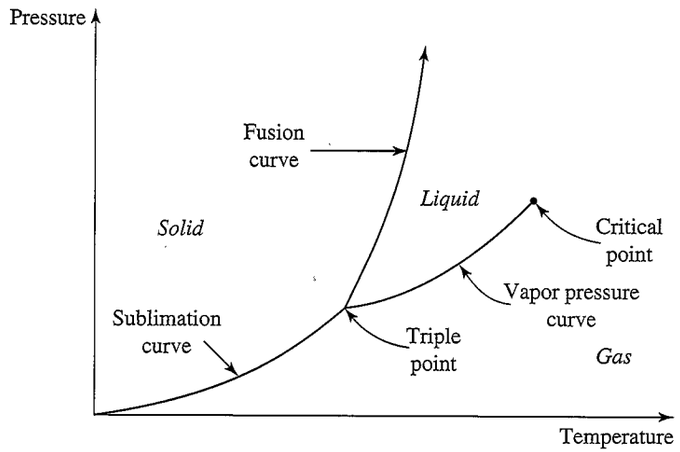

Figure 15.6 A sketch of the phase diagram for a simple material.

density fluctuations and, hence, a probe of the local order in the system. If only two-body forces are present, the mean potential energy per particle can be expressed as (see (8.16))

$$\frac{U}{N} = \frac{\rho}{2}\int g(r)u(r)\,d\mathbf{r}, \tag{15.44}$$

and the (virial) equation of state can be written as (see (8.17))

$$\frac{\beta P}{\rho} = 1 - \frac{\beta\rho}{2d}\int g(r)\,r\frac{du(r)}{dr}\,d\mathbf{r}. \tag{15.45}$$

Hard core interactions. To separate the effects of the short range repulsive interaction from the longer range attractive interaction, we first investigate a model of *hard disks* with the interparticle interaction

$$u(r) = \begin{cases} +\infty & r < \sigma \\ 0 & r \geq \sigma. \end{cases} \tag{15.46}$$

Such an interaction has been extensively studied in one dimension (hard rods), two dimensions (hard disks), and three dimensions (hard spheres). Hard sphere systems were the first systems studied by Metropolis and coworkers.

Because there is no attractive interaction present in (15.46), there is no transition from a gas to a liquid. Is there a phase transition between a fluid phase at low densities and a solid at high densities? Can a solid form in the absence of an attractive interaction?

What are the physically relevant quantities for a system with a hard core interaction? The mean potential energy is of no interest because the potential energy is always zero. The major quantity of interest is $g(r)$ which yields information about the correlations of the particles and the equation of state. If the interaction is given by (15.46), it can be shown

that (15.45) reduces to

$$\frac{\beta P}{\rho} = 1 + \frac{2\pi}{3}\rho\sigma^3 g(\sigma) \quad (d = 3) \tag{15.47a}$$

$$= 1 + \frac{\pi}{2}\rho\sigma^2 g(\sigma) \quad (d = 2) \tag{15.47b}$$

$$= 1 + \rho\sigma g(\sigma) \quad (d = 1). \tag{15.47c}$$

We will calculate $g(r)$ for different values of r and then extrapolate our results to $r = \sigma$ (see Problem 15.23b).

Because the application of molecular dynamics and Monte Carlo methods to hard disks is similar, we discuss the latter method only briefly and do not include a program. The idea is to choose a disk at random and move it to a trial position as implemented in the following:

```
int i = (int)(N*Math.random()); // choose a particle at random
// delta is maximum displacement
xtrial += (2.0*Math.random() - 1.0)*delta;
ytrial += (2.0*Math.random() - 1.0)*delta;
```

If the new position overlaps another disk, the move is rejected and the old configuration is retained; otherwise, the move is accepted. A reasonable, although not necessarily optimum, choice for the maximum displacement δ is to choose δ such that approximately 20% of the trial moves are accepted.

The major difficulty in implementing this algorithm is determining the overlap of two particles. If the number of particles is not too large, it is sufficient to compute the distances between the trial particle and all the other particles, instead of just considering the smaller number of particles that are in the immediate vicinity of the trial particle. For larger systems this procedure is too time consuming, and it is better to divide the system into cells and to only compute the distances between the trial particle and particles in the same and neighboring cells.

The choice of initial positions for the disks is more complicated than it might first appear. One strategy is to place each successive disk at random in the box. If a disk overlaps one that is already present, generate another pair of random numbers and attempt to place the disk again. If the desired density is low, an acceptable initial configuration can be computed fairly quickly in this way, but if the desired density is high, the probability of adding a disk will be very small (see Problem 15.24a). To reach higher densities, we might imagine beginning with the desired number of particles in a low density configuration and moving the boundaries of the central cell inward until a boundary just touches one of the disks. Then the disks are moved a number of Monte Carlo steps and the boundaries are moved inward again. This procedure also becomes more difficult as the density increases. The most efficient procedure is to start the disks on a lattice at the highest density of interest such that no overlap of disks occurs.

We first consider a one-dimensional system of hard rods for which the equation of state and $g(r)$ can be calculated exactly. The equation of state is given by

$$\frac{P}{NkT} = \frac{1}{L - N\sigma}. \tag{15.48}$$

Because hard rods cannot pass through one another, the excluded volume is $N\sigma$ and the available volume is $L - N\sigma$. Note that the form of (15.48) is the same as the van der Waals