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Numerical simulations of the shape and 'phase transitions' in finite systems

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Abstract

Molecular simulations are very convenient to get insight into the structure and thermal behaviour of small atomic clusters. In this paper, we show how the classical Monte Carlo method can be used to tackle both the global optimization problem of molecular structure and the finite temperature properties. Smarter schemes to compute the caloric curves are also illustrated in the example of the histogram reweighting method.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Modern statistical mechanics often relies on numerical simulations as a practical way of validating theories through the use of 'computer experiments'. Many textbooks on the subject now include chapters on simulations, even though applications are commonly limited to discrete, Ising-type models. In material sciences, molecular chemistry and physics, Monte Carlo (MC) and molecular dynamics (MD) [1] methods have become widespread in addressing complex many particle problems that lack an exact solution such as liquid structure [2] or protein folding [3].

Atomic clusters are finite size aggregates containing between a few and millions of particles. Due to their small dimensions, their theoretical study faces a serious challenge, namely that most properties exhibit a strong dependence on the number of atoms [4]. These difficulties actually begin with structure itself, from which other characteristics will derive. It is usually not possible to predict the most stable structure of a finite set of atoms bound via known interactions. The reason for this is simple: the number of stable and distinct atomic arrangements is thought to grow with the system size at least exponentially [5]! The failure of exhaustive enumeration urges one to find approximate numerical solutions to this problem.

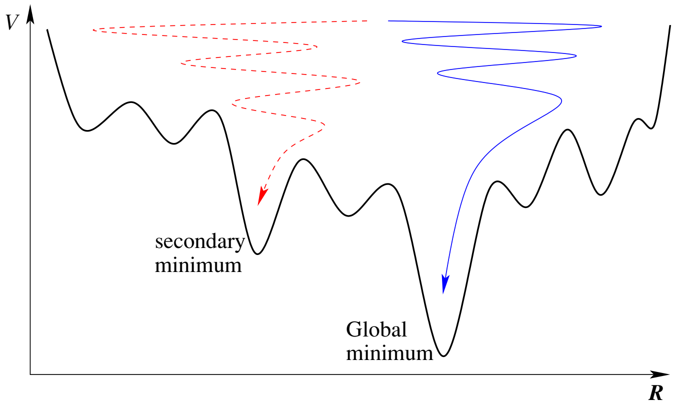

Figure 1. A schematic, one-dimensional potential energy surface. A successful global optimization attempt is represented by the solid arrow; a typical failed attempt is manifested in the trapping into a secondary minimum by the dashed arrow.

Here we present the simulated annealing algorithm, which remains a very general and popular global optimization method.

Another physical problem where the help of numerical methods is usually appreciated is that of phase transitions. Despite being phenomenologically well described, melting of bulk matter is still poorly understood. Finite size clusters also display a solid phase at low temperatures as well as a more disordered, 'liquid-like' phase upon heating. Predicting the temperature where the cluster changes phase also requires simulations. In this paper, the Metropolis Monte Carlo method is chosen to sample configuration space for structural optimization and for simulating thermal equilibrium in small Lennard–Jones (LJ) clusters.

2. Searching for structures by simulated annealing

Since its introduction in 1983 [6], the simulated annealing technique still stands as one of the most general and efficient ways of addressing the global optimization problem. Simulated annealing essentially consists of cooling the system slowly, possibly with regular but sudden heatings in order to facilitate escape from metastable minima. To illustrate how simulated annealing works, we have sketched a typical potential energy surface in figure 1, along with two optimization trajectories ending with different success.

The initial temperature, cooling schedule and total simulation length are the few but important parameters of a simulated annealing optimization. Starting from a random atomic configuration, the MC simulation is carried out following the Metropolis acceptance rule [7], and after some number of steps, the temperature is decreased. Of course, the longer the simulation, the greater chances of success of the optimization. From a more physical perspective, the initial temperature and the temperature after the annealing events also play an important role. If the potential energy surface is characterized by an average energy barrier ΔE, then the temperature should be at least equal to $\Delta E/3N$, otherwise the system will likely be trapped close to its starting basin of attraction. On the other hand, refining the geometry to locate low-energy states requires the final temperature to be rather low. The frequency and magnitude of annealing should also be tuned. Due to the stochastic nature of the simulated annealing algorithm, it can never be guaranteed that the true global minimum has been found after an optimization trajectory. Hence, it is recommended that several independent runs be

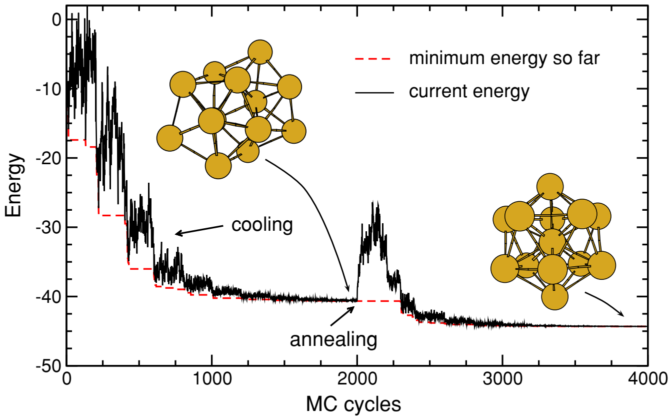

Figure 2. Variations of the minimum and instantaneous potential energy of the LJ_{13} cluster during a typical Monte Carlo simulated annealing trajectory with 20 cooling stages, and one annealing stage at mid trajectory. The final stable structures are also represented, the global minimum being icosahedral.

performed starting from different random configurations. We have illustrated in figure 2 the course of a Monte Carlo simulated annealing optimization, on the example of the 13-atom LJ cluster. The Lennard–Jones units of energy and distance are being used here, that is, the Boltzmann constant k_B is set to 1 and the interaction between particles at distance r is exactly given by

$$V_{\mathrm{LJ}}(r) = 4\left(\frac{1}{r^{12}} - \frac{1}{r6}\right). \tag{1}$$

In the typical trajectory portrayed in figure 2, two cooling schedules are separated by one annealing event. The temperature exponentially varies between 1 and 2×10^{-2} during the first cooling stage and between 0.3 and 10^{-3} during the second cooling state. In the above example the first cooling stage quenches the cluster into a secondary minimum, but upon annealing the system wanders over new parts of configuration space, finding its way to the true global minimum (here, an icosahedron). Locating the most stable structure turns out to be particularly easy at size 13, but this special, ‘magic’ size is not fully representative of LJ clusters. Larger systems generally need much longer trajectories, because the interactions and number of isomers are more numerous, but also because the global minimum is not always separated from the other minima by a substantial energy gap. In such cases, optimization is drastically hampered by the competition between the various low-lying structures.

3. Phases and phase changes: computer calorimetry

Before talking of phase changes, the first task should be to define what a *phase* actually is. Even with the help of computer simulation, it has not yet been possible to find a device which properly identifies phases in small systems. For example, the usual definition of a liquid (something which accommodates the shape of its container) cannot be used here, for any container would so strongly interact with the system that it would completely modify its behaviour. Fortunately, although we do not know what a phase is, we can still tell when a system undergoes a phase change. The tool for this is well known and as old as thermodynamics itself. It is named calorimetry, and consists in measuring the increase of temperature of the system as a function

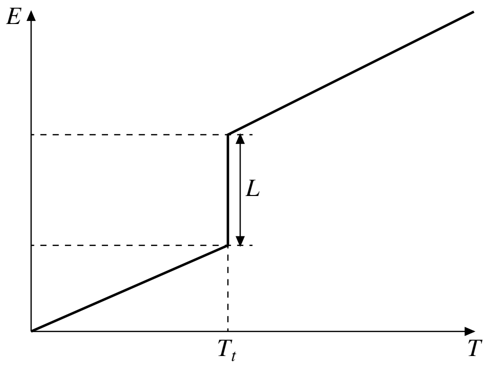

Figure 3. Schematic of a caloric curve in a macroscopic system, across a first-order phase transition.

of the amount of energy injected in it. In a macroscopic system, the increase of temperature is roughly proportional to the injected energy as long as there is a single phase in the system. This steady increase suddenly drops when a second phase appears. Then the temperature remains constant as long as the two phases coexist with each other, and the injected energy is only used for transforming the low-temperature phase into the high-temperature phase. Once the former has disappeared, the temperature starts increasing again. A schematic plot of the energy as a function of temperature (the *caloric curve*) is given in figure 3.

3.1. A computer calorimeter

When using the conventional MC method in the canonical ensemble, no thermometer is needed since the temperature of the system is given as a parameter. On the other hand, the measurement of energy is slightly more subtle: a system at thermodynamical equilibrium constantly changes its configuration, visiting states of total energy E with the corresponding Boltzmann probability $\mathrm{e}^{-\beta E}$. The internal energy of our system is precisely equivalent to the average of all these energies. Furthermore, the kinetic part of E, K, does not have a significant role in phase transitions, because its average varies linearly with temperature, independently of the nature of the phase: $\langle K\rangle = 3Nk_{\mathrm{B}}T/2$. It is thus sufficient to compute the average potential (or configurational) energy of our system. Figure 4 show the results of a Monte Carlo calculation of the internal energy for the 13-atom LJ cluster. The jump in energy is clearly visible in the vicinity of the reduced temperature 0.3. This increase is rounded compared to its macroscopic equivalent. The rounding effect, previously predicted on the basis of fluctuation theory [8], is one of the two main differences with phase transitions in bulk matter. The second difference is less clear in the figure. Simulating bulk melting reveals that the transition temperature takes place at about $T \simeq 0.69$. There is therefore a tremendous decrease of the melting temperature in our small system compared to the bulk. This decrease was predicted as early as 1909 [9] and interpreted qualitatively by capillarity theory.

3.2. Heat capacity

According to classical thermodynamics, the heat capacity C is the derivative of the caloric curve $\langle E\rangle(T)$. Looking at the curve in figure 4, it is evident that the jump in the caloric curve will correspond to a peak in heat capacity. However, computing numerically a derivative is very prone to noise. It is therefore safer to use the property that the heat capacity is

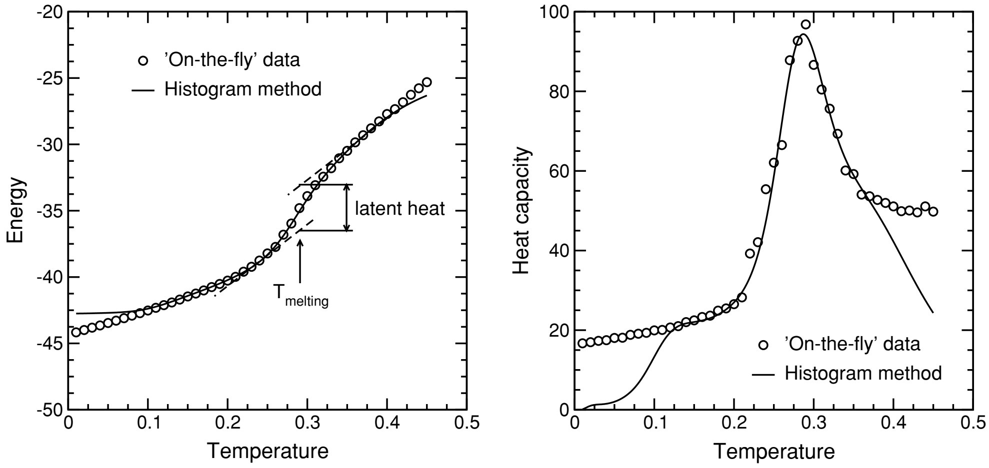

Figure 4. Thermal properties of the LJ_{13} cluster from direct or histogram-reweighted Monte Carlo simulations. Left panel: internal energy; right panel: heat capacity.

also related to the second moment of the distribution of energies at temperature T, namely $C = \Delta E^2/(k_B T^2)$. Such a calculation gives much smoother numerical behaviour. The results for the 13-atom LJ system, represented in figure 4, display a clear peak. This allows us to define more precisely the melting point as the temperature where C reaches its maximum. In the present case, we find $T_t \approx 0.29$.

3.3. More information from the energy distribution: histogram reweighting

In the standard simulation procedure we have been following previously, the energies were computed at each step, and were used for the direct, 'on-the-fly' estimation of the averages and standard deviation at the temperature prescribed in the simulation. But it turns out that a much greater amount of information can be inferred from the energy distribution [10]. The probability $p(E, T)$ to observe a given energy E at temperature T is proportional to the density of states at this energy $\Omega(E)$ times the Boltzmann factor $\mathrm{e}^{-E/k_B T}$. Thus, supposing we have binned together the energies in the histogram of the probability $p(E, T)$, the quantity $p(E, T)\,\mathrm{e}^{E/k_B T}$ is the density of states up to a constant factor. By multiplying $p(E, T)\,\mathrm{e}^{E/k_B T}$ by another Boltzmann factor $\mathrm{e}^{-E/k_B T'}$ we get the unnormalized probability distribution $p(E, T')$ at the new temperature T', from which the new average energy and fluctuation follow. Hence, with only one simulation, it is theoretically possible to obtain the probability distribution at any other temperature. The practical limitation of the method comes from the finite width of the energy distribution. Therefore, the histogram procedure is accurate only if the new temperature is close enough to that of the simulation. Figure 4 shows as solid lines the results obtained from one simulation at $T = 0.3$ reduced units. Here, the agreement with the other data is really good over a wide range of temperatures.

4. Concluding remarks

Even though atomic clusters have only a modest number of particles, they display a wide set of phenomena, ranging from unusual structure to complex dynamics and thermodynamics.

In this paper, simple clusters bound by Lennard–Jones forces were used to deal with two main issues for which the assistance of computers is invaluable.

Locating the optimal geometry is often a difficult task in molecular science, especially in the area of biomolecules where predicting the tertiary structure of a folded polypeptide still stands as one of the ultimate challenges. The simulated annealing algorithm, briefly described in section 2, has been historically introduced in order to solve such problems. Beyond static properties, the finite temperature behaviour of atomic clusters also provides many flavours of phase transitions, as seen from computer experiments. The thermal stability of small systems has recently been shown to exhibit a very strong but unexpected size dependence [11, 12]. This may have a practical importance in the context of growing miniaturization. Brute-force Monte Carlo simulations address this problem directly. However, it is possible to extract much more information from single trajectories than the direct averages, which we have illustrated here with the histogram reweighting technique.

The small Lennard–Jones system was chosen here so that meaningful results can be obtained from simulations within a reasonably short computer time. At this point, we should also mention that particle-based molecular dynamics could have been used instead of Monte Carlo in both the structural and thermodynamical studies. However, based on our own experience we feel that implementing an MD program is more demanding. Obviously, in more complex systems, the methods discussed in the present paper may become less efficient, and we refer the reader to the more advanced techniques described in [1] for possible improvements. Despite these limitations, we believe that atomic clusters offer an original introduction to molecular simulation for undergraduate students, as well as a stimulating illustration of statistical mechanics.

Appendix. An elementary Monte Carlo routine

A basic Monte Carlo simulation in the canonical ensemble is achieved by constructing a Markov chain of configurations $\{\mathbf{R}_i\}$, whose asymptotic distribution is used to calculate thermal observables. At the current configuration $\mathbf{R}_{\text{old}}$ with energy V_{old}, a random atom is chosen and displaced randomly in space within a prescribed distance from its previous location. The configuration $\mathbf{R}_{\text{new}}$ obtained this way, with energy V_{new}, is accepted as the next step of the Markov chain with the Metropolis acceptance rule, which ensures that detailed balance is satisfied:

$$\text{acc}(\mathbf{R}_{\text{old}} \to \mathbf{R}_{\text{new}}) = \min\{1, \exp[-(V_{\text{new}} - V_{\text{old}})/k_{\text{B}}T]\}. \qquad \text{(A.1)}$$

If the configuration is rejected, then $\mathbf{R}_{\text{old}}$ is replicated as the next step of the chain. It is usually wise to adjust the maximum displacement size in order that roughly half of the MC steps are accepted. For a pairwise potential such as Lennard–Jones, one should take care not to calculate the entire configuration energy after each move of a single atom, since only $N - 1$ interaction terms vary for an N-atom system. For better efficiency, the individual energies $V_i(\mathbf{R})$ should be stored along with the Cartesian coordinates, the total potential energy then being calculated according to $V(\mathbf{R}) = \frac{1}{2}\sum_i V_i(\mathbf{R})$.

The atomic coordinates are stored in the `x`, `y` and `z` arrays, the individual energies in the `v` array. Initially the coordinates are saved in the arrays `xold`, `yold` and `zold` in case they will be rejected. We denote by `ran`() a uniform random number in the range [0, 1[. The energy of the current configuration is saved as `Eold`. Only the pair energy between any two atoms `i` and `j` is required to compute V, and we code it into the function `VLJ`:

```
FUNCTION VLJ(x,y,z,i,j)
PARAMETER(n=13)
DIMENSION x(n),y(n),z(n)
r2=(x(i)-x(j))**2+(y(i)-y(j))**2+(z(i)-z(j))**2
rr6=1.0/r2**3
VLJ=4.0*rr6*(rr6-1.0)
RETURN
END
```

The main stages of the Metropolis Monte Carlo simulation are summarized below.

```
j=INT(n*ran()+1)
DO i=1,n
   IF (i.NE.j) v(i)=v(i)-VLJ(x,y,z,i,j)
ENDDO
x(j)=x(j)+hstep*(RAN()-0.5)
y(j)=y(j)+hstep*(RAN()-0.5)
z(j)=z(j)+hstep*(RAN()-0.5)
v(j)=0.
DO i=1,n
   IF (i.NE.j) THEN
      vij=VLJ(x,y,z,i,j)
      v(i)=v(i)+vij
      v(j)=v(j)+vij
   ENDIF
ENDDO
```

Atom `j` is randomly chosen, and all its interactions with other particles are removed. A new location for atom `j` is chosen, the interactions between `j` and the other atoms are then calculated, the array `v` being simultaneously updated.

```
Enew=etot(v)
IF (Enew.GE.Eold) THEN
   comp=EXP((Eold-Enew)/temp)
   IF (RAN().GT.comp) THEN
      DO i=1,n
         x(i)=xold(i)
         y(i)=yold(i)
         z(i)=zold(i)
         v(i)=vold(i)
      ENDDO
      Enew=Eold
   ENDIF
ENDIF
```

The new energy `Enew` is calculated from the individual energies `v`, and the Metropolis acceptance criterion is applied. If the step is rejected, then the previous configuration is restored, thus becoming the next step of the chain.

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