increases as the crack opening increases until it reaches a peak. Subsequently, the normal stress decreases as the crack opening increases further. It is noted that except for the result of the first unit cell, all the peak stresses of the traction-separation relations are close to the theoretic strength. In addition, Figure 6.10 verifies the atomistic traction-separation law is independent of crack lengths.

6.3.3 Cohesive Energy Density

Since the atomistic traction-separation laws estimated at different locations are consistent except for the result obtained from the first unit cell, we use the data of the second unit cell in Figure 6.10(b) to fit the analytical function of the cohesive relation. As Figure 6.11 shows, the displacement corresponding to the peak stress is $0.348 \text{ \AA}$ and the ultimate separation where the normal stress σ_{yy} decays to zero is $u_c = 4.368 \text{ \AA}$. The analytical function enables us to calculate the work of separating the unit area of cohesive surface (so called as the cohesive energy density) defined as

$$\Gamma = \int_0^{u_c} \sigma_{yy}(u_y) du_y \quad (6.8)$$

which is the area under the cohesive relation. Based on the J -integral, the cohesive energy density is equivalent to the critical energy release rate [94]. Figure 6.11 and equation (6.8) derive the corresponding cohesive energy density $\Gamma = 0.4917 \text{ N/m}$, which is higher than the result based on the potential energy difference between the perfect and split model as equation (6.1) shows. The divergence may come from the use of a fixed volume to overestimate the local stress under large deformation.

Figure 6.11 Normal stress σ_{yy} as a function of atomistic separation displacement u_y .

6.4 Conclusions

Compared with the fracture parameter based on singular stress (the critical stress intensity factor or the related energy release rate through the G - K relation) as a function of the size of K -dominance zone, the critical energy release rate on the basis of finite

crack extension, i.e., the results by calculating the difference between the variation of external and internal work in Section 6.2 or the cohesive energy density in Section 6.3, remains a constant with respect to the different specimen geometries. In addition, the critical energy release rate calculated by energy balance is shown to be close to the value of 2γ based on the potential energy difference between the perfect and split model (as equation (6.1) shows). This indicates even though the Griffith energy balance is still valid no matter how specimen geometries is downsized to nanoscale, the concept of continuum fracture mechanics which takes the limit of vanishing crack extension is not directly applicable while the size of K -dominance zone is extremely small. Therefore, if we use the fracture toughness drawing on the stress singularity to predict the failure of nanostructures, the two-parameter model including the contribution of non-singular over the critical distance x_c has to be taken into consideration.

7. CONCLUSION AND FUTURE WORK

7.1 Summary

As a starting point to discuss the applicability of continuum fracture mechanics in atomistic systems, Chapter 1 reviewed the advancement of nanotechnology as the motivation for why this dissertation focuses on the nanoscale and the size effect on the elastic constants of nanostructures, which implies the possible size effect on the fracture toughness inspired by the continuum fracture mechanics based on stress singularity.

Since molecular dynamics was selected to simulate the failure behavior of brittle crystals solids, statistical mechanics, the theoretic foundation of MD simulation, was briefly introduced in Chapter 2. With consideration of a system containing a larger number of atoms, statistical mechanics leads to the issue of the sum of all possible microstates (the atomistic positions and momentums), denoted as partition function, in thermodynamic equilibrium. According to different thermodynamic environments (ensembles), these partition functions provide the reference to modify the Hamiltonian with additional variables (extended phase) to satisfy the statistical property of a many-particle system. The corresponding equations of motion, derived by the Hamiltonian with additional variables, constitute the backbone of molecular dynamics. Accompanied by initial conditions and interatomic potentials, the position and velocity of each atom at any given time can be solved by the numerical integration algorithms.

Even though the trajectory of each atom has been discovered, we still face the problem of how we can interpret the molecular simulation results in terms of continuum mechanics (similar to the Boltzmann's relation stating entropy in terms of the number of microstates). Thus, the virial and Hardy theorems were introduced to measure the stress, one of the macroscopic continuum variables, by homogenizing a group of atoms as a material point. Additionally, coming from the desire to examine the applicability of continuum fracture mechanics, the averaging volume where a local stress can converge is supposed to be as small as possible to reflect the detailed stress concentration near the crack tip. Chapter 3 demonstrates that once the periodic averaging volume is considered, both local virial and Hardy stress can converge within one single lattice. With comparison of the near-tip stress distributions (at the critical strain) between the virial and Hardy's theorems, we demonstrated that the local virial stress based on the square-shaped volume (a periodic averaging spanning over the entire thickness of the specimen) is the most appropriate way to present the characteristic brittle fracture process in NaCl crystals due to the close match between the peak stress and the theoretical strength.

In Chapter 4, based on a NaCl crystal with a central crack initiated by removing interatomic bonds, the capability of actually determining the near-tip stress in discrete systems provides the evidence that the artificial cutting-bond influences the characteristics around the initial crack tip and thus the failure condition is taken as the applied strain corresponding to the maximum normal stress state of the second unit cell (not the first unit cell) ahead of the initial crack. To maintain the equivalence between the MD and the FEM model, except for the periodic boundary condition in the transverse direction and the identical magnitude of applied displacement, one consideration is that

the crack tip no longer stays at the initial position but moves forward a lattice constant since the lattice with the maximum normal stress has been moved from the first unit cell to the second one. Another consideration is that the material properties are not constant but decreasing along with the increasing applied strain due to the nonlinearity of the potential function. Compared with the FEM solution, the near-tip stress of the MD simulation shows even though its maximum value is finite (the maximum stress that a unit cell can sustain is close to the theoretic strength), the distribution follows the trend of inverse square root singularity. Subsequently, with consideration of six models with different crack lengths, the trend of the size-dependent fracture toughness (for both critical stress intensity factor and energy release rate), indicating that fracture toughness decreases with the decreasing crack length, can be obtained by both MD and FEM simulations. This phenomenon can be explained in terms of the size of the K -dominance zone representing the strength of singular stress. The fracture toughness approaches a constant value only when the size of K -dominance is large enough. For the situation of non-constant fracture toughness when the singular stress is not dominant (the small K -dominance zone), the two-parameter model including the contribution of the non-singular term is shown to be accurate in predicting the failure load.

Chapter 5 further focuses on the size-dependent fracture toughness induced by the geometric confinement. It is shown that the diminishing size of the K -dominance zone is still the main reason why fracture toughness decreases with the reduction of the specimen height (the dimension perpendicular to the crack line), like the role of the crack length in the previous chapter. By contrast, for the cases with the ratio of specimen height to crack length larger than 6 (the specimen height is larger than 500 Å in this study), the saturated

size of the K -dominance zone leads to a constant value of fracture toughness. Furthermore, the two parameters in the new fracture criterion (the two-parameter model) are verified as material constants since the prediction and the simulation data based on various specimen heights are consistent with each other. It is also noteworthy that as the specimen height decreases, the type of failure transits from catastrophic (the permanent drop in the stress-strain curve when the applied strain is larger than its critical value) to sustainable (the zigzag distributions in the stress-strain curve before the final failure).

This steady crack growth motivated us to conjecture if it would be possible to estimate the static energy release rate through the overall Griffith energy balance, instead of the G - K relation. Thus, in Chapter 6, we calculated the separation work per unit crack growth by determining the amount of the external work done minus the change of internal energy stored in a body. Since the potential energy obtained by MD simulations cannot reflect the energy loss during the crack extension, the change of internal energy is evaluated by the strain energy in the FEM models. With consideration of secant moduli and crack tip positions updated by the unit cell with the maximum normal stress, the corresponding surface energy (2γ) is found to be independent of the specimen height change and its value is close to that based on the potential energy difference between a perfect and split crystal. Furthermore, following the area underneath the traction-separation relation as the separation work per unit area, the atomistic traction-separation relation is measured by the local virial stress in Chapter 3 and the atomistic opening displacement. Even though the cohesive energy density (the separation work per unit area) is slightly larger than those values from Griffith energy balance, it is noteworthy that the traction-separation distributions and the related cohesive energy density remain the same

no matter how the crack length changes. Thus, different from the critical energy release rate based on the continuum fracture mechanics theory, all these results based on the finite crack extension are size-independent.

7.2 Recommendation for Future Work

This dissertation initiates the frameworks of observing the non-uniform stress distribution in discrete systems and discussing the size-dependent fracture toughness resulting from stress singularity. The following lists some research topics which could possibly be extended from the current work:

1. More sophisticated materials: Due to its brittle behavior, sodium chloride, a simple cubic crystal, was chosen as the main targeted material. Since Chapter 3 has shown that the concept of periodic averaging volume to converge the local atomistic stress is applicable for other kinds of crystals, it is of interest to determine the near-tip stress distributions in the more sophisticated or even nanocrystalline materials. Furthermore, in this study, we only considered the situation of nonlinear softening (see Figure 4.1). Checking whether the size-dependent effect is influenced by the constitutive behavior, i.e., nonlinear stiffening, would be a potential topic.
2. Non-local elasticity and multi-scale simulation techniques: Following the non-local elasticity also averaging the stress around a material point by the “kernel function”, there seems to be similarity between the Hardy stress and non-local elasticity. As discussed in Chapter 3, the same as the virial stress, the convergence of Hardy stress can be accomplished by using the periodic averaging volume. This could

provide the guidelines to choose the kernel function and related averaging volume size in non-local elasticity. On the other hand, the periodic averaging volume could also benefit multi-scale modeling techniques since it ensures a smooth communication between the discrete and continuous domains.

Figure 7.1 Different failure mechanisms in brittle NaCl crystals (a) crack propagation in the removing-bond model; (b) dislocation emission along the $\{110\}$ plane in the removing-atom model.

3. Brittle-ductile transition: In brittle sodium chloride, dislocation, a phenomenon known as ductile failure, could possibly occur if the stress concentration is diminished. As Figure 7.1 shows, two models are created with a crack by cutting 6 interatomic bonds and a vacancy by removing 6 columns of atoms, respectively. Under the tensile loading, in contrast to the cracked model showing crack

propagation, Figure 7.1(b) shows two symmetric dislocations nucleating at the corner of the vacancy and emitting along the $\{110\}$ plane. Determining the stress distributions around the geometric discontinuity would be a significant procedure to determine the competition between the brittle and ductile failure mechanisms and thus develop the proper failure criterion.

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VITA

VITA

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