# 3. Computing Observables

Computer simulation methods are by now an established tool in many branches of science. The motivations for computer simulations of physical systems are manifold. One of the main motivations is that one eliminates approximations. Usually, to treat a problem analytically (if it can be done at all) one needs to resort to some kind of approximation; for example, a mean-field-type approximation. With a computer simulation we have the ability to study systems not yet tractable with analytical methods. The computer simulation approach allows one to study complex systems and gain in-sight into their behaviour. Indeed, the complexity can go far beyond the reach of present analytic methods.

Because they can be used to study complex systems, computer simulation methods provide standards against which approximate theories may be compared. At the same time, they allow the comparison of models with experiment, and provide a means of assessing the validity of a model. There is yet another feature. Computer simulations can fill the gap between theory and experiment. Some quantities or behaviours may be impossible or difficult to measure in an experiment. With computer simulations such quantities can be computed.

At the outset of a simulation stands a well-defined model of a physical system. We are interested in computing properties of the physical system. Our point of view is that the properties or observables appear as averages over some sample space. For example, in the percolation problem the threshold $p_c$, is the average probability of percolation over the space of all configurations. In the spring problem the temperature is computed as the average kinetic energy along the generated path.

## 3.1 Avergaing

For the main part we shall assume that a system under consideration has a model Hamiltonian $\mathcal{H}$. We denote a state of the system by $\mathbf{x} = (\mathbf{x_1}, ..., \mathbf{x_n})$, where $n$ is the number of degrees of freedom. The set of states constitutes the available phase space $\Omega$. The property $A$ to be calculated will be a function of the states of the system. As mentioned above, our point of view is statistical

mechanical. What we need to specify in order to compute the property $A$ is a distribution function $f(.)$. The quantity $A$ is then given by

$$\langle A \rangle = Z^{-1} \int_{\Omega} A(x) f(\mathcal{H}(x)) dx \tag{3.1}$$

where

$$Z = \int_{\Omega} f(\mathcal{H}(x)) dx$$

This is the ensemble average with the partition function $Z$. The distribution function $f$ specifies the appropriate ensemble for the problem at hand.

The ensemble average is often not accessible in computer simulations. In such simulations the quantity $A$ is evaluated along a path in phase space. Take the spring problem. We are not going to evaluate the temperature for a large number of similar systems, rather, we propagate the particle along a trajectory in phase space and evaluate the kinetic energy along the path. What we are computing is a time average

$$\bar{A}_t = (t - t_0)^{-1} \int_{t_0}^{t} A(x(\tau)) d\tau \tag{3.2}$$

The question arising is: Are the two averages the same? For this we must invoke ergodicity, allowing the replacement of ensemble averages by time averages

$$\langle A \rangle = \bar{A}_{\infty} \tag{3.3}$$

At this point, one of the two major limitations of computer simulation methods arises. Clearly a computer simulation cannot follow a path over an infinite time. The observation time is limited to a finite path length so that actually the available phase space is not sampled. One has to be content with

$$\bar{A} \cong \langle A \rangle \tag{3.4}$$

For some problems the finite observation time may be considered infinite. Consider, for example, the computation of a molecular system where the observation time is much larger than the molecular time. What we also have to take into account is the statistical error [**?**, **?**, **?**].

As well as the finite observation time, simulational physics is faced with a second major limitation: finite system size. In general, one is interested in the computation of a property in the thermodynamic limit, i.e., the number of particles tends to infinity. Computer simulations allow, however, only system sizes small compared to the thermodynamic limit so that there are possible finite-size effects. In order to reduce the finite-size effects an approximation is made that has thus far been suppressed, namely the introduction of boundary conditions. Boundary conditions clearly affect some properties.

## 3.2 Averaging and Correlation

Let us follow up the points made above. In deterministic as well as in stochastic computer simulation methods the successive configurations are correlated [**?**, **?**, **?**, **?**, **?**]. What does this mean if we calculate the time average of an observable $A$, which by necessity can cover only a finite observation time? Let us consider the statistical error for $n$ successive observations $A_i, i = 1, ..., n$:

$$\left\langle (\delta A)^2 \right\rangle = \left\langle \left[ n^{-1} \sum_{i=1}^{n} (A_i - \langle A \rangle)^2 \right] \right\rangle \tag{3.5}$$

In terms of the autocorrelation function for the observable $A$

$$\phi_A(t) = \frac{\langle A(0)A(t) \rangle - \langle A \rangle^2}{\langle A^2 \rangle - \langle A \rangle^2} \tag{3.6}$$

and the characteristic correlation time

$$\tau_A^{int} = \int_0^\infty \phi_A(t) dt \tag{3.7}$$

we can rewrite the statistical error as

$$\left\langle (\delta A)^2 \right\rangle \cong \frac{2\tau_A}{n\delta t} \left[ \left\langle A^2 \right\rangle - \langle A \rangle^2 \right] \tag{3.8}$$

where $\delta t$ is the time between observations, i.e., $n\delta t$ is the total observation time $\tau_{\text{obs}}$.

We notice that the error does not depend on the spacing between the observations but on the total observation time. Also the error is not the one which one would find if all observations were independent. The error is enhanced by the characteristic (integral) correlation time between configurations. Only an increase in the sample size and/or a reduction in the characteristic correlation time $\tau_A$ can reduce the error.

## 3.3 Spatial Averaging

Now that we know how the statistical error for an observable $A$ depends on the finite observation time, we can ask for the dependence on the finite system size. For this we define

$$\Delta(n, L) = \sqrt{\left( \langle A^2 \rangle_L - \langle A \rangle_L^2 \right) / n} \tag{3.9}$$

Here $L$ is the linear dimension of the system. Note that we write $< . >_L$ for the average. This is meant as the average with respect to the finite system size. How does this error depend on $L$.

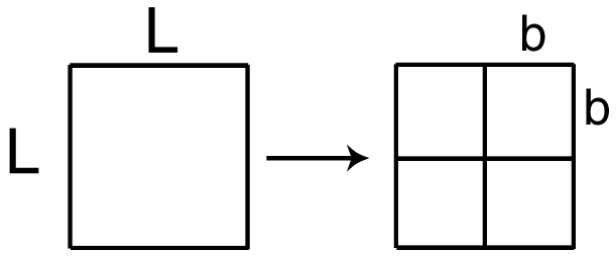


**Fig. 3.1.** Scaling of the number of systems for the self-avarging property

Recall that for thermodynamic equilibrium, for a system of infinite size one observation suffices to obtain $A$. In other words, if $L \to \infty$ then $\Delta(n, L)$ must go to zero, regardless of $n$. Or, if we increase the system size then the effective number of observations should increase. Let $L$ be the system size and $L'$ the new one which we obtain by a scale factor $b$ with $b > 1 : L' = bL$ (c.f. Figure 3.1). The number of effective observations will change to $n' = b^{-d}n$ where $d$ is the dimensionality. More formally we can express the idea by

$$\Delta(n, L) = \Delta(n', L') = \Delta(b^{-d}n, bL) \tag{3.10}$$

We can work out this expression using the definition of $\Delta$ and find

$$\left\langle A^2 \right\rangle_L - \langle A \rangle_L^2 \propto L^{-x}, \quad 0 \leq x \leq d \tag{3.11}$$

In the case where $x = d$ we call the observable $A$ strongly self-averaging and in the cases $0 < x < d$, weakly self-averaging. As we increase $L$, $b$ tends to a finite value, independent of $L$.

The problem of non-self-averaging arises not only at the critical point, where such quantities as the susceptibility or the specific heat exhibit a lack of self-averaging. It occurs also in non-equilibrium situations.

The finite size of the system has an advantage. It enables one to compute second-order thermodynamic properties. In a system of finite size the intensive properties describing the system deviate from their mean values, i.e., they fluctuate around a mean value. These fluctuations depend on the ensemble, of course. Let us take as an example the fluctuations in temperature. We assume that we work with the microcanonical ensemble, as we do in some deterministic methods. It is of interest to relate the fluctuation in the temperature to the specific heat $C_v$, which in thermodynamics is computed from the second derivative of the free energy $F$:

$$C_V = \frac{\partial}{\partial T}\left[T^2 \frac{\partial\,(F/T)}{\partial T}\right]_V \tag{3.12}$$

The fluctuations in temperature are related to the specific heat [**?**, **?**] by

$$\frac{\langle T^2 \rangle - \langle T \rangle^2}{\langle T \rangle^2} = \frac{3}{2N}\left[1 - \frac{3kN}{2C_V}\right] \tag{3.13}$$

Similar relations can be obtained that relate the fluctuations in magnetization in a canonical ensemble to the isothermal susceptibility. The interest in fluctuations stems from the fact that the free energy is difficult to compute in a computer simulation.

Although we are jumping ahead somewhat, it seems appropriate to discuss ensembles at this point. The natural ensemble for the molecular dynamics method is the microcanonical one, where the energy is a constant of motion. Nevertheless, we would like to study systems where the temperature and/or the pressure is a constant of motion. In such a situation the system is not closed and is in contact with a bath. The contact is, however, only conceptual. The approach taken will be to constrain some degrees of freedom. Let us take the case of a constant temperature. For a constant temperature the mean kinetic energy is an invariant. This suggests that an algorithm could be devised such that the mean kinetic energy is constrained to a given value. Due to the constraint we are not really working with a canonical ensemble. Rather, we reproduce only the configurational part of the ensemble. The approach is valid as long as the constraint does not destroy the Markovian character of the transitions from one state to another. The dynamical properties may, however, be influenced by the constraint. In the following we shall always have at the back of our minds that if we impose an ensemble on a system it may be only the configurational part that we evaluate.

## 3.4 Problems

- Assume a Gaussian distribution $P_b(\delta A)$ for the statistical error. Work out the averaging behavior for $(\delta A)^2$ and $(\delta A)^4$
- Show that the susceptibility and the specific heat are non-self-averag ing at the critical point.
- Can you work out an expression for the statistical error which incorporates the behaviour of $\tau_A < L^z$ and averaging behaviour at the critical point?