Chapter 6

Thermal Energy

Due to the nature of the Lennard-Jones energy function, it can be used to model both the limited flexible deformations of a solid and the rapidly varying geometry of a liquid. By varying the dissociation energy of the Lennard-Jones function, we can model a continuous range of materials. For rigid solids, we increase the magnitude of the dissociation energy, and for flexible solids we decrease the magnitude. Further decreases result in fluid like behavior. Thus by varying the dissociation energy as a function of thermal energy, we can create models that "melt" and "freeze". This chapter describes in detail how we model the effects of thermal energy on the potential energy function, and a model of the continuous heat equation in terms of discrete particles.

6.1 The Heat Equation

At the macroscopic level, the thermal energy ψ in a body A is given by integrating over the volume,

$$\psi = \int_V \rho\sigma\theta \, dV = \iiint_A \rho\sigma\theta \, dxdydz, \tag{6.1}$$

where V is the volume, $\rho(x, y, z)$ is the mass density of the body, $\sigma(x, y, z)$ is the specific heat, and $\theta(x, y, z)$ is the temperature. The amount of heat leaving a body per unit time is given by

$$\int_S \mathbf{n} dS = \iiint_A \nabla \cdot (K\nabla\theta) \; dxdydz, \tag{6.2}$$

where S is the surface, $\mathbf{n}$ is the surface normal, and K is a 3×3 symmetric matrix known as the thermal conductivity matrix.

Setting the rate of decrease of thermal energy in the body equal to the amount of thermal energy leaving the body, we arrive at the partial differential equation called the heat equation

$$\frac{\partial \rho\sigma\theta}{\partial t} = \nabla \cdot (K\nabla\theta) \,. \tag{6.3}$$

For a homogeneous and isotropic material $K = kI$, where I is the identity matrix, the equation reduces to the familiar form

$$\frac{\partial \rho\sigma\theta}{\partial t} = k\nabla^2\theta, \tag{6.4}$$

where ∇^2 is the Laplacian.

6.2 Discrete Heat Equation

We use a discrete approximation of the general heat equation (6.3) to solve for the thermal energy and temperature of each particle over time. The thermal energy of a particle is related to the temperature as follows. We assume the specific heat σ and temperature θ are constant for a given particle. The mass m of an object is equal to integrating the mass density ρ over the object's volume. Since we already know the mass, we do not need to specify the mass density or volume of a particle. From (6.1) the thermal energy ψ_i for a particle reduces to

$$\psi_i = \sigma_i\theta_i m_i. \tag{6.5}$$

The change in thermal energy of particle i over a time interval Δt

$$\frac{\psi_i^{t+\Delta t} - \psi_i^t}{\Delta t} \tag{6.6}$$

approximates the left side of the heat equation.

To approximate the right side of the equation, the $\nabla \cdot (K\nabla)$ term, we introduce a thermal conductivity variable k_{ij} between each pair of particles i and j. The thermal conductivity is a measure of the rate of thermal energy transfer within a given material. Insulators, such as Styrofoam, will have a lower thermal conductivity than conductors, such as steel. We compute the approximation on a pairwise basis

$$\nabla \cdot (K\nabla\theta) \approx \sum_{j\in\mathcal{N}_i} \frac{\frac{1}{n_i}k_{ij}\left(\theta_j - \theta_i\right)}{\frac{1}{4}r_{ij}^2}, \tag{6.7}$$

where r_{ij} is the distance between particles i and j, $\mathcal{N}_i$ is the set of nearest neighbors for particle i, and n_i is the cardinality of $\mathcal{N}_i$.

The approximation is based on the finite difference method. To see this, we look at the 2D hexagonal configuration of particles shown in Figure 6.1. Let us consider the case of the center particle, numbered 0, which has 6 neighboring particles, numbered 1 through 6. The Laplacian of the temperature at the center particle $i = 0$ is

$$\nabla^2\theta_0 \approx \frac{\frac{1}{6}\left(\theta_1 + \theta_2 + \theta_3 + \theta_4 + \theta_5 + \theta_6\right) - \theta_0}{\frac{1}{4}r^2} = \sum_{j=1}^{6} \frac{\frac{1}{6}\left(\theta_j - \theta_0\right)}{\frac{1}{4}r^2} \tag{6.8}$$

when approximated by finite differences (Vitasek, 1969). By combining (6.6) and (6.7), we arrive at a discrete version of the heat equation over a three dimensional hexagonal grid. Heat dissipation into the external environment can easily be modeled by adding a term such as $-\beta_h\theta_i$ to the discrete heat equation.

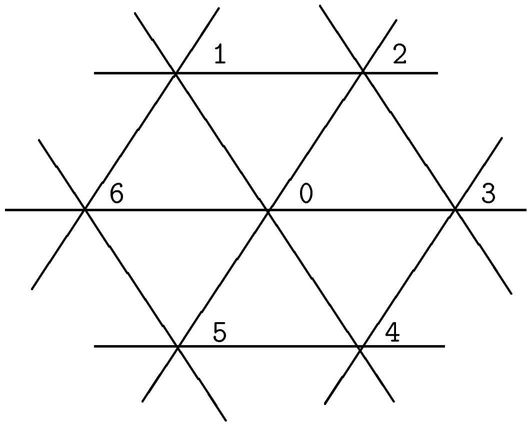

Figure 6.1: Finite difference grid for the Laplacian

6.3 States of Matter

Having laid the basic ground work, we now consider the physical states of matter as a discrete system. Liquids are qualitatively different from solids and the difference is a matter of geometry (Barton, 1974). At the molecular level, when external forces are insignificant, molecules arrange into closely packed structures to minimize their total energy. For spherically symmetrical potential energy functions in 2-D, particles arrange into hexagonal orderings (Figure 3.5). In 3-D, the molecules arrange into hexagonal ordered 2-D layers.

As thermal energy is added to the system, the molecules begin to vibrate and the entropy in the system increases. This movement is quantified at the molecular level as kinetic energy. It is the relationship between molecular kinetic energy and inter-molecular binding energy that determines the amount of entropy, and thus the state of the ensemble. At low temperatures, the mean binding energy is greater than the mean kinetic energy, and the material is highly ordered as a solid. At high temperatures the mean kinetic energy is much greater than the mean binding energy and the material is in total disorder as a gas. In the liquid state the molecules are sufficiently close together for there to be local ordering, with only a small amount of compressibility, but the kinetic energy is large enough to prevent long-range ordering. It is the ability to provide such fluid changes in structure that we which to capture in our approach to modeling.

6.4 Thermal Energy

As an object heats up, we do not increase the kinetic energy of the particles as Greenspan does in his simulations of solids (Greenspan, 1973) or as in the molecular model (Trevena, 1975). Instead, we collapse the mean kinetic energy (thermal energy) of a small volume into a change in potential energy between volumes. We model thermal energy and the inter-particle potential energies together by a continuous

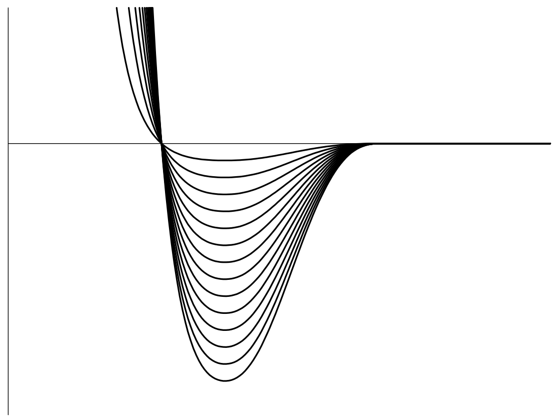

Figure 6.2: Family of inter-particle potential functions.

The weighted Lennard-Jones potential function plotted for $m = 2$, $n = 4$, $r_o = 1$, $r_a = r_o$, $r_b = \sqrt{3}r_o$, and $e = 1 \dots 14$. The potential is weighted to include only nearest neighbors.

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family of inter-particle potential energy functions. Figure 6.2 shows several functions from a family of functions. "Cold" temperatures map to functions with low potential energy minima (deeper energy wells), while "hot" temperatures map to functions with higher potential energy minimal (shallow wells). As thermal energy is added to a system the total energy increases accordingly.

It is instructive to compare the differences between the typical molecular dynamics model using particles and our particle approach. In the molecular dynamics model, the addition of thermal energy increases the kinetic energy and the inter-molecular potential energy function is fixed. The average speed of a volume of molecules corresponds to a measure of thermal energy. The average velocity of a volume corresponds to the rigid body motion of that volume.

In our model, the addition of thermal energy decreases the inter-particle potential energy while the kinetic energy is unchanged. The velocity of a single particle directly parallels the rigid body motion of a small volume of material, i.e. the average velocity of a molecular volume. The dissociation energy of the Lennard-Jones potential corresponds to the combination of the binding properties and thermal energy. Addition of thermal energy increases the total energy of the system *without directly changing particle velocity*, thus avoiding the numerical instabilities, and possible visual artifacts, that would be introduced by increasing kinetic energy. We next discuss how we modify the binding potential. We discuss the practical consequences in the summary (Section 6.7).

6.5 The Thermoelastic Lennard-Jones Function

We now derive a thermoelastic version of the Lennard-Jones potential energy. To insure conservation of energy, we impose the following condition on our system: the addition of an amount of thermal energy to a particle system should increase the total energy of the system by that amount of energy, while leaving the kinetic energy of the system constant. Let us consider some given particle system in two different states, an unheated state $\mathbf{S}_0$ and in a heated state $\mathbf{S}_1$. We let E_{S0} be the energy of the system with zero thermal energy, and E_{S1} be the energy of the same system with the addition of E_H thermal energy. We write the energy conservation condition as

$$E_{S0} + E_H = E_{S1}.$$

Expanding the system energies into kinetic and potential components by (3.9) we have

$$E_{K0} + E_{P0} + E_H = E_{K1} + E_{P1}. \tag{6.9}$$

To derive thermal energy in terms of potential energies, we must formulate the problem in terms of particle pairs. Toward this end, we make several simplifying assumptions. These are:

- particle-particle interaction is limited to nearest neighbors,
- the system is at equilibrium,
- and thermal energy in E_1 is uniform throughout the system.

The first assumption can be easily enforced by setting our weighting function to go to zero at the range of the second nearest neighbor, a distance of $\sqrt{3}r_o$. The second assumption is equivalent to saying the system begins at absolute zero, and thus it must be in equilibrium. Because it is at equilibrium and interaction is including only nearest neighbors, the particles will be separated by the equilibrium spacing.

We begin by rewriting the potential energies E_{P0} and E_{P1} in terms of dissociation energy and thermal energy. The term E_{P0} is equal to the summation of the pairwise potential energies of an unheated system

$$E_{P0} = \sum_i^N \sum_{j \in \mathcal{N}_i} w_{ij} \phi_{ij_0}, \tag{6.10}$$

where ϕ_{ij_0} is potential defined for zero thermal energy. The magnitude of dissociation energy of the Lennard-Jones function for zero thermal energy is equal to some constant value, say e_0. Since the system is near equilibrium, neighboring particles are separated by the equilibrium separation r_o, the weighting function w_{ij} evaluates to unity, and the potential energy ϕ_{ij_0} evaluates to $-e_0$. Thus the inner summation reduces to a product of the average number of neighbors h times the dissociation energy e_o

$$\sum_{j \in \mathcal{N}_i} w_{ij} \phi_{ij_0} = \sum_{j \in \mathcal{N}_i} (1)(-e_0) = -he_0.$$

and (6.10) reduces to

$$E_{P0} = -Nhe_0. \tag{6.11}$$

Now let e_1 be the dissociation energy between a pair of particles in the heated system $\mathbf{S}_1$. Similar to above, the potential energy of $\mathbf{S}_1$ is

$$E_{P1} = -Nhe_1. \tag{6.12}$$

We can now compute a formula for the unknown dissociation energy e_1. Combining (6.9), (6.11), and (6.12) results in

$$E_{K0} - Nhe_0 + E_H = E_{K1} - Nhe_1.$$

By noting that the kinetic energy is constant, that is $E_{K0} = E_{K1}$, this reduces to

$$E_H = -Nh(e_1 - e_0).$$

Since we assume thermal energy is added uniformly to the system, we divide the thermal energy E_H among the N particles assigning each particle ψ thermal energy

$$N\psi = -Nh(e_1 - e_0).$$

The dissociation energy for zero thermal energy e_0 is constant and we solve for e_1,

$$e_1 = e_0 - \frac{\psi}{h}.$$

This describes a method to vary the Lennard-Jones dissociation energy allowing us to account for thermal energy.

To allow for heat transfer throughout the system, we remove the assumption of uniform addition of thermal energy and allow the particles to have differing amounts of thermal energy. We modify the dissociation energy defined between two particles to be a function of the average of both particles, and two constants; the dissociation energy between a pair of particles with zero thermal energy e_o, and the average number of neighbors h (6 for a surface, and 12 for a volume).

$$e_{ij}(\psi_i, \psi_j) = e_o - \frac{\psi_i + \psi_j}{2h}$$

The final form of the thermoelastic Lennard-Jones potential is as follows:

$$\phi(\|\mathbf{r}_{ij}\|, \psi_i, \psi_j) = \frac{-1}{m-n}\left(e_o - \frac{\psi_i + \psi_j}{2h}\right)\left(m\left(\frac{r_o}{\|\mathbf{r}_{ij}\|}\right)^n - n\left(\frac{r_o}{\|\mathbf{r}_{ij}\|}\right)^m\right), \tag{6.13}$$

where $\|\mathbf{r}_{ij}\| = \|\mathbf{x}_j - \mathbf{x}_i\|$ is the magnitude of separation between particles i and j. This formulation is valid for all values of $\psi < e_o h$. Note that negative values of temperature are equivalent to increasing the stiffness of the material, i.e. increasing the magnitude of e_o.

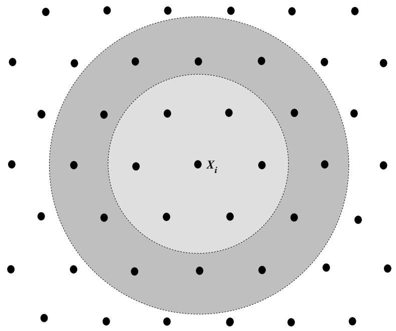

Figure 6.3: Neighborhood Interactions

6.6 Thermal Expansion

When the temperature of a body is raised or lowered, the material will expand or contract. Thermal linear expansion is described by the following formula (Case, 1938)

$$l_2 = l_1 \left(1 + \alpha(\psi_2 - \psi_1)\right) \tag{6.14}$$

where l_1 is the length of a rod at temperature ψ_1, l_2 is the length at temperature ψ_2, and α is the linear expansivity. That is, the rod will expand by the amount $l_1 \alpha \Delta\psi$. If the expansion is opposed, then the resulting stress $E l_1 \alpha \Delta\psi$ will be determined by Young's modulus (3.19). Linear volume expansion is described by

$$V_2 = V_1 \left(1 + \beta(\psi_2 - \psi_1)\right)$$

where V_1 is the volume at temperature ψ_1, V_2 is the volume at temperature ψ_2, and β is the volume or bulk expansivity. For values of less than 2%, the volume expansivity is approximated well by $\beta = 3\alpha$. In general, solids and liquids expand upon heating, and contract upon cooling [CRC mathbook pg. 317]. The expansivity coefficients for liquids tend to be much larger than for solids. Water is a notable exception in which the expansivity depends on temperature and has a negative value over the range of 0^oC and 4^oC.

The thermal energy model for our particle system maintains a common equilibrium separation and collision distance, to avoid unwanted side effects. The expansion or contraction of the particle model due to temperature changes is dependent on the neighborhood range. We consider two cases for which the system is at minimum energy.

In the first case, the neighborhood range is such that a given particle only interacts within the first shell of neighboring particles as shown by the smaller circle in Figure 6.3. At equilibrium, each neighboring particle will be separated by the equilibrium separation r_o and the inter-particle forces will be zero. As the object heats, the equilibrium separation will remain constant and the object neither expands nor contracts. To tailor the equilibrium separation to specific materials, one could vary the equilibrium separation according to (6.14), rewritten here as

$$r_o(\psi_2) = r_o(\psi_1) \left(1 + \alpha(\psi_2 - \psi_1)\right) \tag{6.15}$$

where α is the linear expansivity, $r_o(\psi_1)$ is the equilibrium separation at ψ_1, and $r_o(\psi_2)$ is the equilibrium separation at ψ_2. Coefficients of expansion for a wide variety of solids and liquids can be found in (Miner and Seastone, 1955).

In the second case, the neighborhood range is expanded to include particles beyond the nearest neighbors, i.e. particles within the larger circle shown in Figure 6.3. At equilibrium, there will be compression of the solid due to the long range attractive forces between the center particle and the distant neighbors. As the temperature decreases, these attractive forces will become stronger and the particle system will contract further. In this case, the model mimics the general rule of decrease in volume when the temperature decreases and expansion of volume when the temperature increases.

6.7 Summary

The contributions of this chapter are the introduction of a particle based thermoelastic model with energy conservation and the introduction of a discrete heat transfer model derived from the macroscopic heat equation. Our thermoelastic model states that the elastic force of the Lennard-Jones potential is linearly related to the thermal energy (and thus temperature), as is the thermoelastic model presented by (Terzopoulos, Platt and Fleischer, 1989) for spring-mass systems. It extends their model to particle systems and adds the constraint of conservation of thermal, kinetic, and potential energy over the system. Heat transfer is based on the continuous heat equation at the macroscopic level, which is implemented as a finite difference scheme over a hexagonal grid.

The model includes the physical quantities of thermal energy, volume, mass density, mass, specific heat, temperature, and thermal conductivity. For each particle we need to add only one new variable of state, the thermal energy of the particle, and one variable to accumulate the heat transfer between neighbors. A thermal conductivity variable could also be added to each particle to model non-homogeneous materials. The remaining physical quantities can be defined as constants or derived from existing state variables.

Our model focuses on variations in malleability and does not model a variety of more complex phenomena found in real world materials. For example, it does not necessarily model the changes in volume found in some materials such as the expansion of water upon freezing, the shrinking of many metals when cooled and some plastics upon heating. Instead, the model encourages conservation of volume. Such volumetric changes could be added to the model by defining the equilibrium separation parameter r_o as a function temperature, as given in equation (6.15). Our model is valid for the range $\psi < he_o$ which accounts for solid and fluid behavior. It is invalid when $\psi \geq he_o$. That is, we do not model gaseous behavior.[1]

[1]When $\psi = e_o h$, the Lennard-Jones potential evaluates to zero, and when $\psi > e_o h$ the potential inverts, resulting in long range repulsive forces and short range attractive forces. The long range repulsive forces mimic the nature of a gas. The short range attractive forces encourage nearby particles to occupy the same position, unlike a gas. Thus if we wanted to mimic gaseous behavior,

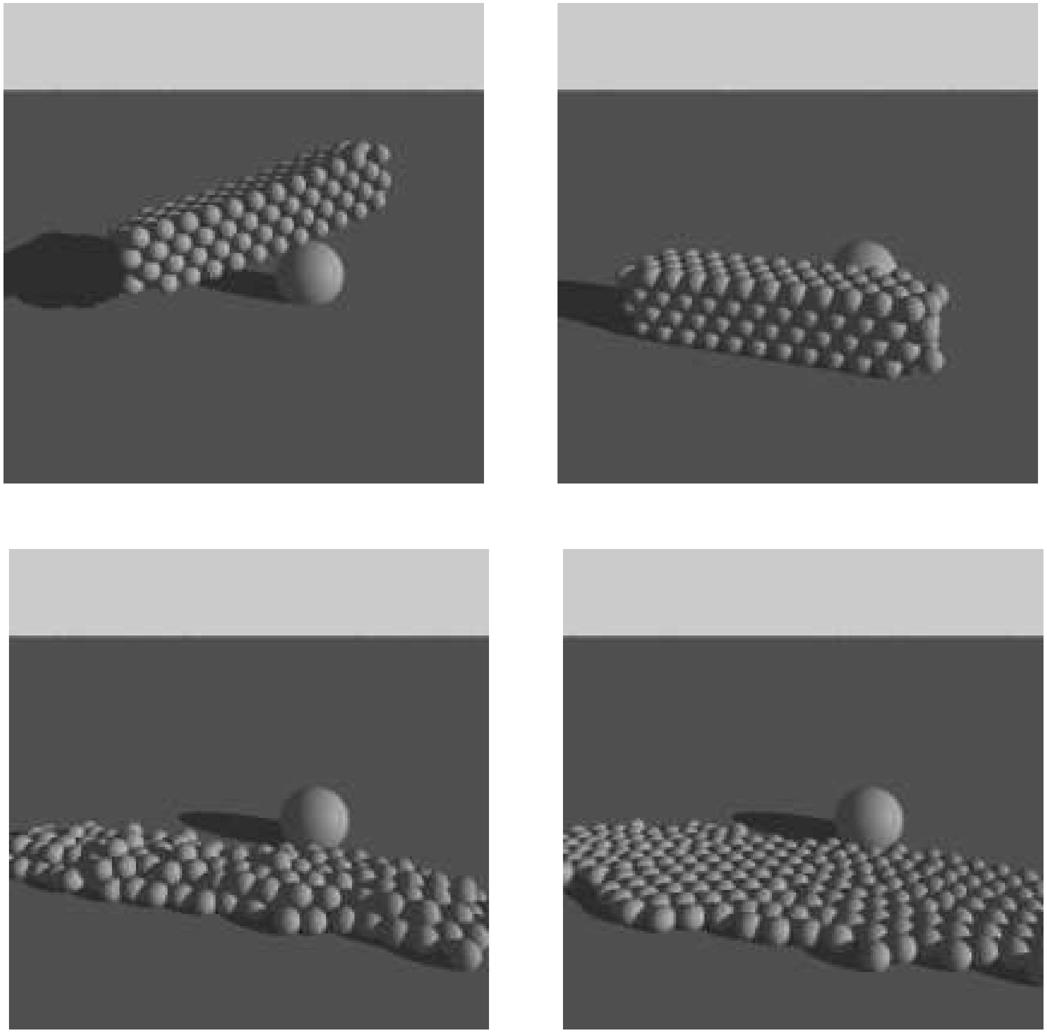

Figure 6.4: Beam colliding and melting

The first two frames shows the initial rigid structure of the beam colliding with an object and coming to rest on the ground plane. It is highly ordered and maintains it's structure even under external forces and collisions. As heat is transferred from the ground plane into the object, the inter-particle bonds weaken and the beam exhibits fluid like behavior with quickly changing structure.

A simple example of melting is shown in Figure 6.4. A solid beam is dropped, colliding with a sphere and the ground plane. After coming to rest, it is "heated" by the ground plane. Heat is transferred through the beam according to the discrete heat transfer model. The resulting weakening of the inter-particle bonds causes the solid to "melt", thus losing its initial structure. Other applications of heat are shown in Figures 8.11 and 8.12, where heat is used to locally modify the properties of a surface, making it more malleable than the surrounding material.

we would need to replace the attractive force with a repulsive force for all values $\psi \geq e_o h$. One possible solution would be to replace the Lennard-Jones with a purely repulsive force at these values.