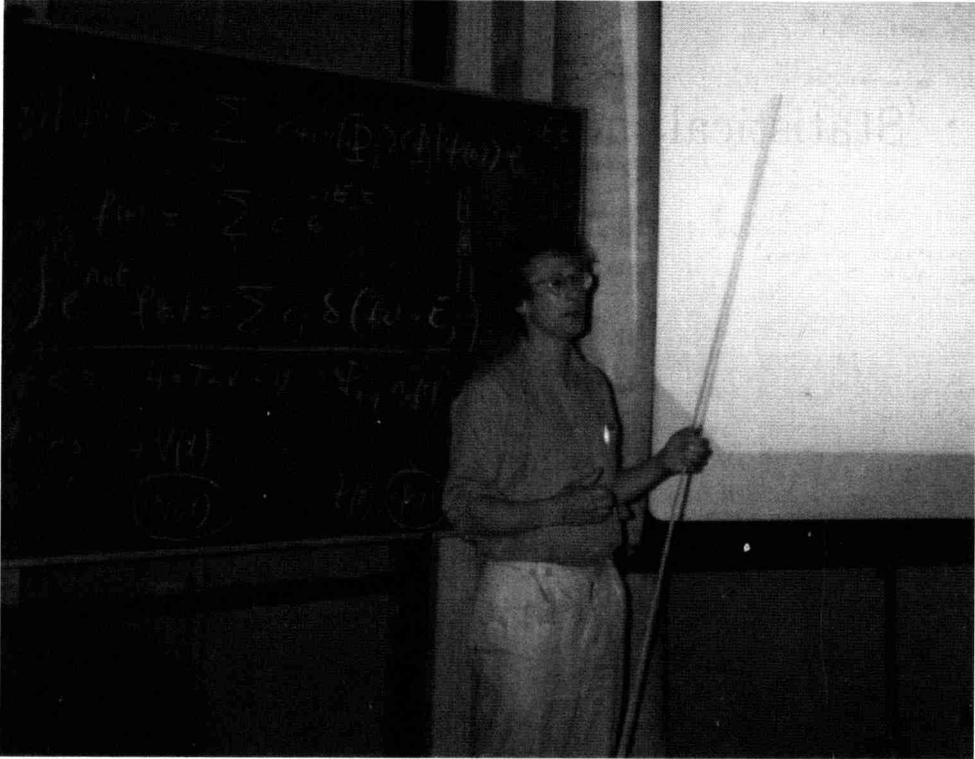


CHAPTER 1

Statistical mechanics for computer simulators

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1. Introduction

The purpose of these lectures is to provide the general statistical mechanics background for computer simulations. This is clearly impossible. I feel a bit like a travel guide who is accompanying a group of tourists on a “Europe in three days” tour. Drastic choices have to be made. In particular, one must choose between a hectic yet superficial visit of all major European attractions or a more focused visit to a few selected sites. In making these choices, the travel guide will take the interests of the tourists into account: while beaches and night life appeal to some, others are more “into” food and drink, while some may even be honestly interested in gothic architecture or 14th century painting. Owners of video equipment will wish to visit as much as possible, because they will only have time to look at it when they are back home.

In preparing these lectures on statistical mechanics for computer simulators I made the choice to focus on a few topics that are either of basic importance, or of special relevance to simulators. Moreover, my choice reflects my own personal bias: some derivations I simply present because I like them. Admittedly, all the topics covered in my lectures are discussed somewhere in the literature, but often in a way that is so cautious, formal or bland that the simple underlying physics remains hidden. In the present lectures, I have therefore included all kinds of quick and dirty derivations that are banned from most serious books on statistical mechanics. Maybe, I even say things that are wrong. But I hope that what I say is sufficiently interesting to provoke the audience into proving me wrong.

1.1. *Who needs statistical mechanics?*

The topic of this school is computer simulation. Computer simulation allows us to study properties of many-particle systems. However, not all properties can be directly measured in a simulation. Conversely, most of the quantities that *can* be measured in a simulation, do not correspond to properties that are measured in real experiments. To give a specific example: in a molecular dynamics simulation of liquid water, we could ‘measure’ the instantaneous positions and velocities of all molecules in the liquid. However, this kind of information cannot be compared to experimental data, because no real experiments provides us with such detailed information. Rather, a typical experiment measures an *averaged* property. Averaged over a large number of particles and, usually, also averaged over the time of the measurement. If we wish to use computer simulation as the numerical counterpart of experiments, we must know what kind of averages we should aim to compute. In order to explain this, we need to introduce the language of statistical mechanics. In statistical mechanics, we encounter thermodynamic concepts such as temperature and entropy and typical mechanical concepts, such as phase space. Although I have no doubt that the reader has, at one time or another, been introduced to all these concepts, I cannot resist sketching how statistical mechanics is “constructed”. The aim of this derivation is to show that there

is nothing mysterious about concepts such as phase space, temperature and entropy and many of the other statistical mechanical objects that will appear time and again in the remainder of this book.

2. Entropy and temperature

Most of the computer simulations discussed in this school are based on the assumption that classical mechanics can be used to describe the motions of atoms and molecules. This assumption leads to a great simplification in almost all calculations and it is therefore most fortunate that it is indeed justified in many cases of practical interest. It is therefore somewhat surprising that, in order to ‘derive’ the basic laws of statistical mechanics, it is easier to use the language of quantum mechanics. I will follow this route of ‘least resistance’. In fact, for our derivation, we need only little quantum mechanics. Specifically, we need the fact that a quantum mechanical system can be found occur in different states. For the time being, I limit myself to quantum states that are eigenvectors of the Hamiltonian H of the system (i.e. energy eigenstates). For any such state $|i\rangle$, we have that $H|i\rangle = E_i|i\rangle$, where E_i is the energy of state $|i\rangle$. Most examples discussed in quantum-mechanics textbooks concern systems with only few degrees of freedom (e.g. the one-dimensional harmonic oscillator or a particle in a box). For such systems, the degeneracy of energy levels will be small. However, for the systems that are of interest to statistical mechanics (i.e. systems with $\mathcal{O}(10^{23})$ particles), the degeneracy of energy levels is astronomically large. In what follows, I denote by $\Omega(E, V, N)$ the number of eigenstates with energy E of a system of N particles in a volume V . I now express the basic assumption of statistical mechanics as follows: *A system with fixed N , V and E is equally likely to be found in any of its $\Omega(E)$ eigenstates.* Much of statistical mechanics follows from this simple (but highly non-trivial) assumption.

To see this, let us first consider a system with total energy E that consists of two weakly interaction sub-systems. In this context, ‘weakly interacting’ means that the sub-systems can exchange energy but that we can write the total energy of the system as the sum of the energies E_1 and E_2 of the sub-systems. There are many ways in which we can distribute the total energy over the two sub-systems, such that $E_1 + E_2 = E$. For a given choice of E_1 , the total number of degenerate states of the system is $\Omega_1(E_1) \times \Omega_2(E_2)$. Note that the total number of states is not the *sum* but the *product* of the number of states in the individual systems. In what follows, it is convenient to have a measure of the degeneracy of the sub-systems that is additive. A logical choice is to take the (natural) logarithm of the degeneracy. Hence:

$$\ln \Omega(E_1, E - E_1) = \ln \Omega_1(E_1) + \ln \Omega_2(E - E_1) \quad (1)$$

We assume that sub-systems 1 and 2 can exchange energy. What is the most likely distribution of the energy? We know that *every* energy state of the total system is equally likely. But the number of eigenstates that correspond to a given distribution of the energy over the sub-systems, depends very strongly on the value of E_1 . We wish to know the most likely value of E_1 , i.e. the one that maximizes $\ln \Omega(E_1, E - E_1)$. The condition for this maximum is that

$$\left(\frac{\partial \ln \Omega(E_1, E - E_1)}{\partial E_1} \right)_{N, V, E} = 0 \quad (2)$$

or, in other words,

$$\left(\frac{\partial \ln \Omega_1(E_1)}{\partial E_1} \right)_{N_1, V_1} = \left(\frac{\partial \ln \Omega_2(E_2)}{\partial E_2} \right)_{N_2, V_2} \quad (3)$$

We introduce the shorthand notation

$$\beta(E, V, N) \equiv \left(\frac{\partial \ln \Omega(E, V, N)}{\partial E} \right)_{N, V} \quad (4)$$

With this definition, we can write Eqn. 3 as

$$\beta(E_1, V_1, N_1) = \beta(E_2, V_2, N_2). \quad (5)$$

Clearly, if initially we put all energy in system 1 (say), there will be energy transfer from system 1 to system 2 until Eqn. 4 is satisfied. From that moment on, there is no net energy flow from one sub-system to the other, and we say that the two sub-systems are in thermal equilibrium. This implies that the condition $\beta(E_1, V_1, N_1) = \beta(E_2, V_2, N_2)$ must be equivalent to the statement that the two sub-systems have the same temperature. When thermal equilibrium is reached, $\ln \Omega$ of the total system is at a maximum. This suggests that $\ln \Omega$ is somehow related to the thermodynamic entropy S of the system. After all, the second law of thermodynamics states that the entropy of a system N, V and E is at its maximum when the system is in thermal equilibrium. There are many ways in which the relation between $\ln \Omega$ and entropy can be established. Here I take the simplest route, i.e. we simply *define* the entropy to be equal to $\ln \Omega$. In fact, for (unfortunate) historical reasons, entropy is not simply equal to $\ln \Omega$, rather we have

$$S(N, V, E) \equiv k_B \ln \Omega(N, V, E) \quad (6)$$

where k_B is Boltzmann's constant which, in S.I. units, has the value $1.380658 \cdot 10^{-23}$. With this identification, we see that our assumption that all degenerate eigenstates of a quantum system are equally likely immediately implies that, in thermal equilibrium, the entropy of a system of a composite system is at a maximum. It would be a bit premature to refer to this statement as 'the second law of thermodynamics', as I have not yet demonstrated that the present definition of entropy is, indeed, equivalent to the thermodynamic definition. I simply take an advance on this result.

The next thing to note is that thermal equilibrium between sub-systems 1 and 2 implies that $\beta_1 = \beta_2$. In every day life, we have another way to express the same thing: we say that two bodies that are brought in thermal contact are in equilibrium if their temperatures are the same. This suggests that β must be related to the absolute temperature. The thermodynamic definition of temperature is

$$1/T = \left(\frac{\partial S}{\partial E} \right)_{V, N} \quad (7)$$

If we use the same definition here, we find that

$$\beta = 1/(k_B T). \quad (8)$$

2.1. System at constant temperature

Now that we have defined temperature, we can consider what happens if we have a system (denoted by S) that is in thermal equilibrium with a large "heat-bath" (B).

The total system is closed, i.e. the total energy $E = E_B + E_S$ is fixed (we assume that the system and the bath are weakly coupled, so that we may ignore their interaction energy). Now suppose that the system S is prepared in a specific state i with energy E_i . The bath then has an energy $E_B = E - E_i$ and the degeneracy of the bath is given by $\Omega_B(E - E_i)$. Clearly, the degeneracy of the bath determines the probability $P(E_i)$ to find system S in state i .

$$P(E_i) = \frac{\Omega_B(E - E_i)}{\sum_i \Omega_B(E - E_i)}. \quad (9)$$

To compute $\Omega_B(E - E_i)$, we expand $\ln \Omega_B(E - E_i)$ around $E_i = 0$.

$$\ln \Omega_B(E - E_i) = \ln \Omega_B(E) - E_i \frac{\partial \ln \Omega_B(E)}{\partial E} + \mathcal{O}(1/E) \quad (10)$$

or, using Eqns. 6 and 7,

$$\ln \Omega_B(E - E_i) = \ln \Omega_B(E) - E_i/k_B T + \mathcal{O}(1/E) \quad (11)$$

If we insert this result in Eqn. 9, we get

$$P(E_i) = \frac{\exp(-E_i/k_B T)}{\sum_i \exp(-E_i/k_B T)} \quad (12)$$

This is the well-known Boltzmann distribution for a system at temperature T . Knowledge of the energy distribution allows us to compute the average energy $\langle E \rangle$ of the system at the given temperature T

$$\begin{aligned} \langle E \rangle &= \sum_i E_i P(E_i) = \frac{\sum_i E_i \exp(-E_i/k_B T)}{\sum_i \exp(-E_i/k_B T)} \\ &= - \frac{\partial \ln (\sum_i \exp(-E_i/k_B T))}{\partial (1/k_B T)} \\ &= - \frac{\partial \ln Q}{\partial (1/k_B T)}, \end{aligned} \quad (13)$$

where, in the last line, I have defined the partition function Q . If we compare Eqn. 13 with the thermodynamic relation

$$E = \frac{\partial F/T}{\partial (1/T)},$$

we see that the Helmholtz free energy F is related to the partition function Q :

$$F = -k_B T \ln Q. \quad (14)$$

Strictly speaking, F is only fixed up to a constant. Or, what amounts to the same thing, the reference point of the energy can be chosen arbitrarily. In what follows, we can use Eqn. 14 without loss of generality. The relation between the Helmholtz free energy and the partition function is often more convenient to use than the relation between $\ln \Omega$ and the entropy. As a consequence, Eqn. 14 is the “workhorse” of equilibrium statistical mechanics.

2.2. Other ensembles

In the previous section, we considered a system that could exchange energy with a large thermal bath. This allowed us to derive the relevant statistical mechanical expressions that describe the behavior of a system of N particles in a volume V at a temperature T . As in the case of a system at constant N, V and E , a system at constant NVT can be found in any one of a very large number of quantum states. Such a collection of states is usually referred to as an *ensemble*. The probability to find the system in any one of these states depends on the external conditions (constant NVE or constant NVT). The choice of ensemble depends on the “experimental” conditions that one aims to model: an isolated system will be described with the NVE -ensemble (which, for historical reasons, is often called the *micro-canonical ensemble*). A system at fixed volume and temperature will be described by the NVT (or *canonical*) ensemble. But often it is convenient to consider systems at constant pressure, or systems that can exchange particles with a reservoir. For every condition, one can introduce the appropriate ensemble. The procedure is very similar to the “derivation” of the canonical ensemble described above. For instance, consider the situation that a system of N particles can exchange energy and volume with a large reservoir. The probability to find the system in a given state with energy E_i and volume V_i is, as before, determined by the number of realizations $\Omega_B(E_{tot} - E_i, V_{tot} - V_i)$ of the “bath”. As before, we expand $\ln \Omega_B$ to first order in E_i , and now also in V_i . Using

$$\frac{\partial S}{\partial E} = \frac{1}{T}$$

and

$$\frac{\partial S}{\partial V} = \frac{P}{T}$$

we obtain

$$\ln \Omega_B(E_{tot} - E_i, V_{tot} - V_i) = \ln \Omega_B(E_{tot}, V_{tot}) - \frac{E_i + PV_i}{k_B T}$$

And the probability to find the system with volume V is given by

$$\mathcal{P}(V) = \frac{Q_{NVT} \exp(-\beta PV)}{\int_0^\infty dV Q_{NVT} \exp(-\beta PV)}. \quad (15)$$

Another ensemble of great practical importance is the constant μVT or *grand-canonical* ensemble. As before, we consider a system of volume V in contact with a large reservoir. The system can exchange energy and particles with the reservoir. The probability to find N particles in the system in a state with energy E_i is determined by the number of realizations of the bath $\Omega(E_{tot} - E_i, N_{tot} - N)$. Using

$$\frac{\partial S}{\partial N} = \frac{-\mu}{T}$$

and following the same procedure as before, we find that the probability to find N particles in the system in volume V at temperature T , is given by

$$\mathcal{P}(N) = \frac{Q_{NVT} \exp(\beta \mu N)}{\sum_{N=0}^\infty Q_{NVT} \exp(\beta \mu N)}. \quad (16)$$

It is obvious that we can use the same procedure to generate a large number of different ensembles. However, the NVT , NPT and μVT ensembles are by far the most important.

3. Fluctuations

We started our discussion of statistical mechanical systems by considering a system of N particles in a volume V with total energy E . We noted that such a system can be found in a very large number ($\Omega(N, V, E)$) eigenstates. Subsequently, we considered a system of N particles in a volume V that could exchange energy with a large thermal "bath". In that case, the probability to find the system in a state with energy E was given by Eqn. 12

$$\mathcal{P}(E) = \frac{\Omega(N, V, E) \exp(-E/k_B T)}{\sum_i \exp(-E_i/k_B T)}$$

using Eqn. 6, we can express Ω in terms of the entropy S and we find

$$\mathcal{P}(E) \sim \exp(-E/k_B T) \exp(S(N, V, E)/k_B)$$

The most likely energy of the system, E^* , is the one for which

$$\left(\frac{\partial S}{\partial E} \right)_{E=E^*} = 1/T.$$

Expanding S in a Taylor series in $\Delta E \equiv E - E^*$, we get

$$\ln \mathcal{P}(\Delta E) = c + \frac{1}{2k_B} \left(\frac{\partial^2 S}{\partial E^2} \right) (\Delta E)^2 + \mathcal{O}((\Delta E)^3); \quad (17)$$

In the limit of large N , we can ignore terms of order ΔE^3 and we find

$$\mathcal{P}(\Delta E) = \text{constant} \times \exp \left[\frac{1}{2k_B} \left(\frac{\partial^2 S}{\partial E^2} \right) (\Delta E)^2 \right] \quad (18)$$

and, recalling that

$$\left(\frac{\partial^2 S}{\partial E^2} \right) = \frac{-1}{C_V T^2},$$

we obtain

$$\mathcal{P}(\Delta E) = (2\pi k_B C_V T^2)^{-\frac{1}{2}} \exp -\frac{(\Delta E)^2}{2k_B C_V T^2}. \quad (19)$$

From Eqn. 19 we immediately see that the mean-square fluctuation in the energy of a system a constant N, V, T is directly related to the heat capacity C_V :

$$\langle (\Delta E)^2 \rangle = k_B T^2 C_V. \quad (20)$$

Using Eqn. 19 we can relate any average in the NVE ensemble to the corresponding average in the NVT ensemble by Taylor expansion:

$$\begin{aligned} \langle A \rangle_{NVT} &= \langle A \rangle_{NVE} + \left(\frac{\partial A}{\partial E} \right) \langle \Delta E \rangle + \\ &\quad \frac{1}{2} \left(\frac{\partial^2 A}{\partial E^2} \right) \langle (\Delta E)^2 \rangle + \mathcal{O}(\langle \Delta E^3 \rangle). \end{aligned} \quad (21)$$

A well-known application of this conversion is the expression derived by Lebowitz, Percus and Verlet for the relation between kinetic energy fluctuations in the NVE and NVT ensembles [1]:

$$\langle (\Delta K)^2 \rangle_{NVE} = \frac{3Nk_B^2 T^2}{2} \left(1 - \frac{3Nk_B}{2C_V} \right) \quad (22)$$

Of course, one can use a similar approach to relate averages in other ensembles. For instance, it is possible to derive an expression for the finite-size correction on the excess chemical potential by comparing the averages in the canonical (NVT) and grand-canonical (μVT) ensembles [2]:

$$\Delta\mu_{ex}(N) = \frac{1}{2N} \left(\frac{\partial P}{\partial \rho} \right) \left[1 - k_B T \left(\frac{\partial \rho}{\partial P} \right) - \rho k_B T \frac{(\partial^2 P / \partial \rho^2)}{(\partial P / \partial \rho)^2} \right]. \quad (23)$$

3.1. Histograms and Landau Free energies

Let us look once more at the probability to find a system with volume V in an NPT ensemble. According to Eqn. 15 this probability is given by

$$\mathcal{P}(V) = c Q(N, V, T) \exp(-\beta P_0 V)$$

where c is a normalization constant. We use the notation P_0 to distinguish that applied pressure (i.e. the pressure of the reservoir) from $P(N, V, T)$, the pressure of the system. Using the relation between the canonical partition function $Q(N, V, T)$ and the Helmholtz free energy $F(N, V, T)$, we can rewrite Eqn. 15 as

$$\mathcal{P}(V) = c \exp(-\beta(F(N, V, T) + P_0 V)). \quad (24)$$

From this equation we see that the probability to find the system in volume V is determined by the behavior of $F + P_0 V$. But this is nothing other than the Gibbs free energy G . The most likely volume is the one for which G is at its minimum. This happens when

$$\frac{\partial F(N, V, T)}{\partial V} \equiv -P(N, V, T) = -P_0$$

i.e. when the thermodynamic pressure of the system is equal to the applied pressure. In fact, if we could measure the histogram $\mathcal{P}(V)$, we could directly measure the variation of the Helmholtz free energy with volume. The higher the free energy of a given volume fluctuation, the less likely we are to observe this fluctuation. In principle, we could determine the complete equation of state of the system from knowledge of $\mathcal{P}(V)$. To see this, consider

$$\frac{\partial \ln \mathcal{P}(V)}{\partial V} = \beta(P(N, V, T) - P_0) \quad (25)$$

One amusing consequence of this expression is the relation between two-phase coexistence and van der Waals loops in the equation of state [3]. Suppose that a system at a given pressure P_0 undergoes a first-order phase transition from a state with volume V_1 to a state with volume V_2 . At coexistence, the system is equally likely to be found in either state, but it is unlikely to be in a state with intermediate density. Hence, the histogram of volumes, $\mathcal{P}(V)$ will be double-peaked. Eqn. 25 immediately shows that the pressure as a function of volume should exhibit an oscillation around P_0 .

The relation between probabilities of fluctuations and free energies is, in fact, quite general. To see this, let us consider a system with N particles in volume V in contact with a reservoir at constant T . Now let us assume that we are not interested in the fluctuations of the energy of the system, but in fluctuations of some other observable property, e.g. the total magnetic moment M . We wish to know the probability that

the system is found in a state with magnetic moment M . To do so, we should sum the probabilities of all states i that satisfy the constraint $M_i=M$.

$$\mathcal{P}(M) = \frac{\sum_i \exp(-\beta E_i) \delta_{M_i, M}}{\sum_i \exp(-\beta E_i)}$$

where the Kronecker delta constrains the sum to those terms that have the required magnetic moment. We see that the restricted sum in the numerator has the form of a partition function and we denote it by $Q(N, V, T, M)$. We also define an associated free energy

$$F(N, V, T, M) \equiv -k_B T \ln(Q(N, V, T, M)) \quad (26)$$

We refer to $F(N, V, T, M)$ as the Landau free energy associated with the variable M . Clearly, there is a close connection between (Landau) free energies and constraints. We define a subset of all possible states of the system by the constraint $M_i=M$. The Landau free energy then determines the probability that the system will spontaneously be found in a state that satisfies this constraint:

$$\mathcal{P}(M) = c \exp(-\beta F(N, V, T, M))$$

In computer simulations, we can measure Landau free energies by sampling a histogram of the spontaneous fluctuations of M . However, this approach in its naive form is not very useful, as we can only hope to sample fluctuations with an associated Landau free energy of at most a few $k_B T$. If we wish to study the Landau free energy over a wider range, non-standard sampling schemes are needed (see e.g. [4, 5]).

4. Classical Statistical Mechanics

Thus far, we have formulated statistical mechanics in purely quantum-mechanical terms. The entropy is related to the density of states of a system with energy E , volume V and number of particles N . And similarly, the Helmholtz free energy is related to the partition function Q , a sum over all quantum states i of the Boltzmann factor $\exp(-E_i/k_B T)$. To be specific, let us consider the average value of some observable A . We know the probability that a system at temperature T will be found in an energy eigenstate with energy E_i and we can therefore compute the thermal average of A as

$$\langle A \rangle = \frac{\sum_i \exp(-E_i/k_B T) \langle i|A|i \rangle}{\sum_i \exp(-E_i/k_B T)}. \quad (27)$$

This equation suggests how we should go about computing thermal averages: first we solve the Schrödinger equation for the (many-body) system of interest, and next we compute the expectation value of the operator A for all those quantum states that have a non-negligible statistical weight. Unfortunately, this approach is doomed for all but the simplest systems. First of all, we cannot hope to solve the Schrödinger equation for an arbitrary many-body. And secondly, even if we could, the number of quantum states that contribute to the average in Eqn. 27 would be so astronomically large ($\mathcal{O}(10^{10^{25}})$) that a numerical evaluation of all expectation values would be unfeasible. Fortunately, Eqn. 27 can be simplified to a more workable expression in the classical limit ($\hbar \rightarrow 0$). To this end, we first rewrite Eqn. 27 in a form that is independent of

the specific basis set. We note that $\exp(-E_i/k_B T) = \langle i | \exp(-H/k_B T) | i \rangle$, where H is the Hamiltonian of the system. Using this relation, we can write

$$\begin{aligned} \langle A \rangle &= \frac{\sum_i \langle i | \exp(-H/k_B T) A | i \rangle}{\sum_i \langle i | \exp(-H/k_B T) | i \rangle} \\ &= \frac{\text{Tr} \exp(-H/k_B T) A}{\text{Tr} \exp(-H/k_B T)} \end{aligned} \quad (28)$$

where Tr denotes the trace of the operator. As the value of the trace of an operator does not depend on the choice of the basis set, we can compute thermal averages using any basis set we like. Preferably, we use simple basis sets, such as the set of eigenfunctions of the position or the momentum operator. The reason why use of these basis sets may be advantageous can be understood as follows. We recall that the Hamiltonian H is the sum of a kinetic part K and a potential part U . The kinetic-energy operator is a quadratic function of the momenta of all particles. As a consequence, momentum eigenstates are also eigenfunctions of the kinetic energy operator. Similarly, the potential energy operator is a function of the particle coordinates. Matrix elements of U are therefore most conveniently computed in a basis set of position eigenfunctions. However, $H = K + U$ itself is not diagonal in either basis set, nor is $\exp(-\beta(K + U))$. However, if we could replace $\exp(-\beta H)$ by $\exp(-\beta K) \exp(-\beta U)$, then we could simplify equation 28 considerably. In general, we cannot make this replacement because

$$\exp(-\beta K) \exp(-\beta U) = \exp(-\beta((K + U) + \mathcal{O}([K, U])))$$

where $[K, U]$ is the commutator of the kinetic and potential energy operators while $\mathcal{O}([K, U])$ is meant to denote all terms containing commutators and higher-order commutators of K and U . It is easy to verify that the commutator $[K, U]$ is of order \hbar . Hence, in the limit $\hbar \rightarrow 0$, we may ignore the terms of order $\mathcal{O}([K, U])$. In that case, we can write

$$\text{Tr} \exp(-\beta H) \approx \text{Tr} \exp(-\beta U) \exp(-\beta K) \quad (29)$$

If we use the notation $|r\rangle$ for eigenvectors of the position operator and $|k\rangle$ for eigenvectors of the momentum operator, we can express Eqn. 29 as

$$\text{Tr} \exp(-\beta H) = \sum_{r,k} \langle r | e^{-\beta U} | r \rangle \langle r | k \rangle \langle k | e^{-\beta K} | k \rangle \langle k | r \rangle \quad (30)$$

All matrix elements can be evaluated directly:

$$\langle r | \exp(-\beta U) | r \rangle = \exp(-\beta U(\mathbf{r}^N))$$

where $U(\mathbf{r}^N)$ on the right hand side is no longer an operator, but a function of the coordinates of all N particles. Similarly,

$$\langle k | \exp(-\beta K) | k \rangle = \exp(-\beta \sum_{i=1}^N p_i^2 / (2m_i))$$

where $p_i = \hbar k_i$. And finally,

$$\langle r | k \rangle \langle k | r \rangle = 1/V^N$$

where V is the volume of the system and N the number of particles. Finally, we can replace the sum over states by an integration over all coordinates and momenta. The final result is

$$\text{Tr} \exp(-\beta H) \approx \frac{1}{h^{dN} N!} \int d\mathbf{p}^N d\mathbf{r}^N \exp(-\beta(\sum_i p_i^2/(2m_i) + U(\mathbf{r}^N))) \quad (31)$$

where d is the dimensionality of the system. The factor $1/N!$ is a direct result of the indistinguishability of identical particles. In almost the same way, we can derive the classical limit for $\text{Tr} \exp(-\beta H)A$ and finally, we can write the classical expression for the thermal average of the observable A as

$$\langle A \rangle = \frac{\int d\mathbf{p}^N d\mathbf{r}^N \exp(-\beta(\sum_i p_i^2/(2m_i) + U(\mathbf{r}^N))) A(\mathbf{p}^N, \mathbf{q}^N)}{\int d\mathbf{p}^N d\mathbf{r}^N \exp(-\beta(\sum_i p_i^2/(2m_i) + U(\mathbf{r}^N)))} \quad (32)$$

Equations 31 and 32 are the starting point for virtually all classical simulations of many-body systems.

4.1. Ergodicity

Thus far, we have discussed the average behavior of many-body systems in a purely static sense: we only introduced the assumption that every quantum state of a many-body system with energy E is equally likely to be occupied. Such an average over all possible quantum states of a system, is called an “ensemble” average. However, this is not the way we usually think about the average behavior of a system. In most experiments we perform a series of measurements during a certain time-interval and then determine the average of these measurements. In fact, the idea behind Molecular Dynamics simulations is precisely that we can study the average behavior of a many-particle system simply by computing the natural time evolution of that system numerically and averaging the quantity of interest over a sufficiently long time. To take a specific example, let us consider a fluid consisting of atoms. Suppose that we wish to compute the average density of the fluid at a distance r from a given atom i , $\rho_i(r)$. Clearly, the instantaneous density depends on the coordinates \mathbf{q}_j of all particles j in the system. As time progresses, the atomic coordinates will change (according to Newton’s equations of motion), and hence the density around atom i will change. Provided that we have specified the initial coordinates and momenta of all atoms ($\mathbf{q}^N(0), \mathbf{p}^N(0)$) we know, at least in principle, the time evolution of $\rho_i(r; \mathbf{q}^N(0), \mathbf{p}^N(0), t)$. In a Molecular Dynamics simulation, we measure the time-averaged density $\overline{\rho_i(r)}$ of a system of N atoms, in a volume V , at a constant total energy E :

$$\overline{\rho_i(r)} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt' \rho_i(r; t'). \quad (33)$$

Note that, in writing down this equation, we have implicitly assumed that, for T sufficiently long, the time-average does not depend on the initial conditions. This is, in fact, a subtle assumption that is not true in general (see, *e.g.* ref. [6]). However, we shall disregard subtleties and simply assume that, once we have specified N , V and E , time-averages do not depend on the initial coordinates and momenta. If that is so, then we would not change our result for $\overline{\rho_i(r)}$ if we average over many different initial conditions, *i.e.* we consider the hypothetical situation where we run a large

number of Molecular Dynamics simulations at the same values for N , V and E , but with different initial coordinates and momenta,

$$\overline{\rho_i(r)} = \frac{\sum_{\text{initial conditions}} \left(\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt' \rho_i(r; \mathbf{q}^N(0), \mathbf{p}^N(0), t') \right)}{\text{number of initial conditions}}. \quad (34)$$

We now consider the limiting case where we average over *all* initial conditions compatible with the imposed values of N , V and E . In that case, we can replace the sum over initial conditions by an integral

$$\frac{\sum_{\text{initial conditions}} f(\mathbf{q}^N(0), \mathbf{p}^N(0))}{\text{number of initial conditions}} \rightarrow \frac{\int_E d\mathbf{q}^N d\mathbf{p}^N f(\mathbf{q}^N(0), \mathbf{p}^N(0))}{\Omega(N, V, E)}, \quad (35)$$

where $\Omega(N, V, E) = \int_E d\mathbf{q}^N d\mathbf{p}^N$ (we have ignored a constant factor¹). The subscript E on the integrals indicates that the integration is restricted to a shell of constant energy E . We denote an ensemble average by $\langle \dots \rangle$, to distinguish it from a time-average, denoted by a bar. If we switch the order of the time-averaging and the averaging over initial conditions, we find

$$\overline{\rho_i(r)} = \lim_{T \rightarrow \infty} \frac{1}{T} \int dt' \langle \rho_i(r; \mathbf{q}^N(0), \mathbf{p}^N(0), t') \rangle_{NVE}. \quad (36)$$

However, the ensemble average in the above equation does not depend on the time t' . This is so, because there is a one-to-one correspondence between the initial phase-space coordinates of a system, and those that specify the state of the system at a later time t' (see *e.g.* [7, 6]). Hence, averaging over all initial phase-space coordinates is equivalent to averaging over the time-evolved phase-space coordinates. For this reason, we can leave out the time averaging in Eqn. 36, and we find

$$\overline{\rho_i(r)} = \langle \rho_i(r) \rangle_{NVE}. \quad (37)$$

The above equation states that, if we wish to compute the average of a function of the coordinates and momenta of a many-particle system, we can *either* compute that quantity by time-averaging (the ‘MD’ approach), *or* by ensemble averaging (the ‘MC’ approach). It should be stressed that the preceding paragraphs are only meant to make Eqn. 37 *plausible*, not as a proof. In fact, that would have been quite impossible because Eqn. 37 is not true in general. However, in what follows, we shall simply assume that the ‘ergodic hypothesis’, as Eqn. 37 is usually referred to, applies to the systems that we study in computer simulations. The reader should, however, be aware that there are many examples of systems that are not ergodic *in practice* (*e.g.* glasses, meta-stable phases) or even *in principle*, *e.g.* nearly harmonic solids.

¹ If we consider a quantum-mechanical system, then $\Omega(N, V, E)$ is simply the number of quantum states of that system, for given N , V and E . In the classical limit, the number of quantum states of a d -dimensional system of N distinguishable, structureless particles is given by $\Omega(N, V, E) = (\int d\mathbf{p}^N d\mathbf{q}^N) / h^{dN}$. For N *indistinguishable* particles, we should divide the latter expression by a factor $N!$.

5. Free energy and phase behavior

5.1. Thermodynamic Integration

The second law of thermodynamics states that for a closed system with energy E , volume V and number of particles N , the entropy S is at a maximum when the system is in equilibrium. From this formulation of the second law it is simple to derive the corresponding equilibrium conditions for systems that can exchange heat, particles or volume with a reservoir. In particular, if a system is in contact with a heat bath, such that its temperature T , volume V and number of particles N are fixed, then the Helmholtz free energy $F \equiv E - TS$ is at a *minimum* in equilibrium. Analogously, for a system of N particles at constant pressure P and temperature T , the Gibbs free energy $G \equiv F + PV$ is at a minimum.

If we wish to know which of two phases (denoted by α and β) is stable at a given temperature and density, we should simply compare the Helmholtz free energies F_α and F_β of these phases. It would seem that the obvious thing to do is simply to measure F_α and F_β by computer simulation. Unfortunately, it is not possible to measure the free energy (or entropy) directly in a simulation. What we *can* measure in a simulation are averages of *mechanical* quantities, *i.e.* averages of functions of the coordinates and momenta of the molecules in the system, such as the pressure or the dielectric constant. If we denote such a mechanical quantity by $A(\mathbf{p}^N, \mathbf{q}^N)$, then the average of A that can be measured in a simulation at constant N , V and T is

$$\langle A \rangle_{NVT} = \frac{\int d\mathbf{p}^N d\mathbf{q}^N A(\mathbf{p}^N, \mathbf{q}^N) \exp(-\beta H(\mathbf{p}^N, \mathbf{q}^N))}{\int d\mathbf{p}^N d\mathbf{q}^N \exp(-\beta H(\mathbf{p}^N, \mathbf{q}^N))} \quad (38)$$

where H is the Hamiltonian of the system expressed as a function of the momenta \mathbf{p}^N and coordinates \mathbf{q}^N . k_B is Boltzmann's constant and $\beta = 1/(k_B T)$.

However, entropy, free energy and related quantities are not simply averages of functions of the phase-space coordinates of the system. Rather they are directly related to the *volume* in phase space that is accessible to a system. For instance, in classical statistical mechanics, the Helmholtz free energy F is directly related to the canonical partition function Q_{NVT} :

$$F = -k_B T \ln Q_{NVT} \equiv -k_B T \ln \left(\frac{\int d\mathbf{p}^N d\mathbf{q}^N \exp(-\beta H(\mathbf{p}^N, \mathbf{q}^N))}{h^{dN} N!} \right) \quad (39)$$

where h is Planck's constant and d is the dimensionality of the system.

It is clear that Q_{NVT} is not of the form of a canonical average over phase space. And this is why F or, for that matter, S or G , cannot be measured directly in a simulation. We call such quantities that depend directly on the available volume in phase *thermal* quantities.

Actually, there is nothing strange about the fact that thermal quantities cannot be measured directly in a simulation: the same problem occurs in the real world – thermal quantities cannot be measured directly.

When considering numerical schemes to determine the free energy, it is therefore instructive to look at the *experimental* techniques to determine entropies or free energies. In experiments, one does not measure the free energy directly, but rather a derivative of the free energy with respect to volume V or temperature T :

$$\left(\frac{\partial F}{\partial V} \right)_{NT} = -P \quad (40)$$

and

$$\left(\frac{\partial F/T}{\partial 1/T}\right)_{VT} = E. \quad (41)$$

As the pressure P and the energy E are mechanical quantities, they *can* be measured both in the experiment and in simulation. In order to compute the free energy of a system at given temperature and density, we should find a reversible path in the $V - T$ plane, that links the state under consideration to a state of known free energy. The change in F along that path can then simply be evaluated by integration of Eqns. 40 and 41. There are only very few thermodynamic states where the free energy of a substance is known. One state is the ideal gas phase, another may be the perfectly ordered ground state at $T = 0K$.

In computer simulations, the situation is quite similar. In order to compute the free energy of a dense liquid, one may construct a reversible path to the very dilute gas phase. It is not really necessary to go all the way to the ideal gas. But at least one should reach a state that is sufficiently dilute that the free energy can be computed accurately, either from knowledge of the first few terms in the virial expansion of the compressibility factor $PV/(NkT)$, or that the chemical potential can be computed by other means. For the solid, the ideal gas reference state is less useful (although techniques have been developed to construct a reversible path from a dense solid to a dilute (lattice) gas [8]). The obvious reference state for solids is the harmonic lattice. Computing the absolute free energy of a harmonic solid is relatively straightforward, at least for atomic and simple molecular solids. However, not all solid phases can be reached by a reversible route from a harmonic reference state. For instance, in molecular systems it is quite common to find a strongly anharmonic plastic phase just below the melting line. This plastic phase is not (meta-) stable at low temperatures.

5.1.1. Artificial paths Fortunately, in computer simulations we do not have to rely on the presence of a ‘natural’ reversible path between the phase under study and a reference state of known free energy. If such a path does not exist, we can construct an artificial path. This is in fact a standard trick in statistical mechanics (see e.g. [9]). It works as follows: Consider a case where we need to know the free energy $F(V, T)$ of a system with a potential energy function U_1 , where U_1 is such that no ‘natural’ reversible path exists to a state of known free energy. Suppose now that we can find another model system with a potential energy function U_0 for which the free energy *can* be computed exactly. We define a generalized potential energy function $U(\lambda)$, such that $U(\lambda = 0) = U_0$ and $U(\lambda = 1) = U_1$. The free energy of a system with this generalized potential is denoted by $F(\lambda)$. Although $F(\lambda)$ itself cannot be measured directly in a simulation, we can measure its derivative with respect to λ :

$$\left(\frac{\partial F}{\partial \lambda}\right)_{NVT\lambda} = \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_{NVT\lambda} \quad (42)$$

If the path from $\lambda = 0$ to $\lambda = 1$ is reversible, we can use eq. 42 to compute the desired $F(V, T)$. We simply measure $\langle \partial U / \partial \lambda \rangle$ for a number of values of λ between 0 and 1.

In the numerical simulation of bio-molecular molecules, ‘artificial’ thermodynamic integration is often used to compute the difference in excess free-energy of similar but distinct molecules (see e.g. [10]). Such calculations are important in many different contexts. For instance, one can thus compute the relative binding strengths of closely

related molecules to an enzyme. In such calculations, the thermodynamic integration involves a gradual replacement of part of the molecule by another building block (for instance, an H could be transformed into a CH_3 group).

5.1.2. Reference systems Let us consider the computation of the free energy of a crystalline solid by thermodynamic integration. In such calculations it is important to select a reasonable reference system, *i.e.* a system that is, in some sense ‘close’ to the system of interest, and can be reached without crossing any first-order phase-transition boundaries. One of the safest choices for a reference system appears to be an Einstein crystal with the same structure as the phase under study [11]. This choice of reference system makes it extremely improbable that the path connecting $\lambda = 0$ and $\lambda = 1$ will cross an (irreversible) first order phase transition from the initial structure to another, only to go back to its original structure for still larger values of λ . Nevertheless, it is important that the parametrization of $U(\lambda)$ be chosen carefully. Usually, a linear parametrization (*i.e.* $U(\lambda) = \lambda U_1 + (1 - \lambda)U_0$) is quite satisfactory. But occasionally such a parametrization may lead to weak (and relatively harmless) singularities in eq. 42 for $\lambda \rightarrow 0$. There are, however, alternative thermodynamic integration schemes that do not suffer from this problem [12]. More details about such free energy computations can be found in ref. [12, 4, 13].

Similar techniques can be used to locate first-order phase transitions involving phases with partial order (e.g. liquid crystals). For details, the reader is referred to refs [14, 15, 16, 17, 18, 19]. Finally, thermodynamic integration techniques are particularly useful to compute the Gibbs free energy of mixtures. An example is the work of Kranendonk and Frenkel, who have computed the melting curve of a substitutionally disordered solid mixture of hard spheres with different size [20]. In this case, thermodynamic integration is used to slowly change the size-ratio of the particles at fixed volume fraction. The reference point is size ratio $\alpha = 1$ (‘isotopic mixture’). The reversible work needed to change the size ratio from 1 to a given value of α is a direct measure for the excess free energy of the solid solution at that composition. This technique was subsequently used by Eldridge et al. [21] to compute the relative stability of the AB_2 and AB_{13} crystal phases of dissimilar hard spheres with a size ratio $\alpha \approx 0.58$. For details, the reader is referred to ref. [22, 23, 24].

5.2. Tracing coexistence curves

Once a single point on the coexistence curve between two phases is known, the rest of that curve can be computed without further free energy calculations. To map out such coexistence curves, Kofke [25, 26] proposed a scheme that is based on a numerical integration of the Clausius-Clapeyron equation (unfortunately, Kofke refers to the method as ‘Gibbs-Duhem’ integration). Let us briefly recall the Clausius-Clapeyron equation. If two phases coexist at a given temperature T and pressure P , then their chemical potentials must be equal. If we now change both the pressure and the temperature by infinitesimal amounts dP and dT respectively, then the difference in chemical potential of the two phases becomes

$$\mu_\alpha - \mu_\beta = -(S_\alpha - S_\beta)dT + (V_\alpha - V_\beta)dP \quad (43)$$

Along the coexistence curve $\mu_\alpha = \mu_\beta$, and hence

$$\frac{dP}{dT} = \frac{S_\alpha - S_\beta}{V_\alpha - V_\beta} = \frac{\Delta H}{T\Delta V} \quad (44)$$

where we have used the fact that, at coexistence, $\Delta S = T\Delta H$, where H_α (H_β) denotes the enthalpy of phase α (β). As ΔH , T and ΔV can all be measured directly in a simulation, dP/dT can be computed from Eqn. 44. Kofke used a predictor-corrector algorithm to solve Eqn. 44 although other integration schemes may be more stable [27]. If one of the two coexisting phases is the (dilute) vapor phase, it is convenient to cast Eqn. 44 in a slightly different form:

$$\frac{d \ln P}{d1/T} = -\frac{\Delta H}{P\Delta V/T} \quad (45)$$

Examples of recent applications of the Kofke method can be found in refs. [28, 29, 30, 31, 27]. It should be stressed that the Kofke method is in no way limited to the computation of coexistence curves in the P, T -plane. A particularly important class of problems that can be treated in an analogous fashion are those where one studies the location of a phase transition as a function of the intermolecular interaction potential. For instance, Agrawal and Kofke have investigated the effect of a change of the steepness of the intermolecular potential in atomic systems on the melting point [32]. In the same spirit, Dijkstra and Frenkel studied the effect of a change in flexibility of rod-like polymers on the location of the isotropic nematic transition [33].

6. Perturbation Theory

The thermodynamic integration scheme discussed in the previous section lies at the root of thermodynamic perturbation theory [9]. The aim of thermodynamic perturbation theory is to arrive at an estimate of the free energy (and all derived properties) of a many-body system, using as input information about the free energy and structure of a simpler reference system. We assume, as before that the potential energy function of this reference system is denoted by U_0 while the potential energy function of the system of interest is denoted by U_1 . In order to compute the free energy difference between the known reference system and the system of interest, we use the linear parametrization of the potential energy function

$$U(\lambda) = \lambda U_1 + (1 - \lambda)U_0 .$$

From Eqn. 42 we know how to compute the derivative of the free energy with respect to λ and hence we can express the free energy difference $F_1 - F_0$ as

$$F_1 - F_0 = \int_0^1 d\lambda \langle U_1 - U_0 \rangle_{NVT\lambda} \quad (46)$$

This expression (first derived by Kirkwood), although useful for simulations, is not particularly useful for theoretical estimates of the free energy difference $F_1 - F_0$. However, we can make progress by considering

$$\left(\frac{\partial^2 F}{\partial \lambda^2} \right)_{NVT\lambda}$$

For the linear parametrization considered here, it is straightforward to show that

$$\left(\frac{\partial^2 F}{\partial \lambda^2} \right)_{NVT\lambda} = -\beta \left(\langle (U_1 - U_0)^2 \rangle_{NVT\lambda} - \langle (U_1 - U_0) \rangle_{NVT\lambda}^2 \right) \quad (47)$$

The important thing to note is that the second derivative of F with respect to λ is always negative (or zero). This implies that

$$\left(\frac{\partial F}{\partial \lambda}\right)_{NVT\lambda=0} \geq \left(\frac{\partial F}{\partial \lambda}\right)_{NVT\lambda}$$

and hence

$$F_1 \leq F_0 + \langle U_1 - U_0 \rangle_{NVT\lambda=0} . \quad (48)$$

This variational principle for the free energy is known as the Gibbs-Bogoliubov inequality. It implies that we can compute an upper bound to the free energy of the system of interest, from knowledge of the average of $U_1 - U_0$ evaluated for the reference system. Of course, the usefulness of Eqn. 48 depends crucially on the quality of the choice of reference system. A good reference system is not necessarily one that is close in free energy to the system of interest, but one for which the fluctuations in the potential energy difference $U_1 - U_0$ are small. Thermodynamic perturbation theory for simple liquids has been very successful, precisely because the structure of the reference system (hard-sphere fluid) and the liquid under consideration (e.g. Lennard-Jones) is very similar. As a result, $\langle U_1 - U_0 \rangle_\lambda$ hardly depends on λ and, as a consequence, its derivative (Eqn. 47) is very small.

In some cases, the fluctuation term can be made to vanish altogether. Consider, for instance, the free energy difference between a hard sphere reference system and a model fluid of particles that have a hard-sphere repulsion and a very weak, attractive interaction $-\epsilon$ that extends over a very large distance R_c . In particular, we consider the limit $\epsilon \rightarrow 0$, $R_c \rightarrow \infty$, such that

$$\frac{4\pi}{3} R_c^3 \epsilon = 2a$$

where a is a constant. In the limit $R_c \rightarrow \infty$, the potential energy of the perturbed fluid can be computed directly. Within a shell of radius R_c , there will be, on average, N_c other particles, all of which contribute $-\epsilon/2$ to the potential energy of the fluid. For $R_c \rightarrow \infty$, the number of neighbors N_c also tends to infinity and hence the relative fluctuation in N_c becomes negligible (as it is of order $1/\sqrt{N_c}$). It then follows that the fluctuations in the perturbation (i.e. $U_1 - U_0$) also become negligible and, as a consequence, the Gibbs-Bogoliubov inequality becomes an identity: in this limit of weak, long ranged forces, perturbation theory becomes exact [34]! I refer to this limit as the ‘‘van der Waals’’ limit, for reason that will become obvious. The free energy per particle of the van der Waals fluid is

$$f_{vdW}(\rho, T) = f_{HS}(\rho, T) - \rho a \quad (49)$$

and the pressure is

$$P_{vdW} = \rho^2 \frac{\partial f_{vdW}}{\partial \rho} = P_{HS}(\rho, T) - a\rho^2 \quad (50)$$

where P_{HS} denotes the pressure of the hard sphere reference system. Of course, van der Waals did not know the equation of state of hard spheres, so he had to make an approximation [35]:

$$P_{HS} = \rho k_B T / (1 - \rho b) \quad (51)$$

where b is the second virial coefficient of hard spheres. If we insert Eqn. 51 in Eqn. 50, the well-known van der Waals equation results. If, on the other hand, we use the “exact” equation of state of hard spheres (as deduced from computer simulations), then we can compute the “exact” equation of state of the van der Waals model (i.e. the equation of state that van der Waals would have given an arm and a leg for). Using this approach, Longuet-Higgins and Widom [36] were the first to compute the true phase diagram of the van der Waals model. As an illustration (Figure 1), I have recomputed the Longuet-Higgins-Widom phase diagram, using more complete data about the hard-sphere equation of state than were available to Longuet-Higgins and Widom.

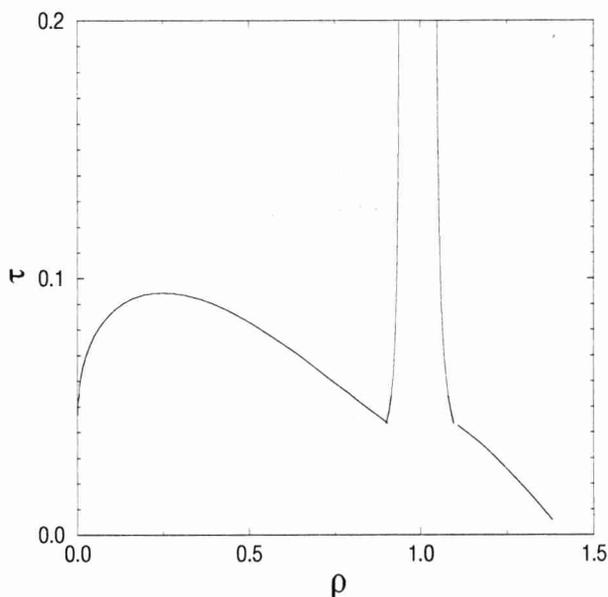


Figure 1. Phase diagram for the van der Waals model. This phase diagram is computed by using the hard-sphere system as reference system and adding a weak, long-ranged attractive interaction. Density ρ in units σ^{-3} , where σ is the diameter of the hard spheres. The ‘temperature’ τ is defined in terms of the second virial coefficient: $B_2/B_2^{HS} \equiv 1 - 1/(4\tau)$, where B_2^{HS} is the second virial coefficient of the hard-sphere reference system.

6.1. Perturbation theory for hard-core systems?

One drawback of the conventional formulation of thermodynamic perturbation theory is that it fails if the perturbation becomes very large, even when it is intuitively clear that the actual free energy difference between the reference system and the perturbed system should be small. Consider for instance a simple fluid with a steeply repulsive, but continuous potential. The free energy of this system will be very close to that of a hard-sphere reference system, provided that we make an optimal choice for the hard-sphere diameter σ (see e.g. [9]). However, if we would try the inverse, i.e. compute the

free energy of the hard-sphere fluid, starting from the continuous reference system, then Eqn. 48 would always predict an infinite free energy for the hard-sphere fluid. Admittedly, this example is not very realistic. But there are many cases where one *would* like to use a reference system with continuous interactions to model a system with hard-core interaction: for instance, one might wish to use an Einstein crystal as a reference system for a hard-sphere crystal, or one might be interested in developing a mean-field (Maier-Saupe [37]) model for a liquid crystal consisting of hard rods or platelets. To my knowledge, this problem seems to bother other people less than it bothers me. In fact, I have never seen the simple derivation that I present below in the literature. But I guess that it must exist somewhere.

Consider the case that we wish to estimate the Helmholtz free energy F_h of a model system characterized by a potential energy function U_h . The subscript h stands for “hard core”, because later, I will consider the case the U_h is a hard-core potential. At this stage, however, I make no assumptions about U_h . In addition, we have a simple reference system with a potential energy function U_r (the r stands reference. U_r may be a continuous function, but again, that is not essential at this stage). In what follows, I denote the configurational part of the partition functions of the two systems by Z_h and Z_r respectively. We assume that the free energy of the reference system (F_r) is known. Now consider two related model systems, one with a potential energy function $U_h/2$ and the other with potential energy $U_r/2$. We construct the following non-negative expression

$$g(\lambda) \equiv (\exp(-\beta U_h/2) + \lambda \exp(-\beta U_r/2))^2$$

where λ is an arbitrary real number. Let us now consider the integral of $g(\lambda)$ over all configuration space.

$$\begin{aligned} \int d\mathbf{r}^N g(\lambda) &= \int d\mathbf{r}^N \exp(-\beta U_h) + 2\lambda \int d\mathbf{r}^N \exp(-\beta(U_h + U_r)/2) + \\ &\quad \int d\mathbf{r}^N \exp(-\beta U_r) \\ &= Z_h + 2\lambda Z_{hr} + \lambda^2 Z_r, \end{aligned} \tag{52}$$

where Z_{hr} is defined as

$$Z_{hr} \equiv \int d\mathbf{r}^N \exp(-\beta(U_h + U_r)/2)$$

As $g(\lambda)$ is non-negative, it follows that the expression in the last line of Eqn. 52 must also be non-negative. But Eqn. 52 is a simple quadratic equation in λ . Hence, we can immediately conclude that

$$Z_r Z_h \geq Z_{hr}^2 \tag{53}$$

We can rewrite this in the form of a simple variational expression for Z_h :

$$Z_h \geq \left(\frac{Z_{hr}}{Z_r} \right)^2 Z_r \tag{54}$$

or,

$$F_h \leq F_r - 2k_B T \ln \left(\frac{Z_{hr}}{Z_r} \right) \tag{55}$$

Now let us consider two applications. First, the (conventional one) where the reference potential U_r describes a hard-core interaction, while U_h is continuous. Then we immediately get,

$$F_h \leq F_r - 2k_B T \ln \langle \exp(-\beta U_h/2) \rangle_r . \quad (56)$$

And, in the limit of weak perturbations (or, more generally, in the case that the fluctuations of U_h in the reference system are negligible), we recover the old result

$$F_h \leq F_r + \langle U_h \rangle_r . \quad (57)$$

Now consider the more interesting limit, where U_h is a hard-core potential and U_r is a continuous reference potential. In that case, we can write Eqn. 55 as

$$F_h \leq F_r - 2k_B T \ln \langle \exp(-\beta(U_h - U_r/2)) \rangle_r . \quad (58)$$

7. Mean-field theory

The Gibbs-Bogoliubov inequality can be used as a starting point to derive mean-field theory, which can be considered as a systematic approximation for the free energy of a many-body system. For the sake of simplicity, we consider a many-body Hamiltonian of interacting spins

$$U_1 = -\frac{J}{2} \sum_{i=1}^N \sum_{jnni} s_i s_j .$$

We wish to approximate this model system, using a reference system with a much simpler Hamiltonian, namely one that consists of a sum of one-particle contributions, e.g.

$$U_0 = \sum_{i=1}^N h s_i$$

where h denotes the effective “field” that replaces the interaction with the other particles. The free energy per particle of the reference system is given by

$$f_0(h) = -k_B T \ln \int ds \exp(-\beta h s)$$

We can easily compute the average value of s in the reference system

$$\langle s \rangle_0 = \frac{\partial f_0(h)}{\partial h} \quad (59)$$

Now, we consider the Gibbs-Bogoliubov inequality Eqn. 48

$$\begin{aligned} f_1 &\leq f_0 + \langle u_1 - u_0 \rangle_0 \\ &= f_0 + \left\langle -\frac{J}{2} \sum_{jnni} s_i s_j - h s_i \right\rangle_0 \\ &= f_0 - \frac{J}{2} z \langle s \rangle^2 - h \langle s \rangle \end{aligned} \quad (60)$$

where, in the last line, we have introduced z , the coordination number of particle i . Moreover, we have used the fact that, in the reference system, different spins are

uncorrelated. We now look for the optimum value of h , i.e. the one that minimizes our estimate of f_1 . Carrying out the differentiation with respect to h , we find

$$\begin{aligned}
 0 &= \frac{\partial f_0 - \frac{J}{2} z \langle s \rangle^2 - h \langle s \rangle}{\partial h} \\
 &= \langle s \rangle - (Jz \langle s \rangle + h) \frac{\partial \langle s \rangle}{\partial h} - \langle s \rangle \\
 &= - (Jz \langle s \rangle + h) \frac{\partial \langle s \rangle}{\partial h}
 \end{aligned} \tag{61}$$

And hence,

$$h = -Jz \langle s \rangle \tag{62}$$

If we insert this expression for h in Eqn. 59, we obtain an implicit equation for $\langle s \rangle$, that can be solved to yield $\langle s \rangle$ as a function of T . The free energy estimate that we obtain when inserting this value of $\langle s \rangle$ in Eqn. 60 is

$$f_{MF} = f_0 + \frac{J}{2} z \langle s \rangle^2 \tag{63}$$

The subscript MF in this expression stands for the ‘‘mean-field’’ approximation. It is very important to note that the free energy that results from the mean-field approximation is *not* simply the free energy of the reference system with the effective field. Many books on statistical mechanics are extremely vague (if not outright wrong) on this matter. A notable exception is the book by Yeomans [38].

The example of mean-field theory that I discussed above was chosen for its simplicity. However, the same variational method can be used to derive more general mean-field theories. Of course, the mean-field ‘‘recipe’’ described here cannot be used to approximate the free energy of hard-core models (for the same reason that conventional perturbation theory will not work in such cases). However, in that case, Eqn. 58 could be used as a starting point to devise a mean-field theory for systems with hard-core interactions.

8. Onsager’s regression hypothesis

Diffusion is the process whereby an initially non-uniform concentration profile (*e.g.* an ink drop in water) is smoothed in the absence of flow (no stirring). Diffusion is caused by the molecular motion of the particles in the fluid. The macroscopic law that describes diffusion is known as Fick’s law: it states that the flux \mathbf{j} of the diffusing species is proportional to (minus) the gradient in the concentration of that species:

$$\mathbf{j} = -D\nabla c \tag{64}$$

where D , the constant of proportionality, is referred to as the diffusion coefficient. In what follows, I shall be discussing a particularly simple form of diffusion, namely the case that the molecules of the diffusing species are identical to the other molecules, but for a ‘label’ that does not affect the interaction of the labeled molecules with the others. For instance, this ‘label’ could be a particular polarization of the nuclear spin of the diffusing species or a modified isotopic composition. Diffusion of a labeled species among otherwise identical solvent molecules is called *self-diffusion*.

Let us now compute the concentration profile of the tagged species, under the assumption that a time $t = 0$, the tagged species was concentrated at the origin of our

coordinate frame. In order to compute the time-evolution of the concentration profile, we must combine Fick's law with an equation that expresses conservation of the total amount of labeled material:

$$\frac{\partial c(r, t)}{\partial t} + \nabla \cdot \mathbf{j}(r, t) = 0 \quad (65)$$

Combining Eqn. 65 with Eqn. 64, we obtain

$$\frac{\partial c(r, t)}{\partial t} - D \nabla^2 c(r, t) = 0 \quad (66)$$

We can solve Eqn. 66 with the boundary condition

$$c(r, 0) = \delta(r) \quad (67)$$

to yield

$$c(r, t) = \frac{1}{(4\pi Dt)^{d/2}} \exp\left(-\frac{r^2}{4Dt}\right). \quad (68)$$

As before, d denotes the dimensionality of the system. In fact, for what follows we do not need $c(r, t)$ itself, but just the time-dependence of its second moment

$$\langle r^2(t) \rangle \equiv \int d\mathbf{r} c(r, t) r^2, \quad (69)$$

where we have used the fact that we have imposed

$$\int d\mathbf{r} c(r, t) = 1. \quad (70)$$

We can directly obtain an equation for the time-evolution of $\langle r^2(t) \rangle$ by multiplying Eqn. 66 by r^2 and integrating over all space. This yields

$$\frac{\partial}{\partial t} \int d\mathbf{r} r^2 c(r, t) = D \int d\mathbf{r} r^2 \nabla^2 c(r, t) \quad (71)$$

The left hand side of this equation is simply equal to

$$\frac{\partial \langle r^2(t) \rangle}{\partial t} \quad (72)$$

Applying partial integration to the right-hand side, we obtain

$$\begin{aligned} \frac{\partial \langle r^2(t) \rangle}{\partial t} &= D \int d\mathbf{r} r^2 \nabla^2 c(r, t) \\ &= D \int d\mathbf{r} \nabla \cdot (r^2 \nabla c(r, t)) - D \int d\mathbf{r} (\nabla r^2) \cdot (\nabla c(r, t)) \\ &= D \int d\mathbf{S} (r^2 \nabla c(r, t)) - 2D \int d\mathbf{r} (\mathbf{r}) \cdot (\nabla c(r, t)) \\ &= 0 - 2D \int d\mathbf{r} (\nabla \cdot \mathbf{r} c(r, t)) + 2D \int d\mathbf{r} (\nabla \cdot \mathbf{r}) c(r, t) \\ &= 0 + 2dD \int d\mathbf{r} c(r, t) \\ &= 2dD \quad (73) \end{aligned}$$

Eqn. 73 relates the diffusion coefficient D to the width of the concentration profile. This relation was first derived by Einstein. It should be realized that, whereas D is a macroscopic transport coefficient, $\langle r^2(t) \rangle$ has a *microscopic* interpretation: it is the mean-square distance over which the labeled molecules have moved in a time-interval t . This immediately suggests how to ‘measure’ D in a computer simulation: for every particle i , we measure the distance traveled in time t , $\Delta \mathbf{r}_i(t)$ and we plot the mean square of these distances as a function of the time t :

$$\langle (\Delta r(t))^2 \rangle = \frac{1}{N} \sum_{i=1}^N (\Delta \mathbf{r}_i(t))^2 \quad (74)$$

The displacement $\Delta \mathbf{r}(t)$ that we are interested in is simply the time-integral of the velocity of the tagged particle:

$$\Delta \mathbf{r}(t) = \int_0^t \mathbf{v}(t') dt' \quad (75)$$

Eqn. 75 allows us to express the diffusion coefficient directly in terms of the particle velocities. We start with the relation

$$2D = \lim_{t \rightarrow \infty} \frac{\partial \langle x^2(t) \rangle}{\partial t} \quad (76)$$

where, for convenience, we consider only one Cartesian component of the mean-square displacement. If we write $x(t)$ as the time-integral of the x -component of the tagged-particle velocity, we get

$$\begin{aligned} \langle x^2(t) \rangle &= \left\langle \left(\int_0^t dt' v_x(t') \right)^2 \right\rangle \\ &= \int_0^t \int_0^t dt' dt'' \langle v_x(t') v_x(t'') \rangle \\ &= 2 \int_0^t \int_0^{t'} dt' dt'' \langle v_x(t') v_x(t'') \rangle \end{aligned} \quad (77)$$

The quantity $\langle v_x(t') v_x(t'') \rangle$ is called the *velocity auto-correlation function*. It measures the correlation between the velocity of a particle at times t' and t'' . The velocity auto-correlation function (VACF) is an *equilibrium* property of the system, because it describes correlations between velocities at different times along an equilibrium trajectory. As equilibrium properties are invariant under a change of the time-origin, the VACF depends only on the *difference* of t' and t'' . Hence,

$$\langle v_x(t') v_x(t'') \rangle = \langle v_x(t' - t'') v_x(0) \rangle \quad (78)$$

Inserting Eqn. 77 in Eqn. 76, we obtain

$$\begin{aligned} 2D &= \lim_{t \rightarrow \infty} 2 \int_0^t dt'' \langle v_x(t - t'') v_x(0) \rangle \\ D &= \int_0^\infty d\tau \langle v_x(\tau) v_x(0) \rangle \end{aligned} \quad (79)$$

In the last line of Eqn. 79 we introduced the coordinate $\tau \equiv t - t''$. Hence, we see that we can relate the diffusion coefficient D to the integral of the velocity auto-correlation

function. Such a relation between a transport coefficient and an integral over a time-correlation function is called a ‘Green-Kubo’ relation. Green-Kubo relations have been derived for many other transport coefficients, such as the shear viscosity η ,

$$\eta = \frac{1}{Vk_B T} \int_0^\infty dt \langle \sigma^{xy}(0) \sigma^{xy}(t) \rangle \quad (80)$$

with

$$\sigma^{xy} = \sum_{i=1}^N \left(m_i v_i^x v_i^y + \frac{1}{2} \sum_{j \neq i} x_{ij} f_y(r_{ij}) \right) \quad (81)$$

the thermal conductivity λ :

$$\lambda = \frac{1}{Vk_B T^2} \int_0^\infty dt \langle j_z^e(0) j_z^e(t) \rangle \quad (82)$$

with

$$j_z^e = \frac{d}{dt} \sum_{i=1}^N z_i \frac{1}{2} \left(m_i v_i^2 + \sum_{j \neq i} v(r_{ij}) \right) \quad (83)$$

and electrical conductivity σ

$$\sigma = \frac{1}{Vk_B T} \int_0^\infty dt \langle J_x^{el}(0) J_x^{el}(t) \rangle \quad (84)$$

with

$$J_x^{el} = \sum_{i=1}^N q_i v_i^x \quad (85)$$

For details, see *e.g.* ref. [9]. Time correlation functions can easily be measured in a Molecular Dynamics simulation. It should be emphasized that for classical systems, the Green-Kubo relation for D and the Einstein relation are strictly equivalent. There may be practical reasons to prefer one approach over the other, but the distinction is never fundamental. In the next section, we shall discuss time-correlation functions from a statistical-mechanical point of view.

9. Linear Response Theory

The Green-Kubo relations presented in the previous section are but an example of the relation that exists between transport phenomena and time-correlation functions. In fact, Onsager was the first to suggest that a disturbance created in a system by a weak external perturbation decays in the same way as a spontaneous fluctuation in equilibrium. The statistical mechanical theory that provides this link between correlation functions and response to weak perturbations is called *linear response theory*. I shall give a very simple introduction to linear response theory, mainly to illustrate the ‘mechanical’ basis of Onsager’s regression hypothesis. For a more detailed discussion, the reader is referred to any modern textbook on statistical mechanics *e.g.* ref. [6]. A simple introduction (very similar to the one presented here) is given in the book by Chandler [39], while an extensive discussion of linear-response theory in the context of the theory of liquids is given in [40].

9.1. Static response

First, we consider the static response of a system to a weak applied field. The field could, for instance be an electric field, and the response might be the electric polarization. Suppose that we are interested in the response of a property that can be expressed as the ensemble average of a dynamical variable A . In the presence of an external perturbation, the average of A changes from its equilibrium value $\langle A \rangle_0$ to $\langle A \rangle_0 + \langle \Delta A \rangle$. Next, we must specify the perturbation. We assume that the perturbation can also be written as an explicit function of the coordinates (and, possibly, momenta) of the particles in the system. The effect of the perturbation is to change the Hamiltonian H_0 of the system, to $H_0 - \lambda B(\mathbf{p}^N, \mathbf{q}^N)$. For instance, in the case of an electric field along the x -direction, the change in H would be $\Delta H = -E_x M_x(\mathbf{q}^N)$, where M_x is the x -component of the total dipole moment of the system. The electric field E_x corresponds to the parameter λ . We can immediately write down the general expression for $\langle \Delta A \rangle$

$$\langle A \rangle_0 + \langle \Delta A \rangle = \frac{\int d\Gamma \exp[-\beta(H_0 - \lambda B)] A}{\int d\Gamma \exp[-\beta(H_0 - \lambda B)]}$$

where we have used the symbol Γ to denote $\{\mathbf{p}^N, \mathbf{q}^N\}$, the phase-space coordinates of the system. Let us now compute the part of $\langle \Delta A \rangle$ that varies linearly with λ . To this end, we compute

$$\left(\frac{\partial \langle \Delta A \rangle}{\partial \lambda} \right)_{\lambda=0}$$

Straightforward differentiation shows that

$$\left(\frac{\partial \langle \Delta A \rangle}{\partial \lambda} \right)_{\lambda=0} = \beta \{ \langle AB \rangle_0 - \langle A \rangle_0 \langle B \rangle_0 \} \quad (86)$$

To take again the example of the electric polarization, let us compute the change in dipole moment of a system due to an applied field E_x :

$$\langle M_x \rangle = E_x \left(\frac{\partial M_x}{\partial E_x} \right)_{E_x=0} = \beta E_x \{ \langle M_x^2 \rangle - \langle M_x \rangle^2 \}$$

Suppose that we wish to compute the electric susceptibility of an ideal gas of non-polarizable dipolar molecules with dipole moment $\boldsymbol{\mu}$. In that case,

$$\begin{aligned} \{ \langle M_x^2 \rangle - \langle M_x \rangle^2 \} &= \sum_{i,j=1}^N \langle \mu_x^i \mu_x^j \rangle \\ &= N \langle (\mu_x^i)^2 \rangle \\ &= \frac{N \mu^2}{3} \end{aligned}$$

and hence,

$$P_x \equiv \frac{M_x}{V} = \frac{\mu^2 \rho}{3k_B T} E_x.$$

Of course, this example is special because it can be evaluated exactly. But, in general, we can only compute the expression (equation (86)) for the susceptibility, numerically. It should also be noted that the computation of the dielectric susceptibility is quite a bit more subtle than suggested in the above example (see *e.g.* the discussion in the book of Allen and Tildesley [41] and the article by McDonald in [42]).

9.2. Dynamic response

Thus far, we only considered the static response to a constant perturbation. Let us now consider a very simple time-dependent perturbation. We begin by preparing the system in the presence of a weak, constant perturbation (λB). The static response of A to this perturbation, is given by equation (86). At time $t=0$, we discontinuously switch off the external perturbation. The response ΔA will now decay to zero. We can write down an expression for the average of ΔA at time t :

$$\langle \Delta A(t) \rangle = \frac{\int d\Gamma \exp[-\beta(H_0 - \lambda B)] A(t)}{\int d\Gamma \exp[-\beta(H_0 - \lambda B)]}$$

where $A(t)$ is value of A at time t if the system started at point Γ in phase space, and then evolved according to the natural time evolution of the *unperturbed* system. For convenience, we have assumed that the average of A in the unperturbed system vanishes. In the limit $\lambda \rightarrow 0$, we can write

$$\begin{aligned} \langle \Delta A(t) \rangle &= \beta\lambda \frac{\int d\Gamma \exp[-\beta H_0] B A(t)}{\int d\Gamma \exp[-\beta H_0]} \\ &= \beta\lambda \langle B(0)A(t) \rangle \end{aligned} \quad (87)$$

To give a specific example, consider once again a gas of dipolar molecules in the presence of a weak electric field E_x . The perturbation is equal to $-E_x M_x$. At time $t=0$, we switch off the electric field. When the field was still on, the system had a net dipole moment. When the field is switched off, this dipole moment decays:

$$\langle M_x(t) \rangle = E_x \beta \langle M_x(0)M_x(t) \rangle$$

In words, the decay of the macroscopic dipole moment of the system is determined by the dipole correlation function, which describes the decay of spontaneous fluctuations of the dipole moment in equilibrium. This relation between the decay of the response to an external perturbation and the decay of fluctuations in equilibrium is an example of Onsager's regression hypothesis.

It might seem that the above example of a constant perturbation that is suddenly switched off, is of little practical use, because we are interested in the effect of an arbitrary time-dependent perturbation. Fortunately, in the linear regime that we are considering, the relation given by equation (87) is enough to derive the general response.

To see this, let us consider a time-dependent external field $f(t)$ that couples to a mechanical property B , *i.e.*

$$H(t) = H_0 - f(t)B .$$

To linear order in $f(t)$, the most general form of the response of a mechanical property A to this perturbation is

$$\langle \Delta A(t) \rangle = \int_{-\infty}^{\infty} dt' \chi_{AB}(t, t') f(t') \quad (88)$$

where χ_{AB} , the 'after-effect' function, describes the linear response. We know several things about the response of the system that allow us to simplify equation (88). First of all, the response must be *causal*, *i.e.* there can be no response *before* the perturbation is applied. As a consequence,

$$\chi_{AB}(t, t') = 0 \text{ for } t < t' .$$

Secondly, the response at time t to a perturbation at time t' depends only on the time difference $t - t'$. Hence,

$$\langle \Delta A(t) \rangle = \int_{-\infty}^t dt' \chi_{AB}(t - t') f(t') \quad (89)$$

Note that, once we know χ , we can compute the linear response of the system to an arbitrary time-dependent perturbing field $f(t')$. To find an expression for χ_{AB} , let us consider the situation described above equation (87), namely an external perturbation that has a constant value λ until $t = 0$ and zero from then on. From equation (89) it follows that the response to such a perturbation is

$$\begin{aligned} \langle \Delta A(t) \rangle &= \lambda \int_{-\infty}^0 dt' \chi_{AB}(t - t') \\ &= \lambda \int_t^{\infty} d\tau \chi_{AB}(\tau) \end{aligned} \quad (90)$$

If we compare this expression with the result of equation (87), we see immediately that

$$\int_t^{\infty} d\tau \chi_{AB}(\tau) = \beta \lambda \langle B(0)A(t) \rangle$$

or

$$\begin{aligned} \chi_{AB}(t) &= -\beta \langle B(0)\dot{A}(t) \rangle \text{ for } t > 0. \\ &= 0 \text{ for } t \leq 0. \end{aligned} \quad (91)$$

To give a specific example, consider the mobility of a molecule in an external field F_x . The Hamiltonian in the presence of this field is

$$H = H_0 - F_x x .$$

The phenomenological expression for the steady-state velocity of a molecule in an external field is

$$\langle v_x(t) \rangle = \mu F_x \quad (92)$$

If we derive this relation in terms of correlation functions, we shall find a microscopic expression for the mobility μ . From equation (89) through 91, we have

$$\begin{aligned} \langle v_x(t) \rangle &= F_x \int_{-\infty}^t dt' \chi_{v_x x}(t - t') \\ &= F_x \int_0^{\infty} d\tau \chi_{v_x x}(\tau) \\ &= -\beta F_x \int_0^{\infty} d\tau \langle x(0)\dot{v}_x(\tau) \rangle \\ &= +\beta F_x \int_0^{\infty} d\tau \langle v_x(0)v_x(\tau) \rangle \end{aligned} \quad (93)$$

In the last line of equation (93), we have made use of the stationarity property of time-correlation functions

$$\frac{d}{dt} \langle A(t)B(t+t') \rangle = 0$$

Carrying out the differentiation, we find

$$\langle \dot{A}(t)B(t+t') \rangle = - \langle A(t)\dot{B}(t+t') \rangle .$$

Combining equation (92) and equation (93), we find

$$\mu = \beta \int_0^\infty dt \langle v_x(0)v_x(t) \rangle \quad (94)$$

If we compare the above result with the Green-Kubo relation for the self-diffusion coefficient (equation (79)) we recover the Einstein relation, $\mu = \beta D$.

9.3. Dissipation

Many experimental techniques probe the dynamics of a many-body system by measuring the absorption of some externally applied field (*e.g.* visible light, infrared radiation, microwave radiation). Linear-response theory allows us to establish a simple relation between the absorption spectrum and the Fourier transform of a time-correlation function. To see this, let us again consider an external field that is coupled to a dynamical variable $A(\mathbf{p}^N, \mathbf{q}^N)$. The time-dependent Hamiltonian of the system is:

$$H(t) = H_0 - f(t)A(\mathbf{p}^N, \mathbf{q}^N) .$$

Note that the only quantity that is explicitly time-dependent is $f(t)$. As the Hamiltonian depends on time, the total energy E of the system also changes with time.

$$E(t) = \langle H(t) \rangle$$

Let us compute the average rate of change of the energy of the system. This is the amount of energy that is absorbed (or emitted) by the system, per unit time.

$$\begin{aligned} \frac{\partial E}{\partial t} &= \left\langle \frac{dH}{dt} \right\rangle \\ &= \left\langle \sum_i \left(\dot{\mathbf{q}}_i \frac{\partial H}{\partial \mathbf{q}_i} + \dot{\mathbf{p}}_i \frac{\partial H}{\partial \mathbf{p}_i} \right) + \frac{\partial H}{\partial t} \right\rangle \end{aligned} \quad (95)$$

But, from Hamilton's equations of motion we have

$$\dot{\mathbf{q}}_i = \frac{\partial H}{\partial \mathbf{p}_i}$$

and

$$\dot{\mathbf{p}}_i = - \frac{\partial H}{\partial \mathbf{q}_i}$$

As a consequence, equation (95) simplifies to

$$\begin{aligned} \frac{\partial E}{\partial t} &= \left\langle \frac{\partial H}{\partial t} \right\rangle \\ &= - \left\langle \dot{f}(t)A(\mathbf{p}^N, \mathbf{q}^N) \right\rangle \\ &= - \dot{f}(t) \langle A(t) \rangle \end{aligned} \quad (96)$$

One should note, however, that $\langle A(t) \rangle$ itself is the response to the applied field f

$$\langle A(t) \rangle = \int_{-\infty}^{\infty} dt' \chi_{AA}(t-t')f(t')$$

Let us now consider the situation where $f(t)$ is a periodic field with frequency ω (e.g. monochromatic light). In that case, we can write $f(t)$ as

$$f(t) = \text{Re} f_{\omega} e^{i\omega t}$$

and

$$\dot{f}(t) = \frac{i\omega}{2} (f_{\omega} e^{i\omega t} - f_{\omega}^* e^{-i\omega t})$$

The average rate of energy dissipation is:

$$\begin{aligned} \frac{\partial E}{\partial t} &= -\dot{f}(t) \langle A(t) \rangle \\ &= -\dot{f}(t) \int_{-\infty}^{\infty} dt' \chi_{AA}(t-t')f(t') \end{aligned} \quad (97)$$

For a periodic field, we have

$$\begin{aligned} \int_{-\infty}^{\infty} dt' \chi_{AA}(t-t')f(t') &= \frac{f_{\omega} e^{i\omega t}}{2} \int_{-\infty}^{\infty} dt' \chi_{AA}(t-t')e^{i\omega(t'-t)} \\ &\quad + \frac{f_{\omega}^* e^{-i\omega t}}{2} \int_{-\infty}^{\infty} dt' \chi_{AA}(t-t')e^{-i\omega(t'-t)} \\ &= \pi (f_{\omega} e^{i\omega t} \chi_{AA}(\omega) + f_{\omega}^* e^{-i\omega t} \chi_{AA}(-\omega)) \end{aligned} \quad (98)$$

where

$$\chi_{AA}(\omega) \equiv \frac{1}{2\pi} \int_0^{\infty} dt \chi_{AA}(t) e^{-i\omega t}$$

To compute \dot{E} , the rate of change of the energy, we must average

$$\left\langle \frac{\partial H}{\partial t} \right\rangle$$

over one period T ($= 2\pi/\omega$), of the field:

$$\begin{aligned} \dot{E} &= \frac{-\pi}{2T} \int_0^T dt \{ i\omega (f_{\omega} e^{i\omega t} - f_{\omega}^* e^{-i\omega t}) \\ &\quad \times [f_{\omega} e^{i\omega t} \chi_{AA}(\omega) + f_{\omega}^* e^{-i\omega t} \chi_{AA}(-\omega)] \} \\ &= -\pi\omega |f_{\omega}|^2 \frac{\chi_{AA}(\omega) - \chi_{AA}(-\omega)}{2i} \\ &= -\pi\omega |f_{\omega}|^2 \text{Im} \chi_{AA}(\omega) \end{aligned} \quad (99)$$

We use the relation between $\chi_{AA}(t)$ and the auto-correlation function of A (Eqn. 91)

$$\chi_{AA}(\omega) = \frac{1}{2\pi} \int_0^{\infty} dt e^{-i\omega t} (-\beta \langle A(0) \dot{A}(t) \rangle)$$

The imaginary part of $\chi_{AA}(\omega)$ is given by

$$\begin{aligned}\text{Im}\chi_{AA}(\omega) &= \frac{\beta}{2\pi} \int_0^\infty dt \sin(\omega t) \langle A(0)\dot{A}(t) \rangle \\ &= \frac{-\beta}{4\pi} \int_{-\infty}^\infty dt \omega \cos(\omega t) \langle A(0)A(t) \rangle\end{aligned}\quad (100)$$

Finally, we obtain

$$\dot{E} = |f_\omega|^2 \frac{\beta\omega^2}{4} \int_{-\infty}^\infty dt \cos(\omega t) \langle A(0)A(t) \rangle\quad (101)$$

Hence, from knowledge of the autocorrelation function of the quantity that couples with the applied field, we can compute the shape of the absorption spectrum. The above relation was derived assuming classical dynamics and is therefore only valid if $\hbar\omega \ll k_B T$. However, it is also possible to derive a quantum-mechanical version of linear-response theory that is valid for arbitrary frequencies (see *e.g.* ref. [6]).

To give a specific example, let us compute the shape of the absorption spectrum of a dilute gas of polar molecules. In that case, the relevant correlation function is the dipole auto-correlation function

$$\langle M_x(0)M_x(t) \rangle = \frac{N}{3} \langle \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(t) \rangle .$$

For molecules that rotate almost freely (*almost*, because otherwise there would be no dissipation), $\boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(t)$ depends on time because each molecule rotates. For a molecule with a rotation frequency ω , we have

$$\boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(t) = \mu^2 \cos(\omega t)$$

and for an assembly of molecules with a thermal distribution of rotational velocities $P(\omega)$, we have

$$\langle \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(t) \rangle = \mu^2 \int d\omega P(\omega) \cos(\omega t)$$

The rate of absorption of radiation is then given by

$$\dot{E} = \frac{\pi\beta\omega^2 N\mu^2}{12} P(\omega) |f_\omega|^2\quad (102)$$

For more details about the relation between spectroscopic properties and time-correlation functions, the reader is referred to the article by Madden in ref. [42].

In the above derivation of linear response theory, we have assumed that the system we prepare the system in an equilibrium state with the perturbation *on* and then allow the system to relax to a new equilibrium state with the perturbation *off*. However, this will not always work. Consider, for instance, electrical conductivity. In that case, the perturbation is an electrical field that will cause a current to flow in the system. Hence, the state in which we prepared the system with the field on is *not* an equilibrium state, but a steady *non-equilibrium* state. The same holds, for instance, for a system under steady shear. It would seem that, under such circumstances, one cannot use the framework of linear response theory in its simplest form to derive transport coefficients such as the electrical conductivity σ or the viscosity η .

9.3.1. *Electrical conductivity* Fortunately, things are not quite as bad as that. Consider, for example, electrical conductivity. Indeed, if we put a conducting system in an external field, we will generate a non-equilibrium steady state. However, what we *can* do is to perturb the system by switching on a weak, uniform *vector potential* \mathbf{A} . The Hamiltonian of the system with the vector potential switched on is

$$H' = \sum_{i=1}^N \frac{1}{2m_i} (\mathbf{p}_i - \frac{e_i}{c} \mathbf{A})^2 + U_{pot}; \quad (103)$$

The system described by this Hamiltonian satisfies the same equations of motion as the unperturbed system (\mathbf{A} is a gauge field) and the system will be in an equilibrium state at $t = 0$. We then abruptly switch off the vector potential. From electrodynamics, we know that a time dependent vector potential generates an electric field:

$$\mathbf{E} = -\frac{1}{c} \dot{\mathbf{A}}. \quad (104)$$

In the present case, the electrical field will be an infinitesimal δ -spike at $t = 0$

$$\mathbf{E}(t) = \frac{1}{c} \mathbf{A} \delta(t). \quad (105)$$

We can compute the current that results, in the standard way. We note that we can write H' in Eqn. 103 as

$$\begin{aligned} H' &= H_0 - \sum_{i=1}^N \frac{e_i}{cm_i} \mathbf{p}_i \cdot \mathbf{A} + \mathcal{O}(A^2) \\ &= H_0 - \frac{\mathbf{A}}{c} \int d\mathbf{r} \sum_{i=1}^N \frac{e_i}{m_i} \mathbf{p}_i \delta(\mathbf{r}_i - \mathbf{r}) \\ &= H_0 - \frac{\mathbf{A}}{c} \int d\mathbf{r} \mathbf{j}(\mathbf{r}) \end{aligned} \quad (106)$$

where $\mathbf{j}(\mathbf{r})$ denotes the current density at point \mathbf{r} . The average current density at time t due to the perturbation is given by

$$\langle \mathbf{j}(t) \rangle = \frac{\mathbf{A}}{cV k_B T} \int d\mathbf{r} d\mathbf{r}' \langle \mathbf{j}(\mathbf{r}, 0) \mathbf{j}(\mathbf{r}', t) \rangle. \quad (107)$$

The phenomenological expression for the current response to an applied δ -function electric field spike is (see Eqn. 89)

$$\begin{aligned} \langle \mathbf{j}(t) \rangle &= \int_{-\infty}^t dt' \sigma(t-t') E(t') \\ &= \sigma(t) \frac{\mathbf{A}}{c} \end{aligned} \quad (108)$$

From this it immediately follows that

$$\sigma(t) = \frac{1}{V k_B T} \int d\mathbf{r} d\mathbf{r}' \langle \mathbf{j}(\mathbf{r}, 0) \mathbf{j}(\mathbf{r}', t) \rangle. \quad (109)$$

The DC conductivity is then given by

$$\sigma(\omega = 0) = \frac{1}{V k_B T} \int_0^{\infty} dt \int d\mathbf{r} d\mathbf{r}' \langle \mathbf{j}(\mathbf{r}, 0) \mathbf{j}(\mathbf{r}', t) \rangle. \quad (110)$$

9.3.2. *Viscosity* The corresponding linear response expression for the viscosity seems more subtle because shear is usually not interpreted in terms of an external field acting on all molecules. Still, we can use, by analogy to the electrical conductivity cases, a canonical transformation, the time-derivative of which corresponds to uniform shear. To achieve this, we consider a system of N particles with coordinates \mathbf{r}^M and Hamiltonian

$$H_0 = \sum_{i=1}^N p_i^2 / (2m_i) + U(\mathbf{r}^N). \quad (111)$$

Now consider another system, described by a set of coordinates \mathbf{r}'^N that is related to \mathbf{r}^N by a linear transformation:

$$\mathbf{r}'_i = \mathbf{h} \cdot \mathbf{r}_i. \quad (112)$$

The Hamiltonian for the new system can be written as

$$H_1 = \sum_{i=1}^N \frac{1}{2m_i} \mathbf{p}'_i \cdot \mathbf{G}^{-1} \cdot \mathbf{p}'_i + U(\mathbf{r}'^N), \quad (113)$$

where \mathbf{G} , the metric tensor is defined as

$$\mathbf{G} \equiv \mathbf{h}^T \cdot \mathbf{h} \quad (114)$$

We assume that \mathbf{h} differs infinitesimally from the unit matrix \mathbf{I} :

$$\mathbf{h} = \mathbf{I} + \epsilon \quad (115)$$

In the case that we are interested in the effect of uniform shear, we could for instance choose $\epsilon_{xy} = \epsilon$, while all other elements of $\epsilon_{\alpha\beta}$ are zero. Now consider the case that we equilibrate the system with Hamiltonian H_1 and, at time $t = 0$, we switch off the infinitesimal deformation ϵ . This means that, at $t = 0$, the system experiences a δ -function spike in the shear rate

$$\frac{\partial v_x}{\partial y} = -\epsilon \delta(t) \quad (116)$$

We can compute the time-dependent response of the shear stress, $\sigma_{xy}(t)$, to the sudden change from H_1 to H_0 .

$$\langle \sigma_{xy}(t) \rangle = -\epsilon \frac{1}{V k_B T} \langle \sigma_{xy}(0) \sigma_{xy}(t) \rangle \quad (117)$$

By combining Eqns. 116 and 117 with Eqn. 89, we immediately see that the steady-state stress that results from a steady shear is given by

$$\sigma_{xy} = \frac{\partial v_x}{\partial y} \times \frac{1}{V k_B T} \int_0^\infty dt \langle \sigma_{xy}(0) \sigma_{xy}(t) \rangle \quad (118)$$

and the resulting expression for the shear viscosity η is

$$\eta = \frac{1}{V k_B T} \int_0^\infty dt \langle \sigma_{xy}(0) \sigma_{xy}(t) \rangle. \quad (119)$$

9.4. Rare Events

We conclude this section with a discussion of a special class of transport phenomena, namely activated processes. Activated processes require special attention because a naive application of linear-response theory will yield results that are essentially useless. As an example, we consider uni-molecular reaction $A \rightleftharpoons B$, in which species A is transformed into species B . We limit our discussion to those cases where the rate-limiting step of the reaction can be described as a classical barrier-crossing problem. Of course, there are many chemical reactions that do not fit this description. On the other hand, there are many other activated processes (e.g. classical diffusion through a membrane) that do. Our discussion of activated processes is based on Chandler's approach [43].

Let us first look at the phenomenological description of uni-molecular reactions. We denote the number density of species A and B by c_A and c_B , respectively. The phenomenological rate equations are

$$\frac{dc_A(t)}{dt} = -k_{BA}c_A(t) + k_{AB}c_B(t) \quad (120)$$

$$\frac{dc_B(t)}{dt} = +k_{BA}c_A(t) - k_{AB}c_B(t)$$

Clearly, as the number of molecules is constant in this conversion reaction, the total number density is conserved.

$$\frac{d(c_A(t) + c_B(t))}{dt} = 0 \quad (121)$$

In equilibrium, all concentrations are time-independent, *i.e.* $\dot{c}_A = \dot{c}_B = 0$. This implies that

$$K \equiv \frac{\langle c_A \rangle}{\langle c_B \rangle} = \frac{k_{BA}}{k_{AB}} \quad (122)$$

where K is the equilibrium constant of the reaction. Let us now consider what happens if we take a system at equilibrium, and apply a small perturbation Δc_A , to the concentration of species A (and thereby of species B). We can rewrite the rate equation that determine the decay of this perturbation as follows

$$\frac{d\Delta c_A(t)}{dt} = -k_{BA}\Delta c_A(t) - k_{AB}\Delta c_A(t) \quad (123)$$

where we have used Eqns. 121 and 122. The solution to this equation is

$$\Delta c_A(t) = \Delta c_A(0)e^{-(k_{BA}+k_{AB})t} \equiv \Delta c_A(0)e^{-t/\tau_R} \quad (124)$$

where we have defined the reaction time constant

$$\tau_R = (k_{AB} + k_{BA})^{-1} = k_{BA}^{-1} \left(1 + \frac{\langle c_A \rangle}{\langle c_B \rangle}\right) = \frac{c_B}{k_{BA}} \quad (125)$$

where we have assumed that the total concentration $c_A + c_B = 1$. With this normalization, c_A is simply the probability that a given molecule is in 'state' A .

Thus far, we have discussed the reaction from a macroscopic, phenomenological point of view. Let us now look at the microscopics. We will do this in the framework of linear response theory. First of all, we must have a microscopic description of

the reaction. This means that we need a recipe that allows us to measure how far the reaction has progressed. In the case of diffusion from one free energy minimum to another, over a barrier, we might use the fraction of the distance traveled as a 'reaction coordinate'. In general, reaction coordinates may be complicated, non-linear functions of the coordinates of all particles. It is convenient to think of the reaction coordinate q simply as a generalized coordinate.

By analogy to the discussion in section 9, we will consider an external perturbation that changes the relative probabilities of finding species A and B . To achieve this, we add to the Hamiltonian a term that *lowers* the potential energy for $q < q^*$, where q^* denotes the value of the reaction coordinate at the top of the barrier.

$$H = H_0 - \epsilon\theta(q^* - q) \quad (126)$$

where $\theta(x)$ is the Heavyside step-function, $\theta(x) = 1$ for $x > 0$ and $\theta(x) = 0$ otherwise. ϵ is a parameter that measures the strength of the perturbation. As we are interested in the linear response, we shall consider the limit $\epsilon \rightarrow 0$. Let us first consider the effect of a static perturbation of this type on the probability to find a given molecule in state A . We note that

$$\Delta c_A = \langle c_A \rangle_\epsilon - \langle c_A \rangle_0 = \langle \theta_A \rangle_\epsilon - \langle \theta_A \rangle_0 \quad (127)$$

From Eqn. 86 of section 9.1, we find immediately that

$$\frac{\partial \Delta c_A}{\partial \epsilon} = \beta (\langle \theta_A^2 \rangle_0 - \langle \theta_A \rangle_0^2) \quad (128)$$

This equation can be simplified by noting that $\theta^2(x) = \theta(x)$, hence

$$\frac{\partial \Delta c_A}{\partial \epsilon} = \beta \{ \langle \theta_A \rangle_0 (1 - \langle \theta_A \rangle_0) \} = \beta \langle c_A \rangle \langle c_B \rangle \quad (129)$$

Now, we consider what happens if we suddenly switch off the perturbation at time $t = 0$. The concentration of A will relax to its equilibrium value as described in Eqn. 87 and we find that, to first order in ϵ

$$\begin{aligned} \delta c_A(t) &= \beta \epsilon \frac{\int d\Gamma e^{-\beta H_0} (\theta(0) - \langle \theta \rangle) (\theta(t) - \langle \theta \rangle)}{\int d\Gamma e^{-\beta H_0}} \\ &= \beta \epsilon \langle \Delta \theta(0) \Delta \theta(t) \rangle \end{aligned} \quad (130)$$

Finally, we can use Eqn. 129 to eliminate ϵ from the above equation, and we find the following expression for the relaxation of an initial perturbation in the concentration of species A

$$\Delta c_A(t) = \Delta c_A(0) \frac{\langle \Delta \theta(0) \Delta \theta(t) \rangle}{\langle c_A \rangle \langle c_B \rangle} \quad (131)$$

If we compare this with the phenomenological expression, Eqn. 124, we see that

$$e^{-t/\tau_R} = \frac{\langle \Delta \theta(0) \Delta \theta(t) \rangle}{\langle c_A \rangle \langle c_B \rangle} \quad (132)$$

Actually, we should be cautious with this identification. For very short times (*i.e.* typical time-scales for molecular motion), we should *not* expect the auto-correlation function of the concentration fluctuations to decay exponentially. Only at times that are long compared to typical molecular processes, should we expect Eqn. 132 to hold.

Let us assume that we are in this regime. Then we can obtain an expression for τ_R by differentiating Eqn. 132:

$$-\tau_R^{-1}e^{-t/\tau_R} = \frac{\langle \dot{\theta}(0)\dot{\theta}(t) \rangle}{\langle c_A \rangle \langle c_B \rangle} = -\frac{\langle \dot{\theta}(0)\theta(t) \rangle}{\langle c_A \rangle \langle c_B \rangle} \quad (133)$$

where we have dropped the Δ 's, because the time-derivative of the equilibrium concentration vanishes. Hence, for times that are long compared to molecular times, but still very much shorter than τ_R , we can write

$$\tau_R^{-1} = \frac{\langle \dot{\theta}(0)\theta(t) \rangle}{\langle c_A \rangle \langle c_B \rangle} \quad (134)$$

or, if we recall Eqn. 125 for the relation between k_{BA} and τ_R , we find

$$k_{BA}(t) = \frac{\langle \dot{\theta}(0)\theta(t) \rangle}{\langle c_A \rangle} \quad (135)$$

In this equation, we have indicated the time-dependence of $k_{BA}(t)$ is indicated explicitly. However, we recall that it is only the long-time plateau value of $k_{AB}(t)$ that enters into the phenomenological rate equation. Finally, we can express the correlation function in Eqn. 135 by noting that

$$\dot{\theta}(q^* - q) = \dot{q} \frac{\partial \theta(q^* - q)}{\partial q} = -\dot{q} \delta(q^* - q) \quad (136)$$

Hence

$$\begin{aligned} k_{BA}(t) &= \frac{\langle \dot{q} \delta(q^* - q(0)) \theta(q(t) - q^*) \rangle}{\langle c_A \rangle} \\ &= \frac{\langle \dot{q} \delta(q^* - q(0)) \theta(q(t) - q^*) \rangle}{\langle \theta(q^* - q) \rangle} \end{aligned} \quad (137)$$

$\langle \theta(q^* - q) \rangle$ denotes the probability to find the system somewhere in valley A (the 'reactant' side, to use the language of chemical reactions). We can rephrase equation (137) in a form that makes the separation in statics and dynamics more obvious. We do this by multiplying and dividing and multiplying the right hand side of equation (137) by $\langle \delta(q^* - q) \rangle$. We then obtain

$$k_{BA} = \lim_{t \rightarrow \infty} \frac{\langle \dot{q}(0) \delta(q^* - q(0)) \theta(q(t) - q^*) \rangle}{\langle \delta(q^* - q(0)) \rangle} \times \frac{\langle \delta(q^* - q) \rangle}{\langle \theta(q^* - q) \rangle} \quad (138)$$

The second term on the right-hand side of equation (138), *i.e.* $\langle \delta(q^* - q) \rangle / \langle \theta(q^* - q) \rangle$ denotes the probability density to find the system at the top of the barrier, divided by the probability that the system is on the reactant side of the barrier. This ratio, is completely determined by the height of the free-energy barrier and can therefore be measured by umbrella sampling. For instance, van Duijneveldt and Frenkel [44] have used umbrella sampling to estimate the free-energy barrier for crystal nucleation.

The first term on the left hand side of equation (138) is a conditional average, namely the average of the product $\dot{q}(0)\theta(q(t) - q^*)$, given that $q(0) = q^*$. We can write this term as

$$\lim_{t \rightarrow \infty} \langle \dot{q}(0)\theta(q(t) - q^*) \rangle_{q(0)=q^*} \quad (139)$$

This dynamic quantity can be computed by Molecular Dynamics. In practice, constraint MD will be used to compute this average, in which the system is prepared under the initial constraint $q(0) = q^*$ and then released. It should be noted that the use of a constraint in the MD sampling does have a (slight) effect on the average in equation (139) [45]. The final result is that we have expressed the rate constant k_{BA} exclusively in microscopic quantities that can be measured in a simulation [46, 43].

Acknowledgments

The work of the FOM Institute is part of the research program of FOM and is supported financially by the Netherlands Organization for Research (NWO).

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