LECTURE NOTES

CHE 622A

MOLECULAR SIMULATION

DEPARTMENT OF CHEMICAL ENGINEERING

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Contents

List of symbols

A	Helmholtz free energy
B	virial coefficient
C	heat capacity
$\mathbf{D}$	dipole moment
E	energy (kinetic energy E^{kin}, potential energy E^{pot})
$F, \mathbf{F}$	force
f	function; in particular, the Mayer f function
G	Gibbs free energy
g	radial distribution function
H	enthalpy
$\mathscr{H}, \hat{\mathscr{H}}$	Hamiltonian (energy) function $\mathscr{H}$ and operator $\hat{\mathscr{H}}$
h	Planck constant, i.e. $h = 6.63 \cdot 10^{-34}$ Js
i, j, k, ℓ	indices
$\mathbf{L}$	angular momentum
$\mathscr{L}$	length
$M, \mathscr{M}$	number of systems or coexisting phases
m	mass (of a single molecule)
$N, \mathbf{N}$	number of molecules or microscopic degrees of freedom
$\mathscr{N}$	number of intensive thermodynamic degrees of freedom
n	repulsive interaction exponent, e.g. $n = 12$
P	pressure
$p, \mathbf{p}$	momentum
Q	electric charge (partial or point charge)
$\mathscr{Q}$	partition function
$q, \mathbf{q}$	position, configuration
R	radius
$r, \mathbf{r}$	distance, radial coordinate
S	entropy
s	surface area
T	temperature
$\mathscr{T}$	instantaneous microscopic temperature
t	time
u	interaction potential
V	volume
w	attractive interaction exponent, e.g. $w = 6$
$\mathscr{X}$	macroscopic thermodynamic quantity
x, y, z	spatial coordinates
$x, \mathbf{x}, y, \mathbf{y}$	mole fraction, composition (in mol mol^{-1})
Y	packing fraction

α polarizability
β_T isothermal compressibility
Γ phase space
$\boldsymbol{\Gamma}^{\mathrm{E}}$ adsorption
γ surface tension
$\gamma, \boldsymbol{\gamma}$ microstate
δ Dirac delta function
ε energy parameter
$\zeta, \boldsymbol{\zeta}$ random number
η binary size parameter
ϑ azimuthal angle
κ number of components in a mixture
Λ normalization length scale
λ logarithmic scaling variable
$\mu, \boldsymbol{\mu}$ chemical potential
$\tilde{\mu}$ reduced residual chemical potential
Ξ multipole moment (charge $\Xi_0 = Q$, dipole $\Xi_1 = \mathbf{D}$, quadrupole Ξ_2, ...)
ξ binary energy parameter
Π virial
π probability
ρ fluid density $\rho = N/V$, phase space density $\rho(\gamma)$
σ size parameter
φ orientational angle
χ microscopic observable
ψ wave function
Ω grand potential
ω frequency

1 Concepts of Statistical Mechanics

1.1 Molecular Mechanics

Molecular mechanics relies on a classical mechanical (non-quantum-mechanical) and particle based (rather than continuous) representation of matter and the forces acting on it.[1]

Continuum mechanics	Molecular mechanics	Quantum mechanics
Continuous matter, continuous energy	Discrete molecules, continuous energy	Particle-wave duality, discrete energy levels
Gradients as driving forces (∇x, ∇T, ∇P, ...)	Forces between molecules (gradients of potentials)	Schrödinger equation
Transport coefficients, equation of state	Classical mechanical force field (pair potential)	Energy levels, wave functions

The hierarchy of these levels implies the following relationship between the simulation approaches:

- Molecular force field parameters are sometimes adjusted using results of quantum mechanical computations (beside experimental data, which should always be used for model parameterization);

- Molecular simulation results can potentially be used to determine thermodynamic properties of fluids which are needed for continuum methods such as CFD (however, this is almost never done in actual practice).

The design of molecular force fields, i.e. molecular modelling, always needs to make compromises between competing objectives:

- Numerical simplicity vs. detailed description of physical reality;

- Presence of free parameters, to allow fitting to experimental data, but *not too many*, so that overfitting is avoided and the models can be used for predictions;

- Agreement with experimental data for property I vs. property II, property III, etc.

Typical force fields for low-molecular fluids are *rigid pair potentials* (absence of internal degrees of freedom and absence of multibody interactions). Quantitative conflicts between multiple design criteria, which concern the parameterization of the model within a given model parameter space, can be treated by multicriteria optimization methods.

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[1] Recommended book for the CHE 622A module: Allen and Tildesley, *Computer Simulation of Liquids*, Clarendon, Oxford, 1987 [1].

1.2 Statistical Ensemble

In statistical mechanics, an ensemble is a set of M systems with different, and varying, microscopic states, but with the same, and constant, macroscopic boundary conditions. Accordingly, each system $1 \leq k \leq M$ has a microstate $\gamma_k(t)$ of the type $\gamma = (\mathbf{p}, \mathbf{q})$, where

- $\mathbf{p}$ is the vector containing all momentum coordinates, i.e. $3N$ scalar values in the case of N point masses, and

- $\mathbf{q}$, which is also called the configuration of the system, is the vector containing all position coordinates, of which there are as many as momentum coordinates,

which evolve over the course of time t. The macroscopic boundary conditions depend on the type of ensemble.

isolated systems	closed systems	open systems (control volumes)	mechanically coupled systems
Each system has constant N, V, E	Each system has constant N and V	Each system has constant V	Each system has constant N
	Exchange of energy (heat is transferred)	Exchange of energy and matter	Exchange of energy (work is done)
	Ensemble invariant: $\sum_i E_i$	Ensemble invariants: $\sum_i N_i$ and $\sum_i E_i$	Ensemble invariants: $\sum_i V_i$ and $\sum_i E_i$
microcanonical (NVE ensemble)	canonical (NVT ensemble)	grand canonical (μVT ensemble)	isothermal-isobaric (NPT ensemble)

Macroscopic thermodynamic properties are associated with the ensemble as a whole, not with the individual systems.

1.3 Phase Space

The phase space Γ is the set[2] of possible microstates $\gamma \in \Gamma$. For systems with N point masses, it is $6N$-dimensional with

$$\gamma = (\mathbf{p}_1, \ \mathbf{p}_2, \ \ldots, \ \mathbf{p}_N, \ \mathbf{q}_1, \ \mathbf{q}_2, \ \ldots, \ \mathbf{q}_N), \tag{1.1}$$
$$\Gamma = \mathbb{R}^3 \times \mathbb{R}^3 \times \cdots \times \mathbb{R}^3 \times V \times V \times \cdots \times V. \tag{1.2}$$

At any time t, the systems have the microstates $\gamma_1(t), \gamma_2(t), \ldots, \gamma_M(t)$. On average, this yields a distribution,[3] the phase space density $\rho(\gamma)$. The phase space density is determined by

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[2]Cf. Allen and Tildesley [1], Section 2.1: Sampling from Ensembles.

[3]Here, both ensemble averages (over the systems) and time averages (for a single system) will be considered, cf. below, Section 2.1: Ergodic Hypothesis. However, for a finite number of systems M, a probability distribution is only obtained by averaging over time. The systems of an ensemble are all assumed to be equal, so that the result is the same for all systems and only depends on the ensemble.

1. the thermodynamic boundary conditions,

2. the intermolecular interactions,

and nothing else. The probability $\pi(\Gamma')$ of finding any given system within a region $\Gamma' \subseteq \Gamma$ of the phase space[4] at any given time is proportional to

$$\int_{\Gamma'} dp_{1x} \cdots dp_{Nz}\, dq_{1x} \cdots dq_{Nz}\, \rho(\gamma),$$

where we simplify the notation to

$$\begin{aligned}
\mathbf{dp} &= dp_{1x}\, dp_{1y} \cdots dp_{Nz}, & (1.3) \\
\mathbf{dq} &= dq_{1x}\, dq_{1y} \cdots dq_{Nz}, & (1.4) \\
d\gamma &= \mathbf{dp}\,\mathbf{dq}. & (1.5)
\end{aligned}$$

Hence, on average, there are

$$M'(\Gamma') = \frac{M \int_{\Gamma'} d\gamma\, \rho(\gamma)}{\int_{\Gamma} d\gamma\, \rho(\gamma)} \tag{1.6}$$

systems of the ensemble to be found within the region Γ'.

1.4 Thermodynamic Limit

Transition to thermodynamically relevant[5] ensembles:

- Large numbers of molecules $(N \gg 10^{20})$, effectively $N \to \infty$;

- Law of large numbers, $M \to \infty$, for statistics over the systems.[6]

For the transition to the limit $N \to \infty$, certain intensive quantities such as the fluid density $\rho = N/V$ and the temperature T can be chosen as invariants, while all extensive quantities such as the volume V, the energy E, and the entropy S diverge.

In the limit $M \to \infty$, the phase space density $\rho(\gamma)$ becomes a distribution of systems over the phase space at any given time, rather than being only a time average. The transition to infinite M is carried out at invariant macroscopic boundary conditions for the systems. The ensemble average of a microscopic observable $\chi(\gamma)$, i.e. of any quantity which depends only on γ and nothing else, is then given by the weighted average

$$\langle \chi \rangle = \frac{\int_{\Gamma} d\gamma\, \chi(\gamma)\rho(\gamma)}{\int_{\Gamma} d\gamma\, \rho(\gamma)}. \tag{1.7}$$

Unless stated otherwise, it will be assumed here that the limit $M \to \infty$ is considered, and that M and all other extensive quantities are large enough to neglect finite-size effects.

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[4]Note the analogy between a system with the microstate $\gamma(t)$, which moves through the phase space Γ, and a particle with the position $\mathbf{q}(t)$, which moves through a volume V. Hence, the same symbol ρ is used here for the fluid density and the phase space density.

[5]Exception: Thermodynamics of small systems, where finite size effects and deviations from the macroscopic behaviour are explicitly of interest [2].

[6]In case of the NVT, μVT, and NPT ensembles, this also corresponds to the limit of an infinite heat bath, and in case of the μVT ensemble, to the limit of an infinite reservoir of molecules surrounding the system.

1.5 Trajectory

The trajectory $\gamma(t)$ of a system is the development of its microstate over time. It is determined here by the initial value $\gamma(t_0)$ and the classical mechanical equations of motion, e.g. following Hamilton

$$
\begin{aligned}
\dot{p}_\ell &= -\frac{\partial \mathscr{H}}{\partial q_\ell} = F_\ell, \\
\dot{q}_\ell &= \frac{\partial \mathscr{H}}{\partial p_\ell} = \frac{p_\ell}{m}.
\end{aligned}
\tag{1.8}
$$

Therein, m is the mass of a particle, for simplicity assumed here to be a point mass, ℓ is one of the $3N$ microscopic degrees of freedom (DOF) for a three-dimensional system with N particles, and the Hamiltonian (function)

$$
\mathscr{H}(\gamma) = \mathscr{H}(p_{1x}, p_{1y}, \ldots, p_{Nz}, q_{1x}, q_{1y}, \ldots, q_{Nz}) = E^{\mathrm{kin}}(\mathbf{p}) + E^{\mathrm{pot}}(\mathbf{q})
\tag{1.9}
$$

evaluates to the total energy of the system. This notation is particularly suitable for the separation of coordinates into momenta $\mathbf{p}$ on the one hand, which determine the kinetic energy

$$
E^{\mathrm{kin}}(\mathbf{p}) = \frac{\mathbf{p}^2}{2m} = \frac{1}{2m} \sum_{1 \le i \le N} \left(p_{ix}^2 + p_{iy}^2 + p_{iz}^2 \right),
\tag{1.10}
$$

and the configuration $\mathbf{q}$, which determines the potential energy $E^{\mathrm{pot}}(\mathbf{q})$, on the other hand.

2 Microcanonical Ensemble

2.1 Ergodic Hypothesis

By following the trajectory $\gamma_k(t)$ of a single system k between two points in time t_0 and t_1, for any microscopic observable $\chi(\gamma)$, a time average can be determined

$$\bar{\chi} = \frac{1}{t_1 - t_0} \int_{t_0}^{t_1} dt \; \chi\left(\gamma(t)\right), \tag{2.1}$$

while the ensemble average $\langle \chi \rangle$ is given[1] by Eq. (1.7).

Ergodic hypothesis: For any system $1 \leq k \leq M$ and any region $\Gamma' \subseteq \Gamma$, the fraction of the time interval $t_0 \leq t \leq t_1 = t_0 + \Delta t$ with $\gamma_k(t) \in \Gamma'$ converges to

$$\lim_{\Delta t \to \infty} \frac{t'}{\Delta t} = \frac{\int_{\Gamma'} d\gamma \; \rho(\gamma)}{\int_{\Gamma} d\gamma \; \rho(\gamma)}. \tag{2.2}$$

This means that all systems travel through the whole phase space in the same way. In the limit $M \to \infty$, it also means that ensemble averaging over all systems (at a single point in time) and time averaging over a trajectory (for a single system) necessarily yield the same outcome, since the distribution of microstates in both cases is exactly the same.

Quasiergodic behaviour: For any system $1 \leq k \leq M$, the time average of a given microscopic observable $\chi(\gamma)$, converges to

$$\lim_{\Delta t \to \infty} \bar{\chi} = \langle \chi \rangle \tag{2.3}$$

in the infinite time limit.

The ergodic hypothesis does not always hold, and even where it holds, this is hard to prove formally. In practice, nonetheless, quasiergodic behaviour holds for all thermodynamically relevant microscopic observables in all thermodynamically relevant cases.[2] The validity of the ergodic hypothesis, i.e. ergodicity, is a property of the ensemble only, whereas quasi-ergodicity is a property of a microscopic observable in combination with the macroscopic boundary conditions.

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[1] For a finite number of systems M in the ensemble, the average value of χ will vary over time, so that $\langle \chi \rangle$ is to be understood as an average over all systems and over time. In the thermodynamic limit $M \to \infty$, the average value at any given time can be taken, and it is constant, assuming (as we do here throughout) that *the ensemble as a whole is in equilibrium at any given time,* whereas the microscopic obervables within a single system may fluctuate over time. In particular, we will assume here that the initial conditions for the ensemble are such that it is in equilibrium already, so that there is no relaxation from initial non-equilibrium conditions towards equilibrium. This assumption does not carry over directly to molecular simulation in practice, where such phenomena in general do occur.

[2] Counterexamples exist. These include cases where a system is subdivided into various compartments which are isolated from each other, where there is no coupling between certain microscopic degrees of freedom, or where a quantity (e.g. the overall angular momentum of the system) is invariant, but not specified mac-

2.2 Liouville's Theorem

It is assumed that the ensemble as a whole is in equilibrium at any given time. Hence, the phase space density is time-independent

$$\frac{\partial \rho}{\partial t} = 0. \tag{2.4}$$

On this basis, Liouville's theorem addresses the question: How does the phase space density vary along a trajectory, i.e. what is the time derivative $D\rho/Dt$ in the moving frame of reference following the trajectory $\gamma(t)$ of a system through the phase space?

The frame of reference follows the evolution of the microstate over time, moving through Γ with the velocity $\dot{\gamma} = (\dot{p}_{1x}, \ldots, \dot{p}_{Nz}, \dot{q}_{1x}, \ldots, \dot{q}_{Nz})$. The time derivative of ρ in this frame of reference is[3]

$$\frac{D\rho}{Dt} \;=\; \sum_{\ell \in \{1x, \ldots, Nz\}} \dot{p}_\ell \frac{\partial \rho}{\partial p_\ell} + \sum_{\ell \in \{1x, \ldots, Nz\}} \dot{q}_\ell \frac{\partial \rho}{\partial q_\ell} \;=\; \dot{\gamma} \nabla \rho. \tag{2.5}$$

By analogy between the motion of systems trough phase space and the motion of fluid matter through a volume, the continuity equation from fluid dynamics

$$\frac{\partial \rho}{\partial t} \;=\; -\sum_\ell \frac{\partial (\rho \dot{p}_\ell)}{\partial p_\ell} - \sum_\ell \frac{\partial (\rho \dot{q}_\ell)}{\partial q_\ell} \;=\; -\nabla(\rho \dot{\gamma}) \tag{2.6}$$

holds for the time derivative $\partial \rho/\partial t$ of the phase space density in the stationary frame of reference. Since $\nabla(\rho \dot{\gamma}) = \rho \nabla \dot{\gamma} + \dot{\gamma} \nabla \rho$, it follows from Eqs. (2.4) to (2.6) that

$$\frac{D\rho}{Dt} \;=\; -\rho \nabla \dot{\gamma} \;=\; -\rho \left(\sum_\ell \frac{\partial}{\partial p_\ell} \dot{p}_\ell + \sum_\ell \frac{\partial}{\partial q_\ell} \dot{q}_\ell \right). \tag{2.7}$$

The classical mechanical equations of motion, cf. Eq. (1.8), permit us to replace $\dot{p}_\ell$ and $\dot{q}_\ell$ such that

$$\frac{D\rho}{Dt} = -\rho \left(-\sum_\ell \frac{\partial}{\partial p_\ell} \frac{\partial \mathcal{H}}{\partial q_\ell} + \sum_\ell \frac{\partial}{\partial q_\ell} \frac{\partial \mathcal{H}}{\partial p_\ell} \right). \tag{2.8}$$

According to Schwarz's theorem, applied to the Hamiltonian $\mathcal{H}(p_{1x}, \ldots, p_{Nz}, q_{1x}, \ldots, q_{Nz})$, the applied partial differentiation operations are commutative[4]

$$\frac{\partial^2 \mathcal{H}}{\partial p_\ell \, \partial q_\ell} = \frac{\partial^2 \mathcal{H}}{\partial q_\ell \, \partial p_\ell}, \tag{2.9}$$

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roscopically, so that different systems which belong to the same ensemble continue to behave differently for an arbitrarily long time. Then the choice of initial conditions for the microstate of a system becomes significant. These counterexamples typically either represent undesired artefacts, which can be removed, or they are designed for the specific purpose of discussing non-ergodic behaviour. *We will not consider such special cases, and (quasi-)ergodicity will be assumed throughout.*

[3]Here, ∇ is the divergence operator, which can be thought of as the vector of partial differentiation operators $\nabla = (\partial/\partial p_{1x}, \ldots, \partial/\partial q_{Nz})$.

[4]Assuming, as we do here, that the mentioned derivatives do exist. This is not strictly the case for systems containing hard bodies, where the potential energy is discontinuous in **q**, corresponding to infinite repulsive forces. However, this case can be treated in the same way, by treating the hard potential as the limit of a series of soft potentials which become increasingly steep.

and Eq. (2.8) simplifies to

$$\frac{D\rho}{Dt} = 0. \tag{2.10}$$

Liouville's theorem: On a trajectory $\gamma(t)$ which obeys the classical mechanical equations of motion, the phase space density $\rho(\gamma(t))$ is constant.

2.3 Dirac Delta Function

The phase space density was shown to be a *conserved quantity* of the equations of motion. However, for mechanical systems in general, the only conserved quantities are

- the total energy E of the system,

- the total momentum $\mathbf{p}$ of the system,

- the total angular momentum $\mathbf{L}$ of the system,

- and functions of these quantities $f(E, \mathbf{p}, \mathbf{L})$.

Hence, it must be possible to express $\rho(\gamma)$ as a function of these quantities. Assuming that the system as a whole is at rest and does not rotate, it follows that the phase space density is a function of the energy only, which is expressed microscopically by the observable $\mathcal{H}(\gamma)$. We can therefore write

$$\rho(\gamma) = \rho(\mathcal{H}(\gamma)). \tag{2.11}$$

In the microcanonical ensemble, E is specified as a macroscopic boundary condition which is constant and equal for all systems. Microstates with $\mathcal{H}(\gamma) \neq E$ cannot occur, hence their probability is zero. Microstates with $\mathcal{H}(\gamma) = E$ may occur, and following Eq. (2.11), the phase space density needs to be the same for all of these values of γ. The probability

$$\pi(\Gamma') = \frac{\int_{\Gamma'} d\gamma \, \rho(\gamma)}{\int_{\Gamma} d\gamma \, \rho(\gamma)} \tag{2.12}$$

of finding a system within a region $\Gamma' \subseteq \Gamma$ of the phase space is therefore given by the fraction of the microstates with $\mathcal{H}(\gamma) = E$ which are inside this region. This is expressed mathematically by

$$\rho_{NVE}(\gamma) = \delta(\mathcal{H}(\gamma) - E), \tag{2.13}$$

where δ is the Dirac delta function. This generalized function is defined by its integral

$$\int dx \, \delta(f(x)) \ = \ \|\{x \mid f(x) = 0\}\|, \tag{2.14}$$

which evaluates to the magnitude of the set of zeros of the function $f(x)$; wherever $f(x) \neq 0$, the Dirac delta function is zero. Hence, $\int_{\Gamma'} d\gamma \, \delta(\mathcal{H}(\gamma) - E)$ is a measure for the size of that part of the region Γ' where the system has the specified value of E.

2.4 Partition Function

In the microcanonical ensemble, the magnitude of the set of microstates that satisfy the condition $\mathscr{H}(\gamma) = E$ is proportional to $\int_{\Gamma} d\gamma\, \rho(\gamma)$, the phase space integral over the phase space density. By normalization, this can be converted into a dimensionless effective number of states, called the partition function $\mathscr{Q}$.

Discretization: Following the Heisenberg uncertainty principle, $\Delta p_{\ell} \Delta q_{\ell} \geq h$ holds for the product of the uncertainties of associated momentum and position coordinates; therein, $h = 6.63 \cdot 10^{-34}$ Js is the Planck constant. A single quantum mechanical state corresponds to a subvolume of h^{3N} of the phase space for a system of N point masses with $3N$ microscopic DOF. Hence, the phase space integral over $\rho(\gamma)$ needs to be divided by h^{3N}. Thereby, the dimension of $d\gamma = \mathbf{dp}\,\mathbf{dq}$, which is $(\text{Js})^{3N}$, cancels out, yielding a dimensionless quantity.

Permutation correction: In the representation

$$\gamma = (\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N, \mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N), \tag{2.15}$$

all N molecules are distinguished by their order; exchanging molecules 1 and 2 yields a different microstate, whether these molecules are physically different or not. For a pure component system, where all molecules are identical, every microstate thereby appears in $N!$ permutations which are indistinguishable physically. Hence, the phase space integral over $\rho(\gamma)$ needs to be divided by $N!$ (or by $N_i!\,N_j!\cdots$ in case of a mixture of the components i, j, etc.).

The partition function is therefore given by

$$\mathscr{Q} = \frac{1}{h^{3N}} \frac{1}{N!} \int_{\Gamma} d\gamma\, \rho(\gamma), \tag{2.16}$$

for the case of a single component.

3 Entropy and Temperature

3.1 Definition of Entropy

The entropy is defined by the logarithm of the partition function in the microcanonical ensemble[1]

$$S \;=\; \ln \mathscr{Q}_{NVE} \;=\; \ln \frac{1}{h^{3N}N!} \int_{\Gamma} d\gamma \; \delta\left(\mathscr{H}(\gamma) - E\right). \tag{3.1}$$

The logarithm of the partition function is an extensive quantity:

$$\boxed{\;\boxed{(1)\; N_1, V_1, E_1}\quad \boxed{(2)\; N_2, V_2, E_2}\quad \cdots \quad \boxed{(\mathscr{M})\; N_{\mathscr{M}}, V_{\mathscr{M}}, E_{\mathscr{M}}}\;}$$

If $\mathscr{M}$ (sub-)systems are combined to a greater system, as above, the microstate of the combined system is given by $\gamma = (\gamma_1, \gamma_2, \ldots, \gamma_{\mathscr{M}})$, the phase space by the product set $\Gamma = \Gamma_1 \times \Gamma_2 \times \cdots \times \Gamma_{\mathscr{M}}$, and hence,[2] the partition function by

$$\begin{aligned}
\mathscr{Q} \;&=\; \mathscr{Q}_1 \mathscr{Q}_2 \cdots \mathscr{Q}_{\mathscr{M}} \\
\ln \mathscr{Q} \;&=\; \ln \mathscr{Q}_1 + \ln \mathscr{Q}_2 + \cdots + \ln \mathscr{Q}_{\mathscr{M}}.
\end{aligned} \tag{3.2}$$

Accordingly, the entropy is an extensive quantity, since its value for the combined system is given by the sum over the entropy of the subsystems.

3.2 Ideal Gas Entropy

The ideal gas is defined by the absence of intermolecular interactions. Hence, $E^{\mathrm{pot}} = 0$ and $\mathscr{H}(\gamma) = E^{\mathrm{pot}}(\mathbf{p}) = \mathbf{p}^2/2m$. For this special case, the partition function can be determined analytically

$$\mathscr{Q}_{NVE} \;=\; \frac{1}{h^{3N}N!} \int_{\mathbb{R}^{3N}} \left[\int_{V^N} d\mathbf{q} \right] d\mathbf{p} \, \delta(E^{\mathrm{kin}}(\mathbf{p}) - E), \tag{3.3}$$

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[1]This equation is often written as $S = k_{\mathrm{B}} \ln \mathscr{Q}$. Here, following a widespread convention in statistical mechanics, we define the Boltzmann constant $k_{\mathrm{B}} = 1.38065 \cdot 10^{-23}$ J/K to be unity, i.e. 1 K $= 1.38065 \cdot 10^{-23}$ J. The Boltzmann constant thereby becomes a conversion factor between units of temperature and energy, which are *commensurable* quantities (with the same dimension), similar to the relation between heat and work as commensurable quantities which convert by the ratio 1 kcal $= 4\,184$ J.

[2]To see this, either separate the partition function as defined by Eq. (2.16) into $\mathscr{M}$ independent factors, or consider its intuitive interpretation as the effective number of available states.

by separation of variables. The configurational integral, given in square brackets, evaluates to V^N. Hence,

$$\mathcal{Q}_{NVE} \;=\; \frac{V^N}{\Lambda^{3N} N!} \;\cdot\; \left(\frac{\Lambda}{h}\right)^{3N} \int\limits_{\mathbb{R}^{3N}} \mathbf{dp}\; \delta\left(\frac{1}{2m}\left[p_{1x}^2 + p_{1y}^2 + \cdots + p_{Nz}^2\right] - E\right), \tag{3.4}$$

which decomposes into a factor from the configurational integral and a factor from the integral over the momentum coordinates

$$\begin{aligned} \mathcal{Q}_{NVE} &= \mathcal{Q}_{NVE}^{\mathrm{conf}} \cdot \mathcal{Q}_{NVE}^{\mathrm{mom}} \\ S &= \ln\mathcal{Q}_{NVE}^{\mathrm{conf}} + \ln\mathcal{Q}_{NVE}^{\mathrm{mom}}. \end{aligned} \tag{3.5}$$

Therein, the length Λ is used to normalize both factors of the partition function.[3] With the Stirling approximation, $\ln N! \approx N(\ln N - 1)$, the configurational contribution simplifies to

$$\ln\mathcal{Q}_{NVE}^{\mathrm{conf}} \;=\; N\ln V\Lambda^{-3} - N(\ln N - 1) \;=\; N\left(1 + \ln\frac{V}{\Lambda^3 N}\right). \tag{3.6}$$

The integral

$$\int\limits_{\mathbb{R}^{3N}} \mathbf{dp}\; \delta\left(\frac{1}{2m}\left[p_{1x}^2 + p_{1y}^2 + \cdots + p_{Nz}^2\right] - E\right)$$

corresponds to the hypersurface area of the hypersphere[4] in the $3N$-dimensional momentum space $\mathbb{R}^{3N}$ with the radius $R = \sqrt{2mE}$. Therefore, the second contribution to the entropy is
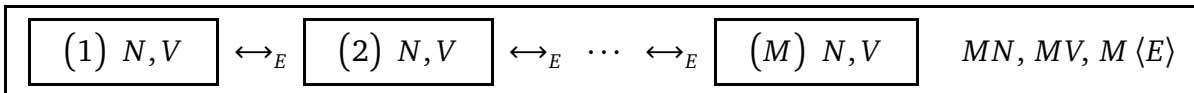
$$\ln\mathcal{Q}_{NVE}^{\mathrm{mom}} \;=\; \ln\left(\frac{\Lambda}{h}\right)^{3N} + \ln\left(\frac{[2\pi mE]^{3N/2}}{(3N/2)!}\right) + O\left(\ln N\right) \;\approx\; \frac{3N}{2}\left(1 + \ln\frac{\Lambda^2}{h^2}\frac{4\pi mE}{3N}\right) \tag{3.7}$$

Combined, in the thermodynamic limit, this yields the Sackur-Tetrode equation

$$\frac{S}{N} \;=\; \frac{5}{2} + \ln\frac{V}{\Lambda^3 N} + \frac{3}{2}\ln\frac{4\pi m\Lambda^2}{3h^2}\frac{E}{N}. \tag{3.8}$$

3.3 Canonical Ensemble

In the NVT ensemble, the systems are closed, but thermally coupled. Hence, they can exchange energy by heat transfer:

$$\boxed{\; \boxed{(1)\; N,V} \;\leftrightarrow_E\; \boxed{(2)\; N,V} \;\leftrightarrow_E\; \cdots \;\leftrightarrow_E\; \boxed{(M)\; N,V} \qquad MN,\, MV,\, M\langle E\rangle \;}$$

The M systems together are described by the state

$$\boldsymbol{\gamma} = (\gamma_1, \gamma_2, \ldots, \gamma_M), \tag{3.9}$$

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[3] Overall, Λ cancels out, so that its magnitude is irrelevant.

[4] The surface area of a k-dimensional sphere with the radius R is $s = 2\pi^{k/2}R^{k-1}/(k/2)!$; for odd values of k, the factorial is replaced with the corresponding value of the gamma function.

and since the ensemble as a whole is isolated, together behave like a microcanonical system.[5] In the thermodynamic limit (infinite heat bath), the microstates of all systems are statistically independent

$$\rho(\boldsymbol{\gamma}) \;=\; \rho_{NVT}(\gamma_1) \cdot \rho_{NVT}(\gamma_2) \cdots \rho_{NVT}(\gamma_M). \tag{3.10}$$

The following questions remain to be clarified:

- How exactly are the boundary conditions related to the temperature?

- What is the canonical partition function $\rho_{NVT}(\gamma_k)$ for a single system k?

3.4 Boltzmann Distribution

The microcanonical phase space density, which characterizes the probability distribution for the M systems of a canonical ensemble together, is given by the Dirac delta function

$$\rho(\boldsymbol{\gamma}) = \delta\left(\sum_{k=1}^{M} \mathscr{H}(\gamma_k) - M\left\langle E \right\rangle \right), \tag{3.11}$$

where $\boldsymbol{\gamma} \in \Gamma^M$ and the energy $M\left\langle E \right\rangle$ describe the systems $1, 2, \ldots, M$ together. Analogously, for the ensemble *without the first system*, $\Gamma' = \Gamma^{M-1}$ denotes the combined phase space, $\boldsymbol{\gamma}' \in \Gamma'$ the vector of microstates, and

$$E'(\boldsymbol{\gamma}') = \sum_{k=2}^{M} \mathscr{H}(\gamma_k) \tag{3.12}$$

the energy of the systems 2 to M together. By separating the first system from the others, Eq. (3.11) transforms to[6]

$$
\begin{aligned}
\rho(\gamma_1, \boldsymbol{\gamma}') \;&=\; \delta\left(\mathscr{H}(\gamma_1) + E'(\boldsymbol{\gamma}') - M\left\langle E \right\rangle \right) \\
&=\; \int_{-\infty}^{\infty} dE_1 \; \delta\left(\mathscr{H}(\gamma_1) - E_1 \right) \; \delta\left(E'(\boldsymbol{\gamma}') - [M\left\langle E \right\rangle - E_1] \right).
\end{aligned}
\tag{3.13}
$$

The relative statistical weight[7] of any given microstate $\gamma_1 \in \Gamma_1$, where $\Gamma_1 = \Gamma$ is the phase space for the first system, is given by the integral over the phase space density in combination

---

[5]As the systems are closed and each molecule is therefore confined to a single system, this is not exactly the case. However, thermal coupling will be discussed here in terms of the exchange of energy, so that the deviations from microcanonical behaviour, which concern the configurational integral only, cancel out.

[6]The delta function $\delta(\mathscr{H}(\gamma_1) - E_1)$ is used here to separate the variables. It is zero except for $\mathscr{H}(\gamma_1) = E_1$, at which point the integral over $\delta(\mathscr{H}(\gamma_1) - E_1)$ yields a contribution of 1. Therefore, in the right hand factor, $\mathscr{H}(\gamma_1)$ can be replaced with E_1, eliminating the variable γ_1 from that factor.

[7]Introducing the canonical phase space density as a *relative* statistical weight permits us to discard constant prefactors which do not depend on γ_1, which we will do repeatedly.

with all microstates $\gamma' \in \Gamma'$ for the other systems

$$\rho_{NVT}(\gamma_1) \quad \sim \quad \int_{\Gamma'} \mathbf{d}\gamma' \, \rho(\gamma_1, \gamma')$$

$$\sim \quad \int_{\Gamma'} \mathbf{d}\gamma' \left[\int_{-\infty}^{\infty} dE_1 \, \delta\left(\mathscr{H}(\gamma_1) - E_1\right) \right] \delta\left(E'(\gamma') - [M \langle E \rangle - E_1]\right)$$

$$\sim \quad \int_{\Gamma'} \mathbf{d}\gamma' \, \delta\left(E'(\gamma') - [M \langle E \rangle - E_1]\right), \tag{3.14}$$

where the integral over dE_1 in square brackets evaluates to 1, since for any given γ_1, there is exactly one energy value E_1 such that $\mathscr{H}(\gamma_1) - E_1 = 0$. By comparison with Eq. (3.1) for the partition function $\mathscr{Q}'$ of the combined system[8] consisting of the systems 2 to M

$$\mathscr{Q}'_{N',V'}(M \langle E \rangle - E_1) = \frac{1}{h^{3N'} N'!} \int_{\Gamma'} \mathbf{d}\gamma' \, \delta\left(E'(\gamma') - [M \langle E \rangle - E_1]\right), \tag{3.15}$$

the canonical phase space density can be given as

$$\rho_{NVT}(\gamma_1) \quad \sim \quad \mathscr{Q}'_{N',V'}(M \langle E \rangle - \mathscr{H}(\gamma_1))$$

$$\sim \quad \exp S'_{N',V'}(M \langle E \rangle - \mathscr{H}(\gamma_1)),$$

$$\sim \quad \exp\left(S'_{N',V'}(M \langle E \rangle) - \mathscr{H}(\gamma_1) \left[\frac{\partial S'}{\partial E'}\right]_{N',V'} + O\left([\mathscr{H}(\gamma_1)]^2\right)\right), \tag{3.16}$$

where the higher-order contribution in $\mathscr{H}(\gamma_1)$ can be neglected in the thermodynamic limit.[9] With the identity

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T} \tag{3.17}$$

from phenomenological thermodynamics, this simplifies to

$$\rho_{NVT}(\gamma_1) \sim \exp S'_{N',V'}(M \langle E \rangle) \cdot \exp\left(-\frac{\mathscr{H}(\gamma_1)}{T}\right). \tag{3.18}$$

Since $M \langle E \rangle$ does not depend on γ_1, the first factor is also constant and can be discarded. The phase space density in the NVT ensemble can therefore be specified as

$$\rho_{NVT}(\gamma) = \exp\left(-\frac{\mathscr{H}(\gamma)}{T}\right), \tag{3.19}$$

which is the Boltzmann distribution. Hence, the probability of a microstate under thermalized boundary conditions is immediately related to the temperature of the system.

---

[8] Since the total number of molecules $N' = (M-1)N$ and volume $V' = (M-1)V$ for the systems 2 to M does not depend on the microstate γ_1 of the first system, these quantities can here be treated as constant. Similarly, the prefactor $1/(h^{3N'} N'!)$ of the partition function $\mathscr{Q}'$ is independent of γ_1.

[9] For $M \to \infty$, the overall energy $M \langle E \rangle$ becomes infinitely greater than the the energy of the first system $\mathscr{H}(\gamma_1)$, and non-linear perturbations of the entropy are strictly absent.

4 Kinetic Gas Theory

4.1 Maxwell Distribution

The Boltzmann distribution can be split into a configurational contribution and a contribution of each individual momentum coordinate

$$\mathcal{H}(\gamma) = E^{\text{pot}}(\mathbf{q}) + \frac{p_{1x}^2}{2m} + \frac{p_{1y}^2}{2m} + \cdots + \frac{p_{Nz}^2}{2m}, \tag{4.1}$$

$$\rho_{NVT}(\gamma) = \exp\left(-\frac{\mathcal{H}(\gamma)}{T}\right)$$

$$= \exp\left(-\frac{E^{\text{pot}}(\mathbf{q})}{T}\right)\exp\left(-\frac{p_{1x}^2}{2mT}\right)\exp\left(-\frac{p_{1y}^2}{2mT}\right)\cdots\exp\left(-\frac{p_{Nz}^2}{2mT}\right). \tag{4.2}$$

Accordingly, different momentum coordinates p_k and p_ℓ are *statistically independent*, and the probability distribution function

$$\rho_{NVT}(p_\ell) \sim \rho_{NVT}(\gamma) \cdot \left[\rho_{NVT}(\mathbf{q})\prod_{k\neq\ell}\rho_{NVT}(p_k)\right]^{-1} \tag{4.3}$$

depends on the temperature only. In this way, an immediate relation between the temperature and the motion of individual molecules can be deduced. By normalization

$$\int_{-\infty}^{\infty} dp_\ell\,\rho_{NVT}(p_\ell) = 1, \tag{4.4}$$

with

$$\int_{-\infty}^{\infty} dx\,\exp(-cx^2) = \sqrt{\frac{\pi}{c}}, \tag{4.5}$$

this yields the Maxwell distribution

$$\rho_{NVT}(p_\ell) = \frac{\exp(-p_\ell^2/2mT)}{\int dp_\ell\,\exp(-p_\ell^2/2mT)} = \frac{1}{\sqrt{2\pi mT}}\exp\left(-\frac{p_\ell^2}{2mT}\right), \tag{4.6}$$

which is a Gaussian bell-shaped function. As a consequence, the fraction of momentum coordinates with $|p_\ell| > p^{\text{ref}}$ is given by a Gaussian error function

$$2\int_{p^{\text{ref}}}^{\infty} dp_\ell\,\rho_{NVT}(p_\ell) = 1 - \text{erf}\left(\frac{p^{\text{ref}}}{\sqrt{2mT}}\right). \tag{4.7}$$

4.2 Equipartition Theorem

At a given temperature, all momentum coordinates obey the Maxwell distribution.[1]

On this basis, the equipartition theorem addresses the question: How much does each microscopic degree of freedom contribute to the ensemble average of the kinetic energy of the system?

By integrating over all permitted values $-\infty < p_\ell < \infty$ for a momentum coordinate p_ℓ, with $\ell \in \{1x, 1y, \ldots, Nz\}$ and

$$\int_{-\infty}^{\infty} dx\, x^2 \exp(-cx^2) = \frac{1}{2}\sqrt{\frac{\pi}{c^3}}, \tag{4.8}$$

one obtains

$$
\begin{aligned}
\left\langle E_\ell^{\text{kin}}\right\rangle_{NVT} = \left\langle \frac{p_\ell^2}{2m} \right\rangle_{NVT} \;&=\; \int_{-\infty}^{\infty} dp_\ell\, \rho_{NVT}(p_\ell)\frac{p_\ell^2}{2m}, \\
&=\; \int_{-\infty}^{\infty} dp_\ell\, \frac{1}{\sqrt{2\pi m T}} \exp\left(\frac{-p_\ell^2}{2mT}\right)\frac{p_\ell^2}{2m} \\
&=\; \frac{T}{2}.
\end{aligned}
\tag{4.9}
$$

For a system with N point masses, it follows that the ensemble average of the total kinetic energy is $3N/2$, from the $3N$ external translational DOF of the point masses. However, the shape of typical molecules is not well represented by point masses, and all microscopic DOF contribute equally to the kinetic energy on average, which is therefore

$$\left\langle E^{\text{kin}}\right\rangle \;=\; N^{\text{DOF}}\frac{T}{2} \tag{4.10}$$

for a system with N^{DOF} degrees of freedom.

4.3 Ideal Gas Heat Capacity

The equipartition theorem for the average contribution of a momentum coordinate p_k to $\mathcal{H}(\gamma)$ was deduced on the following bases:

- The Boltzmann distribution applies, and as a consequence, the value of p_k is statistically independent of all other position and momentum coordinates;

- The contribution of p_k to $\mathcal{H}(\gamma)$ is proportional to p_k^2.

The contribution of a harmonic oscillator to the potential energy can be discussed in the same way, assuming that it is only negligibly coupled to other microscopic DOF. Since the contribution of such a position coordinate q_ℓ to the Hamiltonian is also quadratic, this yields

$$\left\langle E_\ell^{\text{pot}}\right\rangle_{NVT} = \left\langle \frac{cq_\ell^2}{2} \right\rangle_{NVT} = \frac{T}{2} \tag{4.11}$$

---

[1]In particular, the momenta are entirely independent of the configuration of the molecules.

on average, by the same proof as given above.[2] To a reasonable accuracy, the fully excited internal degrees of freedom of a molecule can usually be modelled by harmonic potentials. Therefore, the isochoric ideal gas heat capacity[3] is

$$
\begin{aligned}
\lim_{\rho \to 0} C_V = \lim_{\rho \to 0} \left(\frac{\partial E}{\partial T} \right)_{N,V} &= \lim_{\rho \to 0} \left[\left(\frac{\partial E^{\mathrm{kin}}}{\partial T} \right)_{N,V} + \left(\frac{\partial E^{\mathrm{pot}}}{\partial T} \right)_{N,V} \right], \\
&= \frac{1}{2} N_{\mathrm{ext}}^{\mathrm{DOF}} + N_{\mathrm{int}}^{\mathrm{DOF}}.
\end{aligned}
\tag{4.12}
$$

Therein, $N_{\mathrm{ext}}^{\mathrm{DOF}}$ is the number of external DOF, and $N_{\mathrm{int}}^{\mathrm{DOF}}$ is the effective number of harmonic oscillators corresponding to the excited internal DOF of the molecules. Since each fully excited internal DOF contributes $T/2$ to the kinetic and $T/2$ to the potential energy on average, its overall contribution to the isochoric heat capacity is 1.

Each molecule has three external *translational* DOF and zero to three external *rotational* DOF, depending on the number of axes which carry a significant moment of inertia.[4] The remaining DOF are *internal*;[5] however, the internal DOF are not always fully excited. Whether an internal DOF is fully excited, partially excited, or effectively rigid (in which case it can be neglected), depends on effects which are due to the discretization of the accessible energy levels following quantum mechanics.

4.4 Low-Temperature Effects

At low temperatures, quantum effects may become significant for thermodynamic properties.[6] In quantum mechanics, the wave function $\psi_i(\mathbf{q})$ takes the place of the microstate γ. Solving the Schrödinger equation, which in the stationary case is

$$
\hat{\mathscr{H}}(\psi) = E\psi,
\tag{4.13}
$$

yields an enumerable set of wave functions $\psi_0(\mathbf{q}), \psi_1(\mathbf{q}), \psi_2(\mathbf{q}), \ldots$ which are the *eigenfunctions* of the Hamiltonian (i.e., energy) operator $\hat{\mathscr{H}}$, associated with a series of discrete energy levels $E_0 < E_1 < E_2 < \ldots$ which are the *eigenvalues* of the $\hat{\mathscr{H}}$ operator.

At a given temperature T, the Boltzmann distribution applies

$$
\rho(\psi_i) = \exp\left(\frac{-E_i}{T} \right),
\tag{4.14}
$$

where the following regimes can be distinguished:

---

[2] Since in the result, $T/2$ per DOF, the coefficient $1/2m$ cancels out, the same result is obtained for any quantity with a quadratic contribution to the Hamiltonian, independent of the coefficient of the quadratic term.

[3] Defined by the limit $\rho \to 0$, where intermolecular interactions can be neglected, so that the potential energy only consists of the contributions of the internal degrees of freedom of the molecules.

[4] For an ideal gas atom, the number of external rotational DOF is zero, whereas it is two for molecular oxygen or CO_2 (with a symmetry axis), and three for all molecules which do not have a symmetry axis.

[5] For a system or a molecule with N_a atoms, the overall number of DOF is $3N_a$. The number of internal DOF can be obtained by subtracting the number of external DOF from this value.

[6] The QM results can be included in the present classical mechanical approach by correlations for the ideal contribution, e.g. in the form of correction terms which are added to the molecular simulation results. In many cases, however, no such correction expressions are needed.

- As absolute zero temperature is approached, $T \to 0$, the only permitted state is $\psi_0(\mathbf{q})$, the *ground state*, which is associated with the lowest energy level E_0;

- At low temperatures, the only two relevant energy levels are E_0 and E_1, since the probability of the higher energy levels is comparably small;

- At intermediate temperatures, which are of the same order as the separation between adjacent energy levels E_i and E_{i+1}, many different states need to be considered, but quantum effects remain significant;

- At higher temperatures, so many energy levels become accessible that they can be approximated by a continuum; the system behaves like in classical mechanics.

Due to quantum effects, the isochoric heat capacity converges to $C_V \to 0$ for $T \to 0$. At low temperatures ($T < 0.1\ T_{\mathrm{D}}$), following Debye,[7] the contribution of a DOF which is not fully excited scales with the factor

$$f_{\mathrm{D}}(T) \approx \frac{4\,\pi^4}{5} \left(\frac{T}{T_{\mathrm{D}}} \right)^3 , \qquad (4.15)$$

where T_{D} is the Debye temperature associated with the respective degree of freedom. At intermediate temperatures, $f_{\mathrm{D}}(T)$ becomes more complex (see below), and at high temperatures, the QM correction to the heat capacity converges to unity.
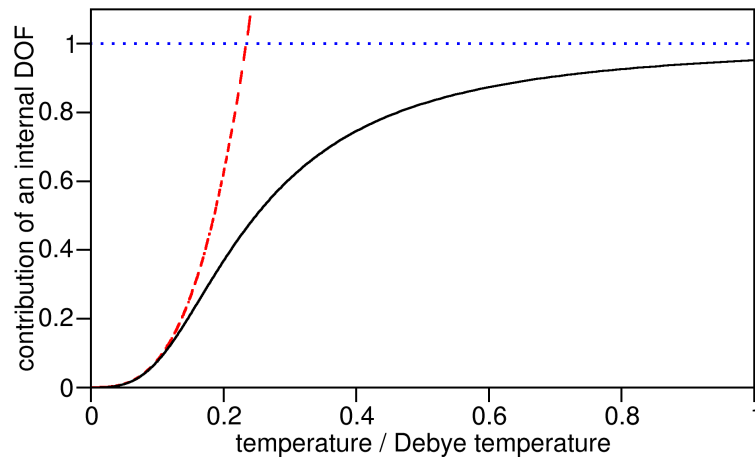
For internal vibrational DOF of molecular fluids, the Debye temperature can be of the order of ambient temperature, e.g. $T_{\mathrm{D}} = 310$ K for I_2, or greater, e.g. $T_{\mathrm{D}} = 2\,200$ K for O_2.

---

[7] P. Debye, Zur Theorie der spezifischen Wärmen, *Ann. Phys.* 344(14), 789–839, **1912**.

5 Equation of State

5.1 Mechanical and Chemical Coupling

The grand canonical $(\mu V T)$ ensemble consists of open systems, which are in chemical and thermal equilibrium with each other:

$$\boxed{(1)\ V \ \longleftrightarrow_{N,E}\ (2)\ V \ \longleftrightarrow_{N,E}\ (3)\ V \ \longleftrightarrow_{N,E}\ \cdots\ \longleftrightarrow_{N,E}\ (M)\ V}$$

The grand canonical phase space density is

$$\rho_{\mu V T}(N, \mathbf{p}, \mathbf{q}) = \exp\left(\frac{\mu N - \mathscr{H}(\mathbf{p}, \mathbf{q})}{T}\right). \tag{5.1}$$

Therein, $\gamma = (N, \mathbf{p}, \mathbf{q})$ is the microstate, and N is a variable quantitiy. The ensemble average of a microscopic observable χ is then obtained by

$$\langle \chi \rangle_{\mu V T} = \frac{1}{\mathscr{Q}_{\mu V T}} \sum_{N=0}^{M\langle N\rangle} \frac{1}{h^{3N} N!} \int_{\mathbb{R}^{3N}} \mathbf{dp} \int_{V^N} \mathbf{dq}\, \rho_{\mu V T}(N, \mathbf{p}, \mathbf{q})\, \chi(N, \mathbf{p}, \mathbf{q}). \tag{5.2}$$

In the isothermal-isobaric (NPT) ensemble, the systems can exchange volume and are in mechanical equilibrium with each other. They can also exchange heat and are therefore in thermal equilibrium:

$$\boxed{(1)\ N \ \left|\begin{smallmatrix}\longleftrightarrow E\\ \longleftrightarrow V\end{smallmatrix}\right.\ (2)\ N \ \left|\begin{smallmatrix}\longleftrightarrow E\\ \longleftrightarrow V\end{smallmatrix}\right.\ (3)\ N \ \left|\begin{smallmatrix}\longleftrightarrow E\\ \longleftrightarrow V\end{smallmatrix}\right.\ \cdots\ \left|\begin{smallmatrix}\longleftrightarrow E\\ \longleftrightarrow V\end{smallmatrix}\right.\ (M)\ N}$$

This yields the phase space density[1]

$$\rho_{NPT}(V, \mathbf{p}, \mathbf{q}) = \exp\left(\frac{-PV - \mathscr{H}(\mathbf{p}, \mathbf{q})}{T}\right), \tag{5.3}$$

where $\gamma = (V, \mathbf{p}, \mathbf{q})$ is the microstate. The NPT ensemble average of an observable is

$$\langle \chi \rangle_{NPT} = \frac{1}{\mathscr{Q}_{NPT}} \frac{1}{h^{3N} N!} \int_{\mathbb{R}^{3N}} \mathbf{dp} \int_{0}^{M\langle V\rangle} dV \int_{V^N} \mathbf{dq}\, \rho_{NPT}(V, \mathbf{p}, \mathbf{q})\, \chi(V, \mathbf{p}, \mathbf{q}). \tag{5.4}$$

Therein, the configurational integral is carried out over system dimensions which depend on the variable value[2] of V.

---

[1] To prove this, consider the effect that a volume change of the system (at constant energy) has on the entropy of the environment (systems 2 to M) if the ensemble consisting of M systems is isolated. To compensate for the volume work done by the system, the same amount of heat is transferred from the environment, which reversibly yields $T \Delta S^{\text{env}} = -P \Delta V^{\text{sys}}$. The same reasoning then applies by which the Boltzmann distribution was also deduced. Similarly, in the grand canonical ensemble, changing the number of molecules in the system (at constant system energy) yields a heat transfer of $\mu \Delta N^{\text{sys}}$ from the system to the environment.

[2] Usually, the limit $M \to \infty$ is considered, so that the upper summation limit $M\langle N\rangle$ in Eq. (5.2) and the upper integration limit $M\langle V\rangle$ in Eq. (5.4) are both replaced with ∞.

5.2 Fundamental Equation of State

The logarithm of the partition function for each of the ensembles is immediately related to the corresponding thermodynamic potential

$$
\boxed{\text{NVT}} \quad -T \ln \mathscr{Q}_{NVT} = -T \ln \frac{1}{h^{3N} N!} \int_{\Gamma} d\gamma \, \exp\left(\frac{-\mathscr{H}(\gamma)}{T}\right),
$$
$$
= \text{Helmholtz free energy } A, \tag{5.5}
$$

$$
\boxed{\text{NPT}} \quad -T \ln \mathscr{Q}_{NPT} = -T \ln \frac{1}{h^{3N} N!} \int_{\mathbb{R}^{3N}} \mathbf{dp} \int_0^{\infty} dV \int_{V^N} \mathbf{dq} \, \exp\left(\frac{-PV - \mathscr{H}(\gamma)}{T}\right),
$$
$$
= \text{Gibbs free energy } G, \tag{5.6}
$$

$$
\boxed{\mu\text{VT}} \quad -T \ln \mathscr{Q}_{\mu VT} = -T \ln \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int_{\Gamma(N)} d\gamma \, \exp\left(\frac{N\mu - \mathscr{H}(\gamma)}{T}\right),
$$
$$
= \text{grand potential } \Omega, \tag{5.7}
$$

i.e. the quantity that is spontaneously minimized under the respective boundary conditions.[3] These potentials are related by

$$
E = A + TS = G + TS - PV = \Omega + TS + G. \tag{5.8}
$$

The dependence of the thermodynamic potential on its associated boundary conditions, e.g. a function $A(N, V, T)$, is a fundamental equation of state (EOS). The other thermodynamic properties can be obtained from it by differentiation[4]

$$
dA = \sum_i \mu_i dN_i - P dV - S dT, \tag{5.9}
$$

$$
dG = \sum_i \mu_i dN_i + V dP - S dT, \tag{5.10}
$$

$$
d\Omega = -\sum_i N_i d\mu_i - P dV - S dT, \tag{5.11}
$$

$$
-dS = \sum_i \frac{\mu_i}{T} dN_i - \frac{P}{T} dV - \frac{1}{T} dE. \tag{5.12}
$$

These and other similar relationships can be memorized using the Guggenheim square.[5]

$$
\begin{array}{ccccc}
S & \leftarrow & E & \rightarrow & V \\
\uparrow & & & & \uparrow \\
H & & & & A \\
\downarrow & & & & \downarrow \\
P & \leftarrow & G & \rightarrow & T
\end{array}
$$

---

[3] In the microcanonical ensemble, the negative entropy $-S = -\ln \mathscr{Q}_{NVE}$ plays a comparable role.

[4] The summation here refers to multiple components i in a mixture; in the preceding discussion, it was implicitly assumed that the system contains a pure fluid. Note that the negative entropy is related to the partition function by $-S = -\ln \mathscr{Q}$, whereas A, G, and Ω are obtained as $-T \ln \mathscr{Q}$. This explains why a factor $1/T$ is present in the coefficients of the total differential for $-S$, but not in the other total differentials.

[5] See also J. M. Phillips, Mnemonic diagrams for thermodynamic systems, *J. Chem. Educat.* 64(8), 674–675, **1987**.

5.3 Ideal Gas Law

If intermolecular interactions are assumed to be absent, the ideal gas law is obtained as an equation of state. With $\mathscr{H}(\gamma) = \mathbf{p}^2/2m$ and[6]

$$
\begin{aligned}
P &= -\left(\frac{\partial A}{\partial V}\right)_{N,T} = T\left(\frac{\partial \ln \mathscr{Q}_{NVT}}{\partial V}\right)_{N,T} \\
&= T\frac{\partial}{\partial V} \ln \frac{1}{h^{3N} N!} \int_{\Gamma} d\gamma \, \exp\left(-\frac{\mathscr{H}(\gamma)}{T}\right) \\
&= T\frac{\partial}{\partial V} \ln \left[\frac{1}{\Lambda^{3N} N!} \int_{V^N} \mathbf{dq} \cdot \left(\frac{\Lambda}{h}\right)^{3N} \int_{\mathbb{R}^{3N}} \mathbf{dp} \, \exp\left(\frac{-\mathbf{p}^2}{2mT}\right)\right],
\end{aligned} \tag{5.13}
$$

and the Stirling approximation $(\ln N! \approx N \ln N - N)$, the pressure is given by

$$
P = T\frac{\partial}{\partial V}\left[N \ln \frac{V}{\Lambda^3 N} + N + \ln\left(\left[\frac{\Lambda}{h}\right]^{3N} \int_{\mathbb{R}^{3N}} \mathbf{dp} \, \exp\frac{-\mathbf{p}^2}{2mT}\right)\right], \tag{5.14}
$$

wherein only the first term depends on V. Accordingly, differentiation eliminates the other terms, and it follows that

$$
P = \frac{T\partial}{\partial V}\left(N \ln \frac{V}{\Lambda^3}\right) = \rho T. \tag{5.15}
$$

Any deviation of real fluid properties from the ideal behaviour is therefore due to the contribution of intermolecular interactions to the partition function.

5.4 Virial Equation of State

The virial equation is the expansion

$$
\frac{P}{T} = \sum_{k=1}^{\infty} B_k \rho^k = \rho + B_2\rho^2 + B_3\rho^3 + B_4\rho^4 + \dots, \tag{5.16}
$$

wherein the parameter B_k is called the k-th virial coefficient. The leading contribution to non-ideal behaviour is therefore given by the second[7] virial coefficient[8]

$$
\begin{aligned}
B_2(T) &= \lim_{\rho \to 0} \frac{1}{\rho}\left(\frac{P}{\rho T} - 1\right) = \lim_{\rho \to 0} \frac{1}{\rho}\left(-1 + \frac{1}{\rho}\frac{\partial}{\partial V} \ln \mathscr{Q}_{NVT}\right) \\
&= \lim_{\rho \to 0} \frac{1}{\rho}\left[-1 + \frac{V\partial}{N\partial V} \ln \int_{V^N} \mathbf{dq} \, \exp\left(-\frac{E^{\mathrm{pot}}(\mathbf{q})}{T}\right)\right]. \tag{5.17}
\end{aligned}
$$

---

[6]A contribution of internal degrees of freedom to the Hamiltonian, if present, cancels out, since it does not depend on the volume.

[7]The first virial coefficient would be $B_1 = 1$, since the contribution $\sim \rho$ is always exactly ρ; hence no such coefficient is used.

[8]The contribution of the momenta (and, similarly, of the $1/N!$ prefactor) does not depend on the volume and therefore cancels out by differentiation, so that only the configurational contribution remains.

The partial derivative is taken at constant N and T. If the potential energy is given by a pair potential

$$E^{\text{pot}}(\mathbf{q}) = \sum_{\{i,j\}} u_{ij}(r_{ij}),\tag{5.18}$$

where r_{ij} is the distance between two molecules i and j, the Mayer f function

$$f_{ij}(r_{ij}) = \exp\left(-\frac{u_{ij}(r_{ij})}{T}\right) - 1 \tag{5.19}$$

can be used for a cluster expansion[9]

$$\begin{aligned}
\exp\left(-\frac{E^{\text{pot}}(\mathbf{q})}{T}\right) &= \prod_{\{i,j\}} \exp\left(-\frac{u_{ij}}{T}\right)\\
&= \prod_{\{i,j\}} \left(1 + f_{ij}\right)\\
&= 1 + \sum f_{ij} + \sum f_{ij} f_{i'j'} + \sum f_{ij} f_{i'j'} f_{i''j''} \cdots, \tag{5.20}
\end{aligned}$$

where the higher-order terms become negligible in the $\rho \to 0$ limit. This justifies the approximation $\exp(-E^{\text{pot}}/T) \approx 1 + \sum f_{ij}$. It follows that[10]

$$\begin{aligned}
B_2(T) &= \lim_{\rho \to 0} \frac{1}{\rho} \left(\frac{\partial}{\partial \ln V^N} \ln \frac{1}{V^N} + \frac{\partial}{\partial \ln V^N} \ln \int_{V^N} \mathbf{dq} \left(1 + \sum_{\{i,j\}} f_{ij} \right) \right)\\
&= \lim_{\rho \to 0} \frac{1}{\rho} \ln \left(\left[\frac{1}{V^N} \int_{V^N} \mathbf{dq} \right] + \frac{1}{V^N} \frac{N^2}{2} \int_{V^N} \mathbf{dq}\, f_{12} \right)\\
&= \lim_{\rho \to 0} \frac{1}{\rho^2} \frac{\partial}{\partial V} \ln \left(1 + \frac{1}{V} \left[\frac{1}{V^{N-1}} \int_{V^{N-1}} \mathbf{dq}_2 \mathbf{dq}_3 \cdots \mathbf{dq}_N \right] \frac{N^2}{2} \int_0^{\infty} dr\, 4\pi r^2 f(r) \right)\\
&= \lim_{\rho \to 0} \frac{1}{\rho^2} \frac{\partial}{\partial V} \ln \left(1 + \frac{N^2}{V} \int_0^{\infty} dr\, 2\pi r^2 f(r) \right)\\
&= \lim_{V \to \infty} \frac{V}{N^2} V \left(\frac{\partial}{\partial V} \frac{N^2}{V} \int_0^{\infty} dr\, 2\pi r^2 f(r) \right) \left(1 + \frac{N^2}{V} \int_0^{\infty} dr\, 2\pi r^2 f(r) \right)^{-1}\\
&= -\lim_{V \to \infty} \left(\frac{1}{\int_0^{\infty} dr\, 2\pi r^2 f(r)} + \frac{N^2}{V} \right)^{-1}\\
&= -\int_0^{\infty} dr\, 2\pi r^2\, f(r). \tag{5.21}
\end{aligned}$$

Hence, the second virial coefficient is given by a volume integral over the Mayer f function.

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[9] J. E. Mayer, The statistical mechanics of condensing systems, *J. Chem. Phys.* 5(1), 67–73, **1937**.

[10] Note that the expressions given in square brackets evaluate to 1.

6 Short Range Interactions

6.1 Repulsive Interaction

In molecular force-field mechanics, the quantum mechanical and multi-body phenomena underlying the inter- and intramolecular interactions are reduced to classical mechanical pair[1] potentials $u_{ij}(r_{ij}, \varphi_i, \varphi_j)$ which are expressed as functions of the distance between two interaction sites r_{ij} and, in some cases, the orientation φ_i and φ_j of the two sites. A molecular model can consist of a single interaction site or of multiple sites. By pairwise additivity, cf. Eq. (5.18), the potential energy of the system is obtained as a sum over all pairwise interactions.

Molecular models need to reflect the physical reality qualitatively, and they need to facilitate accounting for real fluid properties quantitatively by including adjustable model parameters. In all cases, with the single exception of the ideal gas model, it is necessary to reproduce the short-range repulsive interaction between the molecules. At very close distances, the orbitals of adjacent molecules interact

- by overlapping, which causes repulsive forces and an increase in the potential energy of the electrons due to Coulomb's law,

- and by influencing each other, shifting the molecule oribtals to less favourable energy levels, which also induces a repulsive force between the interacting molecules.

Effectively, this yields a soft repulsion of the order of

$$u_{ij}^{\text{rep}}(r_{ij}) \sim \exp(-c r_{ij}). \tag{6.1}$$

For some purposes, it is sufficient to approximate this by a hard repulsion, as in the *hard sphere model*, where the pair potential is given by

$$u_{ij}(r_{ij}) = \begin{cases} \infty, & \text{for } r_{ij} < \sigma_\circ, \\ 0, & \text{for } r_{ij} \geq \sigma_\circ, \end{cases} \tag{6.2}$$

Therein, $\sigma_\circ$ is the diameter of the hard spheres. In this model, the total potential energy of the system is either $E^{\text{pot}}(\mathbf{q}) = 0$, if there is no overlap between particles, or $E^{\text{pot}}(\mathbf{q}) = \infty$, if at least two particles overlap; due to their infinite energy, such configurations never occur,[2] so that E^{pot} is always zero (and $E = E^{\text{kin}}$).

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[1] While this is generally a practical approach for modelling fluids, this simplification is not particularly suitable for most typical solid materials. There, instead, multi-body potentials are commonly used which have the form of a pair potential, but include a parameter which depends on the local order of the surrounding atoms. The most widespread approach in this case is the embedded atom method (EAM) for metals, cf. M. S. Daw *et al.*, *Mater. Sci. Rep.* 9(7–8), 251–310, **1993**; models for carbon, silicon, and ceramics are based on the Tersoff potential, cf. J. Tersoff, *Phys. Rev. B* 39(8), 5566–5568, **1989**.

[2] As a consequence, T has no influence on the configurations of the hard sphere model. Its state is only controlled by the density $\rho = N/V$, which is by convention expressed as a packing fraction $Y = \rho \sigma_\circ^3 \pi / 6$.

6.2 Dispersive Interaction

By fluctuations of the charge distribution (i.e. dispersion), non-polar molecules obtain a dipole moment, which varies at a short time scale. However, assuming that all orientations of these temporary dipoles are equally probable, and that the magnitudes and orientations of the charge fluctuations of multiple molecules are statistically independent, any contributions from this effect would strictly cancel out due to the symmetry of Coulomb's law:
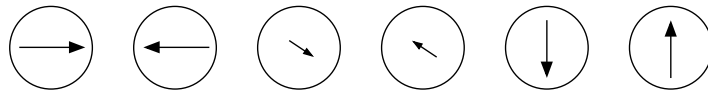
In reality, this symmetry is broken by the influence of the surrounding molecules on the charge fluctuations, since configurations with a lower potential energy are favoured by the Boltzmann term $\exp(-E^{\text{pot}}/T)$ in the phase space density.[3] In this way, a temporary dipole moment is *induced* by the charge distribution in the immediate environment of a molecule.
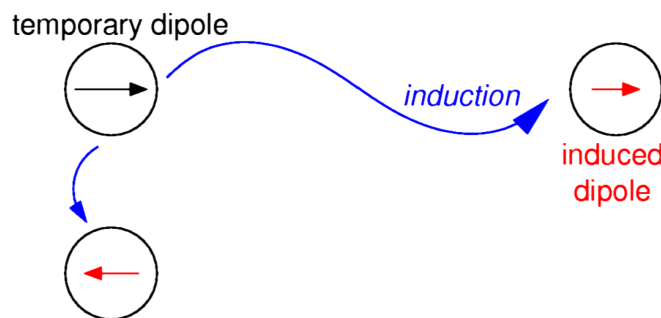
By dispersion, the potential energy of the system is reduced, and molecules are attracted to each other by *London forces*, which are also called *van der Waals forces*. Following London,[4] for two interacting sites with the polarizabilities α_i and α_j coupled to harmonic potentials with the eigenfrequencies ω_i and ω_j, the average interaction potential is

$$u_{ij}^{\text{disp}}(r_{ij}) \; = \; -\,\frac{3\alpha_i\alpha_j}{2(\omega_i^{-1}+\omega_j^{-1})}\,r_{ij}^{-6} + O\!\left(r_{ij}^{-7}\right). \tag{6.3}$$

Hence, the leading contribution of dispersion to the potential energy is negative and $\sim r_{ij}^{-6}$, and the leading contribution to the force $F_{ij} = -du_{ij}/dr_{ij}$ is attractive and $\sim r_{ij}^{-7}$.

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[3] Even in the NVE ensemble, where the phase space density does not contain a Boltzmann factor explicitly, the same relation holds, at least for changes $\Delta E^{\text{pot}}(\mathbf{q})$ which are small compared to E. The reason is that a lower value of $E^{\text{pot}}(\mathbf{q})$ increases $E^{\text{kin}}(\mathbf{p})$, by which a greater region of of the phase space becomes available.

[4] F. London, Über einige Eigenschaften und Anwendungen der Molekularkräfte, *Z. Phys. Chem.* 11, 222–251, **1930**.

6.3 Lennard-Jones Potential

The Lennard-Jones (LJ) potential[5]

$$u_{ij}^{\mathrm{LJ}}(r_{ij}) = 4\varepsilon\left(\left[\frac{\sigma}{r_{ij}}\right]^{12} - \left[\frac{\sigma}{r_{ij}}\right]^{6}\right), \qquad (6.4)$$

with the energy parameter ε and the size parameter σ, is a model for short-range repulsive and dispersive interactions. The force[6] corresponding to this pair potential

$$F_{ij}^{\mathrm{LJ}}(r_{ij}) = -\frac{du_{ij}^{\mathrm{LJ}}}{dr_{ij}} = \frac{24\varepsilon}{\sigma}\left(2\left[\frac{\sigma}{r_{ij}}\right]^{13} - \left[\frac{\sigma}{r_{ij}}\right]^{7}\right), \qquad (6.5)$$

is repulsive at close distances $r_{ij} < 2^{1/6}\sigma$ and attractive for greater distances $r_{ij} > 2^{1/6}\sigma$.
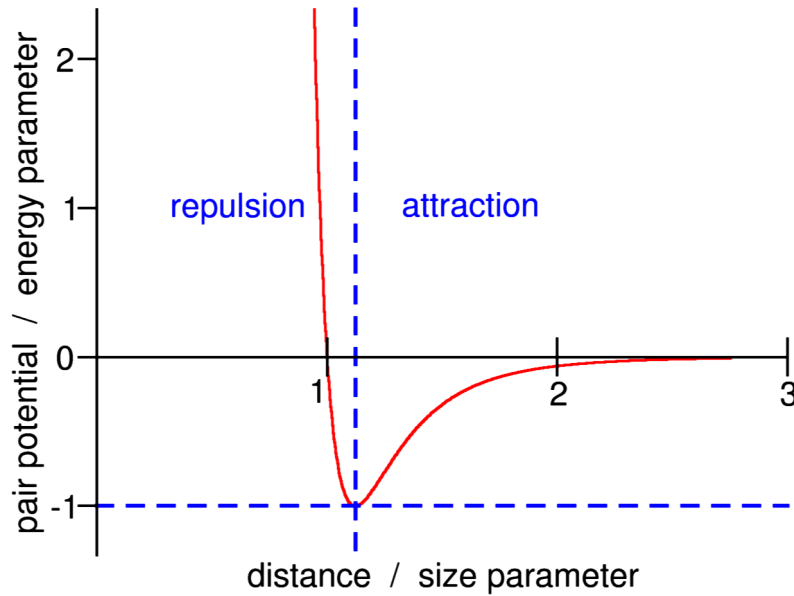
A modification of the LJ potential consists in *truncating and shifting* it

$$u_{ij}(r_{ij}) = \begin{cases} u_{ij}^{\mathrm{LJ}}(r_{ij}) - u_{ij}^{\mathrm{LJ}}(r_{\mathrm{c}}), & \text{for } r_{ij} < r_{\mathrm{c}}, \\ 0, & \text{for } r_{ij} \geq r_{\mathrm{c}}, \end{cases} \qquad (6.6)$$

at a cutoff radius r_{c}. This modification eliminates all long-range interactions over distances beyond r_{c} from the model, which decreases the computational effort. The shift by $u^{\mathrm{LJ}}(r_{\mathrm{c}})$ avoids a discontinuity in the pair potential. With a cutoff at the potential minimum,

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[5]Conventionally credited to J. E. Jones, *Proc. Roy. Soc. A*, 106(738), 463–477, **1924**. While this work indeed considers intermolecular forces of the general form $F(r) = c_n r^{-n} - c_w r^{-w}$, it proposes to specify $14 \leq n \leq 25$ and $w = 5$, so that the attractive contribution to the pair potential is $\sim r^{-4}$. Such generalized forms of the LJ potential are today, also incorrectly, attributed to Mie, see below.

[6]Here, by convention, negative forces $F_{ij} < 0$ indicate an attraction, and positive forces $F_{ij} > 0$ indicate a repulsion between two sites i and j. The distance vector between i and j is defined by $\mathbf{r}_{ij} = \mathbf{q}_j - \mathbf{q}_i$, so that the unit vector pointing from i to j is $\mathbf{r}_{ij}/r_{ij}$. The force (vector) exerted by i on j is $F_{ij}\mathbf{r}_{ij}/r_{ij}$, and the force (vector) exerted by j on i is $F_{ji}\mathbf{r}_{ji}/r_{ji}$, where $F_{ij} = F_{ji}$ according to Newton's third law.

$r_{\mathrm{c}} = 2^{1/6}\sigma$, where the potential shift has the magnitude $+1\varepsilon$, this yields the Weeks-Chandler-Andersen (WCA) potential,[7] a model for soft repulsion. Following Binder,[8] a cutoff at $r_{\mathrm{c}} = 2^{7/6}\sigma$ is used. The most common implementation of this approach[9] is the Lennard-Jones truncated-shifted (LJTS) potential with $r_{\mathrm{c}} = 2.5\,\sigma$.

Generalizations of the LJ potential include the Mie potential[10]

$$u_{ij}(r_{ij}) = \frac{n}{n-w}\left(\frac{n}{w}\right)^{1/(nw^{-1}-1)}\varepsilon\left(\left[\frac{\sigma}{r_{ij}}\right]^{n} - \left[\frac{\sigma}{r_{ij}}\right]^{w}\right), \tag{6.7}$$

which has four parameters (energy ε, size σ, repulsive exponent n, attractive exponent w), and the Buckingham potential[11]

$$u_{ij}(r_{ij}) = \frac{c_1}{\exp(c_2 r_{ij})} - \frac{c_3}{r_{ij}^6}, \tag{6.8}$$

which has three parameters. The Buckingham potential correctly reproduces the exponential soft repulsion, cf. Eq. (6.1), as well as the r^{-6} scaling of the dispersive interaction. As a downside, it contains an exponential function, which is computationally unfavourable.

All of these potentials aim at accounting for all short-range *intermolecular* interactions,[12] repulsive and dispersive, by a single expression.

6.4 Unlike Interaction

The force field for a mixture is defined by the *like* interaction – i.e. the interaction site i is *like* the interaction site j – and the *unlike* interaction which applies to interactions between different species.[13] A combining rule may be required for this purpose, depending on the type of the pair potential.[14] For hard spheres, the unlike interaction is given by the Lorentz

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[7]J. C. Weeks, D. Chandler, H. C. Andersen, Role of repulsive forces in determining the equilibrium structure of simple liquids, *J. Chem. Phys.* 54(12), 5237–5247, **1971**.

[8]Originally introduced by Virnau *et al.*, *J. Chem. Phys.* 121(5), 2169–2179, **2004**.

[9]See also Allen and Tildesley [1], Section 5.2.4 (Shifted and shifted-force potentials).

[10]Incorrectly attributed to Mie [*Ann. Phys.* 316(8), 657–697, **1903**] who, instead, employed a Taylor expansion of the pair potential around $r = \sigma$. It would be more just to refer to Grüneisen [*Ann. Phys.* 344(12), 257–306, **1912**] as a source; however, the term *Mie potential*, whether correct or not, is now established.

[11]R. A. Buckingham, The classical equation of state of gaseous helium, neon and argon, *Proc. Roy. Soc. A* 168(933), 264–283, **1938**.

[12]The *intramolecular* interactions, corresponding to internal degrees of freedom, are also short-range interactions. They can be modelled by harmonic potentials, cf. Section 4.3, but for many purposes, in particular for relatively small molecules, they can be neglected and rigid models can be used. In both cases, whether rigid or internally flexible molecular models are employed, it may be necessary to include correction expressions for quantum mechanical effects, cf. Section 4.4, to reach a good accuracy for the heat capacity and related properties. In the temperature range $0.1\,T_{\mathrm{D}} \le T \le T_{\mathrm{D}}$, where T_{D} is the Debye temperature, it is impossible to account for a partially excited IDF correctly by classical mechanics.

[13]For molecular models with multiple LJ interaction sites, the interaction between sites with different LJ parameters is also a unlike interaction, even if the interacting molecules are identical.

[14]Cf. Allen and Tildesley [1], Section 1.4.2 (Building the model potential). It should be noted that the long range electrostatic interactions, which will be discussed below, do not require any combining rule; there, Coulomb's law can be applied without any further considerations.

combining rule[15]

$$\sigma_{ij} = \frac{1}{2}\left(\sigma_i + \sigma_j\right). \tag{6.9}$$

The Lorentz combining rule is often also applied to the LJ potential, together with the Berthelot combining rule[16]

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}. \tag{6.10}$$

In case of the LJ potential, the unlike interaction is often adjusted to experimental data for the mixture. For this purpose, two binary interaction parameters η and ξ are introduced for each pair of components (both are usually close to 1) and used in the modified Lorentz-Berthelot combining rule

$$\sigma_{ij} = \frac{\eta_{ij}}{2}\left(\sigma_i + \sigma_j\right), \tag{6.11}$$

$$\varepsilon_{ij} = \xi_{ij}\sqrt{\varepsilon_i \varepsilon_j}. \tag{6.12}$$

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[15]H. A. Lorentz, Über die Anwendung des Satzes vom Virial in der kinetischen Theorie der Gase, *Ann. Phys.* 12(1), 127–136, **1881**; Addendum: *Ann. Phys.* 12(4), 660–661, **1881**.

[16]D. Berthelot, Sur le mélange des gaz, *Compt. Rend. Hebd. Acad. Sci.* 126, 1703–1706, 1857–1858, **1898**.

7 Long Range Interactions

7.1 Electrostatic Interactions

The electrostatic interaction between two charged bodies, approximated by point charges, is given by Coulomb's law[1]

$$u_{ij} = \frac{Q_i Q_j}{r_{ij}}. \tag{7.1}$$

This is a long range interaction, as the pair potential decays with $u \sim r^{-1}$, and the force with

$$F_{ij} = -\frac{du_{ij}}{dr_{ij}} = \frac{Q_i Q_j}{r_{ij}^2} \sim r_{ij}^{-2}. \tag{7.2}$$

A series of higher order polarities, which interact over a long range[2] electrostatically, is given by the multipole expansion of the charge distribution.[3]

$Q_i = \Xi_i^0$ charge	$\mathbf{D}_i = \Xi_i^1$ dipole	Ξ_i^2 quadrupole	Ξ_i^3 octopole	$\ldots$ $\ldots$	Ξ_i^j 2^j-pole	$\ldots$ $\ldots$
$Q_i = \sum_k Q_{ik}$ *scalar*	$\mathbf{D}_i = \sum_k \mathbf{q}_{ik} Q_{ik}$ *vector*	see Eq. (7.3) *matrix*	*3-tensor*	$\ldots$	*j-tensor*	$\ldots$

The quadrupole tensor is given by

$$\begin{aligned}
\left(\Xi_i^2\right)_{jj} &= \sum_k Q_{ik}\left(3\left[q_{ik}^{(j)}\right]^2 - \mathbf{q}_{ik}^2\right), \\
\left(\Xi_i^2\right)_{j\ell} &= \sum_k 3 Q_{ik} q_{ik}^{(j)} q_{ik}^{(\ell)} \quad \text{(for } j \neq \ell\text{).}
\end{aligned} \tag{7.3}$$

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[1] By convention, the Coulomb constant $k_C = 1/4\pi\varepsilon_0 = 8.988 \cdot 10^9$ V m C^{-1} = $1.4400 \cdot 10^{-9}$ eV m e^{-2} is specified to be $k_C = 1$, where $e = 1.602 \cdot 10^{-19}$ C is the elementary charge, and $\varepsilon_0 = 0.005\,526\ e(\text{V\AA})^{-1}$ is the vacuum permittivity.

[2] Defined here by $u \sim r^{-k}$ with $k \leq 5$. For electrostatic interactions with $k \geq 6$, the effective pair potential can either be fused with dispersion (case $k = 6$, 7, or 8, probably), e.g. by adjusting the LJ parameter ε accordingly, or it is dominated by the dispersive interactions and can be neglected (case $k \gg 6$). The orientational contribution also plays a role. The deviation of the pair potential from radial symmetry becomes less pronounced for higher-order multipole moments. Up to the quadrupole-quadrupole interaction, however, a significant preference is found for intermolecular orientations which are energetically more favourable; this is neglected whenever the quadrupole is fused with dispersion, even though the r^{-5} scaling of the quadrupolar interaction is similar to the r^{-6} scaling of the dispersive interaction.

[3] The following expressions assume that the charge distribution of molecule i is given by a set of point charges Q_{ik}. If the charge distribution is given as a continuum, e.g. by a wave function, all summation terms need to be replaced by integrals.

The unit of the dipole moment is the Debye (D), with $1\,\text{D} = 0.208\,19\,\text{e\AA}$; e.g., water has a dipole moment of 1.85 D, and for carbon monoxide it is 0.1 D. The unit of the quadrupole moment is the Buckingham (B) or Debye Ångström (DÅ); e.g., the quadrupole moment of CO is 2 DÅ, for CO_2 it is 4.4 DÅ. While D and DÅ are not SI units, they are most frequently used for this purpose.

The series of multipoles is usually expanded around the centre of the lowest-order multipole with a non-zero moment.[4] In many cases, however, it is sufficient to consider only the lowest-order multipole moment, i.e. the charge of an ion, neglecting its dipole moment, or the dipole moment of an uncharged, but polar molecule (neglecting its quadrupole moment).

The interaction potentials and forces between a k-th order multipole at the site i as well as a ℓ-th order multipole at the site j scale as

$$u\left(\Xi_i^k, \Xi_j^\ell\right) \ \sim \ r_{ij}^{-k-\ell-1}, \tag{7.4}$$

$$F\left(\Xi_i^k, \Xi_j^\ell\right) \ \sim \ r_{ij}^{-k-\ell-2}. \tag{7.5}$$

These interactions can become repulsive or attractive, and the contribution to the potential energy can be positive or negative, depending on the orientation, e.g.

$$u_{ij}^{\text{D,D}}(r_{ij}, \varphi_i, \varphi_j, \vartheta_{ij}) \ = \ \left(\sin\varphi_i \sin\varphi_j \cos\vartheta_{ij} - 2\cos\varphi_i \cos\varphi_j\right) \frac{|\,\mathbf{D}_i\,|\,|\,\mathbf{D}_j\,|}{r_{ij}^3}, \tag{7.6}$$

for the pair potential acting between two dipoles. Therein, the orientational angle φ_i is the angle between $\mathbf{D}_i$ and $\mathbf{r}_{ij}$, and φ_j is defined in the same way. The azimuthal angle ϑ_{ij} is the angle between a plane which is parallel to φ_i and $\mathbf{r}_{ij}$ and another plane which is parallel to φ_j and $\mathbf{r}_{ij}$. The trigonometric functions in Eq. (7.6) simplify to scalar product expressions and can therefore be computed with comparably little numerical effort.

7.2 Force Field Design

The following pair potentials are most frequently used to model the different types of interactions:

interaction		pair potential
long range (intermolecular)	electrostatics (charge distribution)	point charges, point dipoles, point quadrupoles
short range (intermolecular)	dispersion and repulsion	Lennard-Jones potential, Mie potential, etc.
short range electrostatics (intermolecular)	hydrogen bonding	point charges
intramolecular interactions	internal degrees of freedom	harmonic potential or rigid models (neglecting IDF)

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[4]For an ion, e.g., the centre of charge $Q_i^{-1} \sum_k q_{ik} Q_{ik}$ should be used as the origin of the multipole expansion.

Multiple interaction sites can be used as building blocks and combined to construct a force field which accounts for all, or the most important, interactions between the molecules. Three basic approaches corresponding to different degrees of abstraction can be distinguished.

- *All-atom models:* There is at least one interaction site for each atom.[5]

- *United-atom models:* Interaction sites can correspond to multiple atoms. A functional group or two small adjacent functional groups are represented by a single site.[6]

- *Coarse grained models:* Force fields at a higher level of abstraction may simplify the detailed chemical structure of the molecule – e.g. polymers represented by connected beads – or the intermolecular interactions, e.g. with a Mie potential for water.[7]

The decision for a particular force field design controls the number of adjustable parameters, i.e. the dimension of the parameter space.

A greater number of parameters increases the adjustability of the model to experimental data; however, this carries the risk of overfitting, by which a model actually becomes worse even though its agreement with specified numerical values is improved. This occurs whenever the avaialble data set does not provide a sufficient amount of information, e.g. because of redundant or contradictory data, or simply due to a lack of data. The principle of *Ockham's razor* applies:[8] For two models which reach the same accuracy for a given data set and both capture the essential aspects of the modelled phenomenon qualitatively, the model with fewer parameters usually has the greater predictive power.

Furthermore, it is harder to characterize a parameter space with a greater dimension. Rapid fine-tuning of a model or a systematic exploration of the entire parameter space (e.g., by multicriteria optimization) may be easy for a coarse grained model, but very hard or impossible to achieve for an all-atom model of the same compound.

7.3 Separation of Scales

Even if pairwise additivity is assumed, $E^{\mathrm{pot}} = \sum u_{ij}$, it is usually too expensive computationally to evaluate the pairwise interactions between all $N(N-1)/2$ pairs of molecules explicitly. Therefore, a cutoff radius r_c is introduced[9] to separate the near field from the far field. For low-molecular fluids, r_c is often of the order of 15 to 20 Å. In the near field

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[5]The molecular models with the greatest level of detail are *reactive force fields*. There, even the formation of covalent bonds is modelled by classical mechanical multi-body potentials. The reactive force field approach is at the boundary to *quantum mechanics/molecular mechanics* or *Car-Parrinello molecular dynamics* where the classical mechanics are coupled to a QM solver from which effective forces are obtained at run time.

[6]Most typically, this means that the hydrogen atoms are fused with the atom to which they are bonded.

[7]All molecular force fields, even with coarse graining, represent each molecule as a discrete entity. At a higher level of abstraction, *dissipative particle dynamics* and the *discrete element method*, which also employ classical mechanical pair potentials, neglect the role of individual fluid molecules.

[8]«Frustra fit per plura quod potest fieri per pauciora» – i.e., it is useless to do by more what can be done by fewer; from W. Ockham, *Summa Totius Logicæ*, **1323/26**.

[9]The separation between the near field and the far field by a cutoff radius is a *numerical technique* for evaluating a pair potential which includes long-range effects. This needs to be distinguished from truncated pair potentials such as WCA and LJTS, where the cutoff is part of the *molecular model* and long range interactions are strictly absent.

$(r_{ij} < r_c)$, the discrete nature of the molecules needs to be taken into account; the pair potentials are evaluated explicitly, at an effort which scales with $O\left(N\rho r_c^3\right)$.

In the far field, the fluid matter is treated as a continuum, and the interactions beyond the cutoff radius $(r_{ij} \geq r_c)$ are taken into account by a *long range correction* (LRC). For a homogeneous LJ system, the LRC contribution to the potential energy is given by

$$E_{\text{LRC}}^{\text{LJ}} = \frac{1}{2} \sum_{i=1}^{N} \int_{r_c}^{\infty} dr \cdot 4\pi r^2 \cdot \rho \cdot 4\varepsilon \left(\frac{\sigma}{r}\right)^6 = -\frac{8\pi}{3} \frac{\sigma^6}{r_c^3} \rho N. \tag{7.7}$$

The division into short range and and long range terms

$$E^{\text{LJ}}(\mathbf{q}) \approx -\frac{8\pi\sigma^6\rho N}{3r_c^3} + \sum_{\{i,j\}}^{r_{ij}<r_c} u_{ij}^{\text{LJ}}(r_{ij}) \tag{7.8}$$

significantly reduces the number of pair potentials which have to be evaluated individually. For electrostatic interactions, multiple LRC approaches exist.

- *Reaction field method:* Assumption of a dielectric continuum in the far field which balances the local polarity of the near field; this approach is very straightforward, but applies to homogeneous systems only.[10]

- *Ewald summation techniques:* The electrostatic interactions are split into a truncated and shifted short range term and a term which contains long range effects; the long range interactions are computed in inverse space, i.e. by Fourier transformation.[11]

- *Fast multipole method*: Recursive subdivision of the volume into subvolumes for which the multipole expansion is developed up to a high order; the summation is conducted in Cartesian space.[12].

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[10]L. Onsager, Electric moments of molecules in liquids, *J. Am. Chem. Soc.* 58(8), 1486–1493, **1936.**

[11]P. P. Ewald, Die Berechnung optischer und elektrostatischer Gitterpotentiale, *Ann. Phys.* 369(3), 253–287, **1921.**

[12]V. Rokhlin, Rapid solution of integral equations of classical potential theory, *J. Comp. Phys.* 60(2), 187–207, **1985**

8 Molecular Simulation Algorithms

8.1 Molecular Dynamics

Molecular dynamics (MD) simulation follows the trajectory of a system by numerical integration of the classical mechanical equations of motion on the basis of a given molecular force field model. This approach was introduced by Alder and Wainwright in 1957.[1]

Starting with a given initial configuration, the evolution of the system is simulated over time. For numerical purposes, time is discretized into time steps corresponding to intervals Δt which are usually[2] of the order of 1 fs $\leq \Delta t \leq 5$ fs. The force[3] acting on molecule i is obtained by summation over all interaction partners[4]

$$\mathbf{F}_i \;=\; \sum_j \mathbf{F}_{ji} \;=\; -\sum_j \frac{du_{ji}}{dr_{ji}} \frac{\mathbf{r}_{ji}}{r_{ji}}. \tag{8.1}$$

Therein, for multi-site models, the intermolecular pair potential u_{ji} is given by the sum of all pairwise interactions of the sites of molecule i with the sites of molecule j. Following Verlet,[5]

$$\begin{aligned} \text{new velocity} \;&=\; \text{old velocity} \;+\; \text{change by acceleration}, \\ \frac{\mathbf{q}_i(t+\Delta t)-\mathbf{q}_i(t)}{\Delta t} \;&=\; \frac{\mathbf{q}_i(t)-\mathbf{q}_i(t-\Delta t)}{\Delta t} + \frac{\mathbf{F}_i\,\Delta t}{m_i}, \end{aligned} \tag{8.2}$$

so that

$$\mathbf{q}_i(t+\Delta t) = 2\mathbf{q}_i(t)-\mathbf{q}_i(t-\Delta t)-\frac{\Delta t^2}{m_i}\sum_j \frac{du_{ji}}{dr_{ji}}\frac{\mathbf{r}_{ji}}{r_{ji}}, \tag{8.3}$$

and the integration can be carried out without the explicit computation (and storage) of velocities; however, the previous position of all particles needs to be stored. Implicitly, the velocities at half time steps are used here.

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[1] B. J. Alder, T. E. Wainwright, Phase transition for a hard sphere system, *J. Chem. Phys.* 27, 1208–1209, **1957**.

[2] For solids and dense liquids, $\Delta t \approx 1$ fs; if molecular models with internal degrees of freedom are used, and the vibration of covalent bonds is simulated explicitly, much smaller time steps $\Delta t \ll 1$ fs may be required. The magnitude of the time step also depends on the numerical integration scheme which is used.

[3] Analogously, for *multi-site models* with external rotational degrees of freedom, the position coordinates include the orientation of the molecule, which can be efficiently implemented by using *quaternion* notation, cf. Rapaport [*J. Comp. Phys.* 60, 306–314, **1985**], and the tangential components of the intermolecular forces are added up to determine the torques.

[4] Index order ji is used here to signify that j acts on i. By Newton's third law, $u_{ij} = u_{ji}$ and $F_{ij} = F_{ji}$, each pair of molecules needs to be considered only once in each time step, rather than twice. Interactions beyond the cutoff radius r_c are neglected at this stage and evaluated separately by a long range correction scheme.

[5] L. Verlet, Computer «experiments» on classical fluids. I. Thermodynamical properties of Lennard-Jones molecules, *Phys. Rev.* 159, 98–103, **1967**.

If the velocities need to be computed, e.g. to obtain microscopic observables and to regulate the temperature, the *Verlet leapfrog algorithm* can be used.[6] This integration scheme explicitly determines position coordinates and forces at full time steps and momentum coordinates at half time steps, iteratively proceeding as follows:

1. Computation of position coordinates $\mathbf{q}_i(t) = \mathbf{q}_i(t - \Delta t) + \mathbf{p}_i(t - \Delta t/2)\,\Delta t / m_i$,

2. computation of forces $\mathbf{F}_i(t) = \sum_j \mathbf{F}_{ji}(\mathbf{q}_j(t), \mathbf{q}_i(t))$ as given by Eq. (8.1),

3. computation of momentum coordinates $\mathbf{p}_i(t + \Delta t/2) = \mathbf{p}_i(t - \Delta t/2) + \mathbf{F}_i(t)\,\Delta t$.

Many integration algorithms exist; ideally, these algorithms are all equivalent realizations of the classical equations of motion, exactly following the system trajectory which is uniquely defined by the initial conditions $\gamma(t_0)$ and the intermolecular interactions.

In fact, all numerical schemes have a certain error, and the nonlinear character of multibody dynamics causes the simulated trajectory $\gamma^{\mathrm{sim}}(t)$ to diverge exponentially, in $t - t_0$, from the exact solution $\gamma(t)$. This deviation is of little importance, however, since the simulated and exact trajectories are similar enough to be equivalent for practical purposes.[7]

8.2 Thermostat and Barostat

The integration of the equations of motion conserves the energy of the system (as well as N and V), corresponding to the microcanonical ensemble. For an MD simulation at a specified temperature, a *thermostat* is introduced.

- Isokinetic thermostat: It is ensured that the instantaneous microscopic temperature $\mathscr{T}(\gamma) = \mathbf{p}^2/mN^{\mathrm{DOF}}$ is constant,[8] with $\mathscr{T}(\gamma) = T$, by rescaling all momentum coordinates by the factor $\sqrt{T/\mathscr{T}(\gamma)}$ in every time step.[9]

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[6]R. W. Hockney, The potential calculation and some applications, pp. 135–211 in B. Alder, S. Fernbach, M. Rotenberg (eds.), *Methods in Computational Physics*, vol. 9 (Plasma Physics), London: Academic Press, **1970**.

[7]The same phenomenon is found for weather forecasts which also follow nonlinear dynamics. For 24 hours, a good precision is expected, and beyond, the quality of the prediction will decay. Nonetheless, even over months, the predicted weather will follow the general tendencies of the local climate and therefore give a correct description of the average weather.

[8]This method is both simple and efficient and therefore used very often; however, it fails to capture the fluctuations of the total kinetic energy of the system. In this way, e.g., the NVT ensemble is approximated by a NVE^{kin} ensemble.

[9]Rescaling all momentum coordinates by the same factor becomes a problem whenever a collision of two molecules i and j is not resolved at sufficient accuracy by the integrator, which can lead to an extremely high value of u_{ij}. The scaling factor is then extremely small, so that only i and j continue to move, and the rest of the system is frozen. Similarly, in case of simulations where the average integration error is significant, but not of the same magnitude everywhere in the simulation volume (e.g. phase coexistence, with a greater deviation from energy conservation in the phase with greater density), the isokinetic thermostat artificially produces a temperature gradient.

- Andersen thermostat: Random degrees of freedom ℓ are assigned new, Maxwell distributed, random momenta p_ℓ.[10]

- Nosé-Hoover thermostat: An additional microscopic degree of freedom with the momentum $\tilde{p}$ (units of kg m^2 s^{-1}), the position $\tilde{q}$ (dimensionless), and the mass $\tilde{m}$ (units of kg m^{-2}) is introduced. The Hamiltonian is extended such that

$$\mathscr{H}(\mathbf{p}, \tilde{p}, \mathbf{q}, \tilde{q}) = \frac{1}{2m}\left(\frac{\mathbf{p}}{\tilde{q}}\right)^2 + \frac{\tilde{p}^2}{2\tilde{m}} + E^{\mathrm{pot}}(\mathbf{q}) + N^{\mathrm{DOF}}T\ln\tilde{q}, \qquad (8.4)$$

by which the Maxwell distribution is correctly reproduced.[11]

The pressure can be regulated by a *barostat*, e.g. following Andersen[12]

$$\mathscr{H}(\mathbf{p}', p_V, \mathbf{q}', V) = \frac{1}{2m}(V^{1/3}\mathbf{p}')^2 + \frac{p_V^2}{2m_V} + E^{\mathrm{pot}}(V^{1/3}\mathbf{q}') + PV, \qquad (8.5)$$

where P is specified, the volume V becomes an additional microscopic DOF, m_V is an effective *piston mass* associated with the volume, and reduced coordinates are employed

$$(\mathbf{p}', \mathbf{q}') = \frac{(\mathbf{p}, \mathbf{q})}{V^{1/3}}. \qquad (8.6)$$

In this way, at each small change of the volume ΔV, all momenta and positions are scaled proportionally, $\Delta \ln \mathbf{p} = \Delta \ln \mathbf{q} = (\Delta \ln V)/3$.

8.3 Monte Carlo Method

The ensemble average of any observable χ is formally given by

$$\langle \chi \rangle = \frac{\int_\Gamma d\gamma\, \chi(\gamma)\rho(\gamma)}{\int_\Gamma d\gamma\, \rho(\gamma)}, \qquad (8.7)$$

which is a high-dimensional integral, since the dimension of Γ is greater than 1000 for all reasonable values of N. A numerical evaluation of this integral cannot be based on a grid of points in Γ, since the grid would have to consist of over 2^{1000} microstates.

To address this challenge, former Manhattan Project scientists at Los Alamos developed the Monte Carlo (MC) method as a randomized integration approach. The general basic idea[13] is to compute a high-dimensional integral by an averaging over the value of the

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[10]See H. C. Andersen, *J. Chem. Phys.* 72(4), 2384–2393, **1980**; This thermostat should not be used for simulations of nonequilibrium scenarios, e.g. in nanofluidics, where deviations from the Maxwell distribution occur. In equilibrium scenarios, the ensemble average of microscopic observables is obtained correctly (assuming ergodicity). However, time-dependent quantities such as transport coefficients are perturbed if new momenta are assigned too frequently.

[11]S. Nosé, A molecular dynamics method for simulations in the canonical ensemble, *Mol. Phys.* 52(2), 255–268, **1984**; W. G. Hoover, Canonical dynamics: Equilibrium phase-space distributions, *Phys. Rev. A* 31(3), 1695–1697, **1985**.

[12]Ibid.

[13]N. Metropolis, S. Ulam, The Monte Carlo method, *J. Am. Stat. Assoc.* 44(247), 335–341, **1949**.

integrand at a series of random points. The accuracy increases as the number of points increases; if the integration space is sufficiently homogeneous with respect to the integrand, i.e. quasiergodicity holds, the required effort becomes computationally tractable.

In case of phase space integrals for molecular systems where the momenta are known to follow the Maxwell distribution, we define[14]

$$\chi(\mathbf{q}) = \frac{1}{(2\pi m T)^{3N/2}} \int_{\mathbb{R}^{3N}} \mathbf{dp} \, \exp\left(-\frac{\mathbf{p}^2}{2mT}\right) \chi(\mathbf{p}, \mathbf{q}), \tag{8.8}$$

and only random configurations $\mathbf{q}^{(1)}, \mathbf{q}^{(2)}, \dots$ need to be generated. If these configurations are chosen at random from V^N following a *uniform distribution*, the ensemble average is obtained as

$$\langle \chi \rangle \approx \frac{\sum_k \chi(\mathbf{q}^{(k)}) \rho(\mathbf{q}^{(k)})}{\sum_k \rho(\mathbf{q}^{(k)})}, \tag{8.9}$$

where the definition of $\rho(\mathbf{q})$ is also given by Eq. (8.8).

8.4 Metropolis Algorithm

A uniform distribution for $\mathbf{q}^{(k)} \in V^N$ is unsuitable in practice, since most configurations generated in this way contain overlapping particles; hence, $E^{\text{pot}}(\mathbf{q})$ is large, $\rho(\mathbf{q})$ is very small, and the relevant contributions to the quantity $\chi(\mathbf{q})\rho(\mathbf{q})$ are sampled very poorly.

Solution following Metropolis *et al.*:[15] If a configuration $\mathbf{q}^{(k)}$ has already been *accepted* as a representative state of the system, it can be used to obtain a new configuration $\mathbf{q}'$ by altering the position of a random molecule i such that

$$\mathbf{q}'_j = \begin{cases} \mathbf{q}^{(k)}_j, & \text{for } i \neq j, \\ \mathbf{q}^{(k)}_i + \tilde{r}\boldsymbol{\zeta}, & \text{for } i = j, \end{cases} \tag{8.10}$$

where $\boldsymbol{\zeta}$ is a vector containing (uniformly distributed) random values between -1 and $+1$, and the displacement length scale $\tilde{r}$ is a simulation parameter. Following the *Metropolis acceptance criterion*, the new configuration is accepted as representative with the probability

$$\pi(\mathbf{q}^{(k)}, \mathbf{q}') = \min\left(1, \frac{\rho(\mathbf{q}')}{\rho(\mathbf{q}^{(k)})}\right), \tag{8.11}$$

which compares the phase space densities of the old and the new state;[16] in particular, configurations with $\rho(\mathbf{q}') > \rho(\mathbf{q}^{(k)})$, corresponding to a decrease in potential energy, are always accepted. Iteratively, the Metropolis algorithm proceeds as follows:

1. Select a random molecule i and generate a random test configuration $\mathbf{q}'$ on the basis of the present configuration $\mathbf{q}^{(k)}$ according to Eq. (8.10).

---

[14]The integral over momentum space is also high dimensional. However, since all individual momentum coordinates p_ℓ are statistically independent, this can usually be simplified further, yielding the ideal gas result for the considered observable.

[15]N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. N. Teller, E. Teller, Equation of state calculations by fast computing machines, *J. Chem. Phys.*, 21(6), 1087–1092, **1953**.

[16]For a good sampling performance, the displacement length scale $\tilde{r}$ should be tuned such that about 50% of the generated configurations are accepted and 50% are rejected.

2. Compute the potential energy change

$$E^{\text{pot}}(\mathbf{q}') - E^{\text{pot}}(\mathbf{q}^{(k)}) = \sum_{i \neq j} \left(u_{ij}(\mathbf{q}'_i - \mathbf{q}^{(k)}_j) - u_{ij}(\mathbf{q}^{(k)}_i - \mathbf{q}^{(k)}_j) \right) \qquad (8.12)$$

and the acceptance probability[17] from Eq. (8.11)

$$\pi(\mathbf{q}^{(k)}, \mathbf{q}') = \min\left(1, \exp([E^{\text{pot}}(\mathbf{q}^{(k)}) - E^{\text{pot}}(\mathbf{q}')]/T)\right). \qquad (8.13)$$

3. Accept $\mathbf{q}'$ with the probability $\pi(\mathbf{q}, \mathbf{q}')$. If accepted, $\mathbf{q}^{(k+1)} = \mathbf{q}'$; if rejected, $\mathbf{q}^{(k+1)} = \mathbf{q}^{(k)}$.

The Metropolis acceptance criterion ensures that the distribution of the accepted configurations agrees with the phase space density. Hence, the series of configurations $\mathbf{q}^{(1)}, \mathbf{q}^{(2)}, \dots, \mathbf{q}^{(\ell)}$ is representative for the ensemble, and an unweighted arithmetic mean

$$\langle \chi \rangle \approx \frac{1}{\ell} \sum_{k=1}^{\ell} \chi(\mathbf{q}^{(k)}) \qquad (8.14)$$

yields the ensemble average of the observable χ.

Remark: Periodic Boundary Conditions

Both for MC and MD simulation, periodic boundary conditions are usually employed to approximate the macroscopic surroundings by periodically displaced identical replicas of the system:
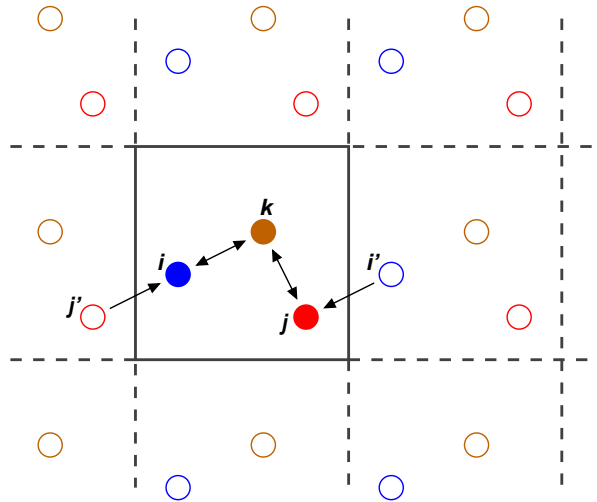
Accordingly, e.g., whenever a molecule leaves the simulation volume on the left side, it reappears on the right side.

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[17]In general, all degrees of freedom need to be considered; this includes the external rotational DOF and the internal DOF of the molecules (if present in the molecular model) and additional quantities which may be varied within the ensemble, e.g. V in the isothermal-isobaric ensemble, or N in the grand canonical ensemble. All microscopic DOF need to be varied stochastically, and the Metropolis acceptance criterion needs to be applied accordingly; thereby, Eq. (8.11) holds in general, whereas Eq. (8.13) only applies to the variation of the position of a selected molecule i.

9 Microscopic Observables

9.1 Computation of Macroscopic Quantities

By MD simulation, a series of microstates

$$\gamma^{(1)}, \gamma^{(2)}, \ldots, \gamma^{(\ell)},$$

is obtained, which are representative[1] for the thermodynamic boundary conditions corresponding to the simulated ensemble. Accordingly, for a microscopic observable χ which is known to correspond to the macroscopic thermodynamic quantity $\mathscr{X}$, the value of $\mathscr{X}$ is determined from

$$\mathscr{X} = \lim_{\ell \to \infty} \frac{1}{\ell} \sum_{k=1}^{\ell} \chi\left(\gamma^{(k)}\right). \tag{9.1}$$

In a MC simulation, a series of configurations

$$\mathbf{q}^{(1)}, \mathbf{q}^{(2)}, \ldots, \mathbf{q}^{(\ell)}$$

is obtained, and $\mathscr{X}$ is given by

$$\mathscr{X} = \lim_{\ell \to \infty} \frac{1}{\ell} \sum_{k=1}^{\ell} \chi\left(\mathbf{q}^{(k)}\right), \tag{9.2}$$

where $\chi(\gamma)$ and $\chi(\mathbf{q})$ are related by Eq. (8.8). Examples for the canonical ensemble:

$$E(N, V, T) = \langle \mathscr{H}(\gamma) \rangle_{NVT} = \frac{N^{\mathrm{DOF}}}{2} T + \langle E^{\mathrm{pot}}(\mathbf{q}) \rangle_{NVT}, \tag{9.3}$$

$$C_V = \frac{\langle \mathscr{H}(\gamma)^2 \rangle - \langle \mathscr{H}(\gamma) \rangle^2}{T^2} = \frac{N^{\mathrm{DOF}}}{2} + \left(\langle E^{\mathrm{pot}}(\mathbf{q})^2 \rangle - \langle E^{\mathrm{pot}}(\mathbf{q}) \rangle^2 \right). \tag{9.4}$$

An observable χ matching a quantity $\mathscr{X}$ can in many cases be found by expressing $\mathscr{X}$ as a derivative of the thermodynamic potential and evaluating this derivative in terms of the partition function. This is shown below for the pressure

$$P = -\left(\frac{\partial A}{\partial V} \right)_{N,T}, \tag{9.5}$$

cf. Section 9.2, and the chemical potential

$$\mu = \left(\frac{\partial A}{\partial N} \right)_{V,T}, \tag{9.6}$$

cf. Section 9.3, in the canonical ensemble.

---

[1]Assuming quasiergodic behaviour, and excluding the initial equilibration stage, during which the sampled microstates cannot be assumed to be representative of the ensemble.

9.2 Virial and Pressure

For a cuboid system with $V = \mathscr{L}_x \mathscr{L}_y \mathscr{L}_z$, a variation of the volume, cf. Eq. (9.5), can be carried out in different ways. In general, the pressure is a tensorial quantity.[2] A surface oriented perpendicular to the x axis experiences the pressure

$$P^{xx} = -\left(\frac{\partial A}{\partial V}\right)_{\mathscr{L}_y,\mathscr{L}_z,N,T} = -\frac{1}{\mathscr{L}_y \mathscr{L}_z}\left(\frac{\partial A}{\partial \mathscr{L}_x}\right)_{\mathscr{L}_y,\mathscr{L}_z,N,T} = -\frac{\mathscr{L}_x}{V}\left(\frac{\partial A}{\partial \mathscr{L}_x}\right)_{\mathscr{L}_y,\mathscr{L}_z,N,T}, \quad (9.7)$$

corresponding to a variation of the volume where all x coordinates are proportionally scaled by a differential amount

$$d\lambda = d\ln V = d\ln\mathscr{L}_x = d\ln q_{ix}\,(\forall i) = d\ln r_{ij}\,(\forall i,j), \quad (9.8)$$

while the y and z coordinates are unaffected. The reduced coordinates

$$q_i' = \left(\begin{array}{c} q_{ix}' \\ q_{iy}' \\ q_{iz}' \end{array}\right) = \left(\begin{array}{c} q_{ix}/\mathscr{L}_x \\ q_{iy}/\mathscr{L}_y \\ q_{iz}/\mathscr{L}_z \end{array}\right), \quad (9.9)$$

for all molecules i, are invariant during this transformation. Accordingly, $\mathbf{dq}_i' = \mathbf{dq}_i/V$ and

$$\mathbf{dq}' = \mathbf{dq}_1'\mathbf{dq}_2'\cdots\mathbf{dq}_N' = V^{-N}\mathbf{dq}. \quad (9.10)$$

For radially symmetrical pair potentials $u_{ij}(r_{ij})$, separating $\mathscr{Q}_{NVT} = \mathscr{Q}_{NVT}^{\mathrm{id}}\mathscr{Q}_{NVT}^{\mathrm{conf}}$ such that[3]

$$\mathscr{Q}_{NVT}^{\mathrm{conf}} = V^{-N}\int_{V^N}\mathbf{dq}\,\exp\left(-\frac{E^{\mathrm{pot}}(\mathbf{q})}{T}\right) = \int_{(0,0,\ldots,0)}^{(1,1,\ldots,1)}\mathbf{dq}'\,\exp\left(-\frac{1}{T}\sum_{\{i,j\}}u_{ij}(r_{ij})\right), \quad (9.11)$$

with $d\lambda = V^{-1}dV$ and $d\ln\mathscr{Q}_{NVT}^{\mathrm{conf}} = (\mathscr{Q}_{NVT}^{\mathrm{conf}})^{-1}d\mathscr{Q}_{NVT}^{\mathrm{conf}}$, Eq. (9.7) in terms of $\mathscr{Q}_{NVT}^{\mathrm{conf}}$ becomes

$$\begin{aligned} P^{xx} &= \frac{T\partial}{\partial V}\ln\mathscr{Q}_{NVT} = \frac{T}{V}\frac{\partial}{\partial\lambda}\left(\ln\mathscr{Q}_{NVT}^{\mathrm{id}} + \ln\mathscr{Q}_{NVT}^{\mathrm{conf}}\right) \\ &= \rho T + \frac{T}{V\mathscr{Q}_{NVT}^{\mathrm{conf}}}\frac{\partial}{\partial\lambda}\int_{(0,\ldots,0)}^{(1,\ldots,1)}\mathbf{dq}'\,\exp\left(-\frac{1}{T}\sum_{\{i,j\}}u_{ij}(r_{ij})\right) \\ &= \rho T + \frac{T}{V}\frac{1}{\mathscr{Q}_{NVT}^{\mathrm{conf}}}\int_{(0,\ldots,0)}^{(1,\ldots,1)}\mathbf{dq}'\,\exp\left(-\frac{1}{T}\sum_{\{i,j\}}u_{ij}(r_{ij})\right)\left[-\frac{1}{T}\sum_{\{i,j\}}\frac{du_{ij}}{dr_{ij}}\frac{\partial r_{ij}}{\partial\lambda}\right], \quad (9.12) \end{aligned}$$

where the partial derivative is taken at constant $\mathscr{L}_y,\mathscr{L}_z,N,T$. Therein, $\exp(-E^{\mathrm{pot}}(\mathbf{q}')/T)$ is the statistical weight of the reduced configuration $\mathbf{q}'$, while $\mathscr{Q}_{NVT}^{\mathrm{conf}}$ is the integral of $\exp(-E^{\mathrm{pot}}(\mathbf{q}')/T)$ over the reduced configuration space,[4] cf. Eq. (9.11).

---

[2]In case of a homogeneous fluid system in equilibrium, without a phase boundary and in absence of an external potential, the diagonal elements of the pressure tensor are all equal, $P^{xx} = P^{yy} = P^{zz} = P$, and the off-diagonal elements, which are not discussed here, are all zero.

[3]Using this normalization, $\mathscr{Q}_{NVT}^{\mathrm{conf}} = 1$ holds for the ideal gas. Hence, in case of the ideal gas, the configurational contribution to the pressure vanishes; accordingly, the contribution from $\mathscr{Q}_{NVT}^{\mathrm{id}}$ yields ρT, cf. Section 5.3.

[4]Hence, for an observable $\chi(\mathbf{q}')$, the canonical ensemble average is $(\mathscr{Q}_{NVT}^{\mathrm{conf}})^{-1}\int\mathbf{dq}'\,\chi(\mathbf{q}')\exp(-E^{\mathrm{pot}}(\mathbf{q}')/T)$.

Eq. (9.12) can be simplified to

$$P^{xx} = \rho T + \frac{T}{V}\left\langle -\frac{1}{T}\sum_{\{i,j\}}\frac{du_{ij}}{dr_{ij}}\frac{\partial r_{ij}}{\partial \lambda}\right\rangle_{NVT} = \rho T + \frac{\langle \Pi^{xx}\rangle}{V},\qquad(9.13)$$

where Π^{xx}, given by[5]

$$\begin{aligned}
\Pi^{xx}(\mathbf{q}) &= -\sum_{\{i,j\}}\frac{du_{ij}}{dr_{ij}}\frac{\partial r_{ij}}{\partial \lambda}\\
&= \sum_{\{i,j\}}F_{ij}\frac{\partial}{\partial \lambda}\left(r_{ij,x}^2 + r_{ij,y}^2 + r_{ij,z}^2\right)^{-1/2} = \sum_{\{i,j\}}F_{ij}\frac{1}{2(r_{ij}^2)^{1/2}}\frac{\partial}{\partial \lambda}\left(r_{ij,x}^2 + r_{ij,y}^2 + r_{ij,z}^2\right)\\
&= \sum_{\{i,j\}}\frac{F_{ij}r_{ij,x}^2}{r_{ij}} = \sum_{\{i,j\}}F_{ij,x}r_{ij,x},\qquad(9.14)
\end{aligned}$$

is the x component of the virial,[6] i.e. the microscopic observable corresponding to the configurational contribution to the pressure acting in x direction. The thermodynamic pressure, as a directional average[7]

$$P = \frac{P^{xx} + P^{yy} + P^{zz}}{3} = \rho T + \frac{\langle \Pi\rangle}{3V},\qquad(9.15)$$

is obtained from the virial

$$\Pi(\mathbf{q}) = \Pi^{xx} + \Pi^{yy} + \Pi^{zz} = \sum_{\{i,j\}}\frac{F_{ij}}{r_{ij}}\left(r_{ij,x}^2 + r_{ij,y}^2 + r_{ij,z}^2\right) = \sum_{\{i,j\}}F_{ij}r_{ij}.\qquad(9.16)$$

9.3 Widom's Test Particle Method

The chemical potential can be expressed in terms of the partition function as

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{V,T} = \left[-T\frac{\partial \ln \mathcal{Q}_{NVT}^{\mathrm{id}}}{\partial N}\right] + T\cdot\left[-\frac{\partial \ln \mathcal{Q}_{NVT}^{\mathrm{conf}}}{\partial N}\right] = \mu^{\mathrm{id}} + T\tilde{\mu},\qquad(9.17)$$

where μ^{id} is the ideal contribution to μ, and $\tilde{\mu}$ is referred to as the reduced residual chemical potential. If $\mathcal{Q}_{NVT}^{\mathrm{conf}}$ is defined by Eq. (9.11), the ideal partition function is

$$\begin{aligned}
\mathcal{Q}_{NVT}^{\mathrm{id}} = \frac{\mathcal{Q}_{NVT}}{\mathcal{Q}_{NVT}^{\mathrm{conf}}} &= \frac{V^N}{h^{3N}N!}\int_{\mathbb{R}^{3N}}\mathbf{dp}\,\exp\left(\frac{-\mathbf{p}^2}{2mT}\right)\\
&= \frac{V^N}{N!}\left[\frac{1}{h}\int_{-\infty}^{\infty}dp\,\exp\left(\frac{-p^2}{2mT}\right)\right]^{3N} = \frac{V^N}{N!}\left(\frac{\sqrt{2\pi mT}}{h}\right)^{3N}.\quad(9.18)
\end{aligned}$$

---

[5]For the present variation, $dr_x^2/r_x^2 = d\ln r_x^2 = 2d\ln r_x = 2\,d\lambda$, whereas $dr_y^2 = dr_z^2 = 0$, for all distances $\mathbf{r}$.

[6]In the same way as the pressure, the virial can be expressed as a tensor; Π^{xx} is on the diagonal of this tensor. However, Π is also often used as a scalar quantity, defined by summation over the diagonal elements of the virial tensor, cf. Eq. (9.16).

[7]This expression for the pressure corresponds to $P = -(\partial A/\partial V)_{N,T}$ for a variation of the volume where *all* coordinate axes are scaled equally, i.e. $d\lambda = d\ln \mathcal{L}_x = d\ln \mathcal{L}_y = d\ln \mathcal{L}_z = (d\ln V)/3$.

With $\Lambda = h/\sqrt{2\pi m T}$, and approximating $\ln(1/N!) \approx -N \ln N - N = -\int dN \ln N$, this yields

$$\mu^{\mathrm{id}} = -T \frac{\partial \ln \mathcal{Q}^{\mathrm{id}}_{NVT}}{\partial N} \approx -T \frac{\partial}{\partial N} \left(N \ln V \Lambda^{-3} - N \ln N - N \right) = T \ln \rho \Lambda^3. \tag{9.19}$$

For the reduced residual chemical potential,[8]

$$\tilde{\mu} = -\left(\frac{\partial \ln \mathcal{Q}^{\mathrm{conf}}_{NVT}}{\partial N} \right)_{V,T} = -\ln \mathcal{Q}^{\mathrm{conf}}_{N+1,V,T} + \ln \mathcal{Q}^{\mathrm{conf}}_{NVT} = -\ln \frac{\mathcal{Q}^{\mathrm{conf}}_{N+1,V,T}}{\mathcal{Q}^{\mathrm{conf}}_{NVT}}, \tag{9.20}$$

where the configuration of the molecules 1 to N will be denoted by $\mathbf{q} = (\mathbf{q}_1, \ldots, \mathbf{q}_N)$ and the position of the additional molecule by $\mathbf{q}_{N+1}$. Defining $\Delta E^{\mathrm{pot}}(\mathbf{q}, \mathbf{q}_{N+1})$ by

$$E^{\mathrm{pot}}_{N+1,V,T}(\mathbf{q}, \mathbf{q}_{N+1}) = E^{\mathrm{pot}}_{NVT}(\mathbf{q}) + \Delta E^{\mathrm{pot}}(\mathbf{q}, \mathbf{q}_{N+1}), \tag{9.21}$$

for the system containing $N+1$ molecules, Eq. (9.11) becomes

$$\begin{aligned}
\mathcal{Q}^{\mathrm{conf}}_{N+1,V,T} &= V^{-N-1} \int_{V^{N+1}} \mathbf{dq} \; \mathbf{dq}_{N+1} \; \exp\left(-\frac{E^{\mathrm{pot}}_{N+1,V,T}(\mathbf{q}, \mathbf{q}_{N+1})}{T} \right) \\
&= V^{-N} \int_{V^N} \mathbf{dq} \left[V^{-1} \int_V \mathbf{dq}_{N+1} \; \exp\left(-\frac{\Delta E^{\mathrm{pot}}}{T} \right) \right] \exp\left(-\frac{E^{\mathrm{pot}}_{NVT}(\mathbf{q})}{T} \right). \tag{9.22}
\end{aligned}$$

In this way, inserting Eq. (9.11) for $\mathcal{Q}^{\mathrm{conf}}_{NVT}$,

$$\begin{aligned}
\tilde{\mu} &= -\ln \frac{V^{-N} \int \mathbf{dq} \left[V^{-1} \int \mathbf{dq}_{N+1} \exp(-\Delta E^{\mathrm{pot}}/T) \right] \exp(-E^{\mathrm{pot}}_{NVT}/T)}{V^{-N} \int \mathbf{dq} \; \exp(-E^{\mathrm{pot}}_{NVT}/T)} \\
&= -\ln \left\langle \frac{1}{V} \int_V \mathbf{dq}_{N+1} \; \exp\left(\frac{-\Delta E^{\mathrm{pot}}}{T} \right) \right\rangle = -\ln \left\langle \left\langle \exp\left(\frac{-\Delta E^{\mathrm{pot}}}{T} \right) \right\rangle_{\mathbf{q}_{N+1}} \right\rangle_{NVT} \tag{9.23}
\end{aligned}$$

a microscopic observable for $\tilde{\mu}$ is found.[9] It can be computed by test particle insertion:[10]

- Conduct a regular MC or MD simulation with N molecules, as usual.

- Between simulation steps, insert a virtual test particle at a uniformly distributed random position $\mathbf{q}_{N+1} \in V$ and, if applicable, with a random orientation. The test particle does not remain in the system, and it does not influence the other molecules.

- For each test particle insertion, compute $\Delta E^{\mathrm{pot}} = \sum_i u_{i,N+1}$ from the pairwise interactions of the test particle with all other molecules i. The simulation result for $\tilde{\mu}$ is determined from Eq. (9.23) using the average value of $\exp(-\Delta E^{\mathrm{pot}}/T)$.

---

[8]Since N is a discrete quantity which can only be varied in steps of ± 1, the partial derivative is replaced by a difference quotient. This is not an approximation, but rather the more accurate expression.

[9]For the implementation as a simulation method, it is crucial that in Eq. (9.23), $\mathbf{q}$ is distributed according to the phase space density for the N-molecule system, whereas $\mathbf{q}_{N+1}$ is distributed uniformly.

[10]B. Widom, Potential-distribution theory and the statistical mechanics of fluids, *J. Chem. Phys.* 86(6), 869–872, **1982**. The method is not restricted to the canonical ensemble or to pure fluids. Analogous expressions are obtained for the NVE and NPT ensembles and for mixtures, where $\tilde{\mu}_i$ is obtained in the same way, i.e. from the potential energy of virtual test particles which belong to the component i.

10 Local Order

10.1 Radial Distribution Function

Beside computing thermodynamic properties from ensemble averages of microscopic observables, cf. Section 9, MC and MD simulation can be employed to investigate the structure of fluid matter at the molecular level.
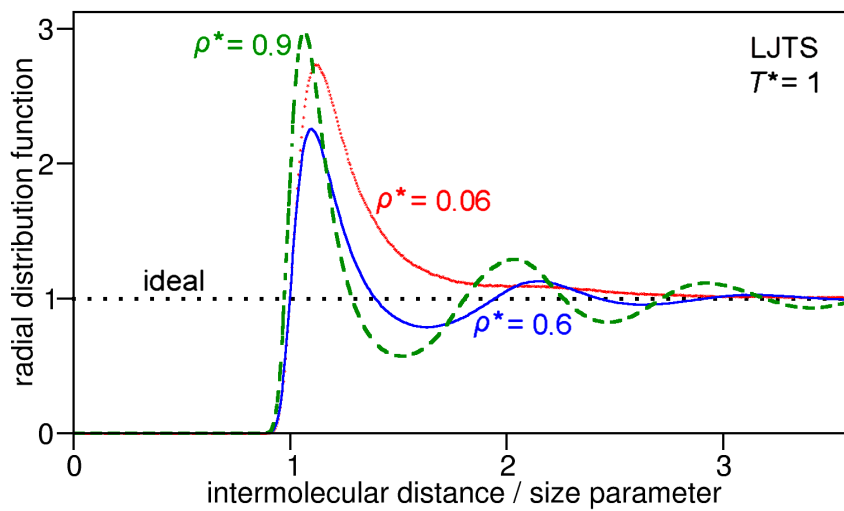
The radial distribution function (RDF), which is also known as the pair correlation function and denoted by $g(r)$, expresses the local density at a given distance r from a molecule; this density is normalized by the overall density $\rho = N/V$, i.e.

$$
\begin{aligned}
g(r) &= \frac{\text{local density at distance } r \text{ from a molecule}}{\text{overall density } \rho} \\
&= \frac{\text{fraction of } N}{\text{fraction of } V} \\
&= \frac{V}{4\pi r^2} \left\langle \delta(r_{ij} - r) \right\rangle,
\end{aligned}
\tag{10.1}
$$

such that $g(r) \to 1$ holds at $r \to \infty$, for a Dirac function with[1]

$$
\int_0^\infty dr \; \delta(r_{ij} - r) = 1, \quad \forall 0 \le r_{ij} < \infty,
\tag{10.2}
$$

considering any given, but arbitrary, pair of molecules i and j. Hence, it is impossible for $g(r)$ to be smaller than 1 everywhere, or greater than 1 everywhere; any local density surplus

---

[1]Accordingly, the value of $\delta(r_{ij} - r)$ is not dimensionless here; it needs to have units of m^{-1}.

needs to cancel out with a local density deficit

$$\int_0^\infty dr \; g(r) \frac{4\pi r^2}{V} \;=\; \int_0^\infty dr \; \langle \delta(r_{ij} - r) \rangle \;=\; 1. \tag{10.3}$$

The RDF is determined by a combination of

- effects of the pairwise interaction – where $u(r)$ is smaller, $g(r)$ tends to be greater,

- and multibody order effects, which become relevant at high densities.

In the case of an ideal gas, and similarly, for a real fluid in the $T \to \infty$ limit,[2] all configurations are equally probable, so that $g(r) = 1$ holds for all r.

10.2 Local Order and Thermodynamics

In systems with pairwise additive interactions, some thermodynamic properties are immediately related to the RDF. In particular, assuming that $g(r)$ is known, the potential energy[3]

$$\begin{aligned}
E^{\text{pot}} &= \left\langle \sum_{\{i,j\}} u_{ij}(r_{ij}) \right\rangle \\
&= \int_0^\infty dr \; u(r) \; \frac{N \left\langle \# \text{ neighbours } j \text{ of } i \text{ with } r_{ij} = r \right\rangle}{2} \\
&= \frac{N^2}{2} \int_0^\infty dr \; u(r) \left\langle \delta(r_{ij} - r) \right\rangle = \frac{2\pi N^2}{V} \int_0^\infty dr \; r^2 \, g(r) u(r),
\end{aligned} \tag{10.4}$$

and the ensemble average of the virial[4]

$$\langle \Pi \rangle \;=\; \left\langle \sum_{\{i,j\}} F_{ij} r_{ij} \right\rangle \;=\; \frac{2\pi N^2}{V} \int_0^\infty dr \; r^2 \, g(r) \, \Pi(r) \tag{10.5}$$

can be determined, and accordingly, the energy $E = E^{\text{kin}} + E^{\text{pot}}$ and the pressure

$$P \;=\; \rho T + \frac{\langle \Pi \rangle}{3V} \;=\; \rho T + \frac{2\pi\rho^2}{3} \int_0^\infty dr \; r^2 \, g(r) \, \Pi(r). \tag{10.6}$$

---

[2] The strongly repulsive region needs to be excluded, however, since it is unrealistic that sufficiently high temperatures can be reached.

[3] The identity $\langle \delta(r_{ij} - r) \rangle = 4\pi r^2 g(r)/V$ is used here.

[4] Notation: $\Pi(r) = \Pi_{ij}(r_{ij}) = r_{ij} F_{ij}(r_{ij})$, cf. Eq. (9.16), and $\Pi = \Pi(\mathbf{q}) = \sum \Pi_{ij}(r_{ij})$.

11 Fluid Phase Equilibria

11.1 Thermodynamic Equilibrium

For a thermodynamic equilibrium between $\mathscr{M}$ phases in a mixture of κ components, the chemical, mechanical, and mechanical equilibrium conditions apply as follows:

$$
\begin{array}{ccccccc}
\mu_1' & = & \mu_1'' & = & \dots & = & \mu_1^{(\mathscr{M})} \\
\vdots & & \vdots & & \vdots & & \vdots \\
\mu_\kappa' & = & \mu_\kappa'' & = & \dots & = & \mu_\kappa^{(\mathscr{M})}
\end{array} \quad \Rightarrow \quad \text{chemical equilibrium}
$$

$$
P' = P'' = \dots = P^{(\mathscr{M})} \quad \Rightarrow \quad \text{mechanical equilibrium}
$$

$$
T' = T'' = \dots = T^{(\mathscr{M})} \quad \Rightarrow \quad \text{thermal equilibrium}
$$

In this way, the phase equilibrium is characterized by $\kappa + 2$ scalar variables which need to have identical values in all coexisting phases. However, these quantities are not independent. By the equation of state, a relation of the type

$$
f^{(i)}\left(\mu_1^{(i)}, \dots, \mu_\kappa^{(i)}, P^{(i)}, T^{(i)}\right) = 0 \tag{11.1}
$$

is given for each phase $1 \leq i \leq \mathscr{M}$, yielding $\mathscr{M}$ additional conditions in terms of μ, P, and T. The number of remaining *intensive thermodynamic properties* which can be varied independently, i.e. the number of intensive thermodynamic degrees of freedom $\mathscr{N}$ is therefore related to the number of phases $\mathscr{M}$ and the number of components κ by

$$
\mathscr{M} + \mathscr{N} = \kappa + 2, \tag{11.2}
$$

which is known as the Gibbs phase rule.[1] For equilibria between two phases,[2] e.g. vapour-liquid equilibria (VLE) and liquid-liquid equilibria (LLE), this reduces to $\mathscr{N} = \kappa$.

11.2 Grand Equilibrium Method

For a VLE, μ, P, and T are the same in the vapour phase and the liquid phase. In case of a pure fluid, this is represented by the intersection of an isotherm in a $\mu - P$ diagram with itself; since $(\partial\mu/\partial P)_T = 1/\rho$, the steep branch of the isotherm corresponds to the vapour (greater value of $1/\rho$), and the flat branch corresponds to the liquid.

---

[1] Additionally, the size of each phase can be varied freely, so that $\mathscr{M}$ extensive thermodynamic DOF exist at given μ, P, T. Counting both intensive and extensive thermodynamic quantities, there are $(\kappa + 2 - \mathscr{M}) + \mathscr{M} = \kappa + 2$ macroscopic DOF, irrespective of $\mathscr{M}$. This corresponds to the number of properties that determine the ensemble, e.g. $N_1, \dots, N_\kappa, V, T$ for canonical boundary conditions.

[2] For the VLE of a pure fluid ($\kappa = 1$), the thermodynamic state of the coexisting phases is determined by a single intensive property, such as the boiling temperature or the saturated vapour pressure. For the VLE or LLE of a mixture, κ independent intensive thermodynamic properties need to be given.
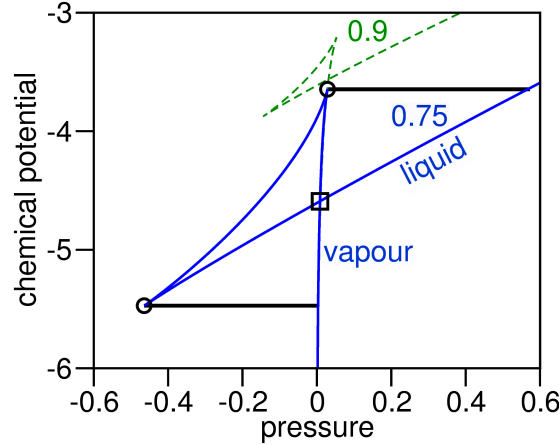
Two isotherms ($T = 0.75$ und 0.9 ε) of the LJTS fluid in a $\mu - P$ diagram;[3] all values are given in LJ units, i.e., in units of ε for the chemical potential and in units of ε/σ^3 for the pressure.

For the liquid phase, the dependence of μ on P can usually be captured as follows:[4] In the NPT ensemble at a given reference pressure $P = P_{\text{ref}}$, the density $\rho'(P_{\text{ref}})$ is given by $N/\langle V \rangle$ and its first derivative by the isothermal compressibility

$$\beta_T = \left(\frac{\partial \ln \rho}{\partial P} \right)_T = \frac{1}{\langle V \rangle T} \left(\langle V^2 \rangle - \langle V \rangle^2 \right). \tag{11.3}$$

If $\mu'(P_{\text{ref}})$ is also available, e.g., by Widom's test particle method, the *liquid branch* of the isotherm in the $\mu - P$ diagram can be expanded to second order as

$$\mu'(P) = \mu'(P_{\text{ref}}) + \frac{1}{\rho'(P_{\text{ref}})} [P - P_{\text{ref}}] - \frac{\beta_T(P_{\text{ref}})}{2\rho'(P_{\text{ref}})} [P - P_{\text{ref}}]^2 + O\left([P - P_{\text{ref}}]^3 \right). \tag{11.4}$$

For the vapour phase, ρ depends strongly on P, and such an expansion would be unsuitable. Instead, by Grand Equilibrium simulation,[5] consecutive simulation runs are conducted for the liquid phase and the vapour phase, and for the vapour, an adaptive chemical potential is imposed to ensure a convergence to thermodynamic equilibrium conditions:

- Given properties:[6] Temperature T and liquid composition $\mathbf{x}$.

- First simulation: Liquid phase, isothermal-isobaric ensemble, at the temperature T (in case of a mixture, with the specified composition $\mathbf{x}$) and a reference[7] pressure P_{ref}. Widom's test particle method or a different method for μ is employed. Computed quantities: $\mu'(P_{\text{ref}})$, $\rho'(P_{\text{ref}})$, $\beta_T(P_{\text{ref}})$; for a mixture: $\mu_i(P_{\text{ref}})$ and $v_i(P_{\text{ref}})$, for all i.

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[3] arXiv:1703.08719 [cond-mat.soft], *J. Chem. Phys.* (submitted), **2017**.

[4] This is discussed for a pure fluid here; for mixtures, an analogous treatment can be developed. There, the first derivative of μ_i, for component i, is given by the partial molar volume v_i (instead of $1/\rho$). Widom's test particle method can be extended to compute v_i; cf. D. M. Heyes, *Mol. Sim.* 8(3–5), 227–238, **1992**.

[5] J. Vrabec, H. Hasse, Grand Equilibrium: Vapour-liquid equilibria by a new molecular simulation method, *Mol. Phys.* 100(21), 3375–3383, **2002**.

[6] As above, properties of the κ components are denoted by vectors, i.e., $\mathbf{x} = (x_1, x_2, \ldots, x_\kappa)$, $\boldsymbol{\mu} = (\mu_1, \ldots, \mu_\kappa)$, and so on. The compositions $\mathbf{x}$ and $\mathbf{y}$ are given as mole fractions, i.e., in units of mol mol^{-1}. Since the sum over all mole fractions is $\sum_k x_k = 1$, only $\kappa - 1$ independent quantities are given by specifying $\mathbf{x}$; counting T also, κ intensive quantites are specified, in agreement with the Gibbs phase law.

[7] The reference pressure is not the actual saturated vapour pressure, which is not known in advance, but an estimate. The method is quite robust; even $P_{\text{ref}} = 0$ works in many cases.

From these results, the vapour pressure P^{sat} and the chemical potential μ^{sat} at saturation, for both phases, are known to be related by Eq. (11.4) or its generalization to mixtures; therein, the higher-order terms are neglected.

- Second simulation: Vapour phase, pseudo-grand-canonical simulation, at the temperature T, specifying a chemical potential μ'' which is calclulated, and varied, at runtime by $\mu'' = \mu'(P(\mathbf{q}))$ following Eq. (11.4), where $P(\mathbf{q}) = \rho T + \Pi(\mathbf{q})/3V$ is obtained[8] from the instantaneous virial $\Pi(\mathbf{q})$.

- Determined properties: Pressure P and vapour composition $\mathbf{y}$.

The Grand Equilibrium method can be implemented both by MC and MD simulation. In this way, a phase equilibrium can be simulated with relatively small homogeneous systems (e.g., $N = 1000$), considering the coexisting phases separately and avoiding the presence of an interface in the simulation volume.

11.3 Interfacial Properties

- Phenomenological point of view: The phase boundary is a strictly two-dimensional surface; thermal, chemical, and mechanical equilibrium conditions apply.

- Molecular point of view: Between adjacent fluid phases, a three-dimensional boundary region exists; equilibrium conditions apply for average quantities, but instantaneous deviations occur due to fluctuations.

Approach developed by Gibbs:[9] Quantities and relations from phenomenological thermodynamics are applied to configurations and observables at the molecular level by introducing a virtual, strictly two-dimensional microscopic *dividing surface* which partitions the volume of the system into coexisting phases

$$V = V' + V''. \tag{11.5}$$

At a point far away from the interface (and, in particular, macroscopically), the coexisting phases are characterized by their intensive properties $\boldsymbol{\mu}$, P, and T which are related to each other – and to all other intensive properties – by the equation of state. In the Gibbs approach, thermodynamic properties of the two phases are *formally* identified with the thermodynamic properties of *homogeneous reference systems* which have the respective intensive properties and the respective volumes, i.e. V' and V''.[10]

By comparing extensive properties of the two-phase system with the homogeneous reference systems, interfacial excess quantities are obtained from[11]

$$
\begin{aligned}
E^{\text{E}} &= E - E' - E'', \\
S^{\text{E}} &= S - S' - S'',
\end{aligned}
$$

---

[8]For a mixture, analogously, chemical potentials $\mu_i'' = \mu_i'(P(\mathbf{q}))$ are calculated on the fly from $\Pi(\mathbf{q})$.

[9]J. W. Gibbs, On the equilibrium of heterogeneous substances, *Transact. Connectic. Acad. Arts Sci.* 3, 343, **1878**. Recommended literature: Chapter 2, J. S. Rowlinson, B. Widom, *Molecular Theory of Capillarity*, **1982** [3].

[10]The properties of the reference systems need not agree with the actual, microscopically observed behaviour of the two-phase system; e.g., from the thermodynamic conditions, ρ' is known, from which with V' we obtain $N' = \rho'V'$. The average number of molecules present in the liquid region of the two-phase system, however, may deviate from this value. This deviation contributes to the adsorption.

[11]From Eq. (11.5), the excess volume is $V^{\text{E}} = 0$.

$$\mathbf{N}^{\mathrm{E}} = \mathbf{N} - \mathbf{N}' - \mathbf{N}'',$$
$$A^{\mathrm{E}} = A - A' - A'', \tag{11.6}$$

and so on. In this way, the established relations from phenomenological thermodynamics can be applied to interfacial properties as well, since the right-hand side of these expressions contains only properties of homogeneous systems. The microscopic dividing surface may be positioned arbitrarily as long as it is parallel to the macroscopic dividing surface.[12] The specific excess number of molecules is known as the adsorption

$$\mathbf{\Gamma}^{\mathrm{E}} = \frac{\mathbf{N}^{\mathrm{E}}}{s} = \left(\frac{N_1^{\mathrm{E}}}{s}, \frac{N_2^{\mathrm{E}}}{s}, \ldots, \frac{N_\kappa^{\mathrm{E}}}{s} \right), \tag{11.7}$$

where s is the surface area. The surface tension is defined by [3]

$$\gamma = \left(\frac{\partial A^{\mathrm{E}}}{\partial s} \right)_{\mathbf{N}^{\mathrm{E}}, T} = \left(\frac{\partial A}{\partial s} \right)_{\mathbf{N}, V', V'', T}, \tag{11.8}$$

where depending on the position of the dividing surface, A^{E} varies, whereas γ does not [3].

For a differential distortion of the volume $V = \mathscr{L}_x \mathscr{L}_y \mathscr{L}_z$ by $d \ln \mathscr{L}_x = d \ln q_{ix} = d\lambda_x$, $d \ln \mathscr{L}_y = d \ln q_{iy} = d\lambda_y$, and $d \ln \mathscr{L}_z = d \ln q_{iz} = d\lambda_z$, cf. Section 9.2 and therein Eqs. (9.7) to (9.10), the invariant volume boundary condition of the partial derivative corresponds to

$$d \ln V = d \ln \mathscr{L}_x + d \ln \mathscr{L}_y + d \ln \mathscr{L}_z = d\lambda_x + d\lambda_y + d\lambda_z = 0, \tag{11.9}$$

while in case of two interfaces[13] perpendicular to the z axis, the area $s = 2\mathscr{L}_x \mathscr{L}_y$ varies by

$$d \ln s = d \ln \mathscr{L}_x + d \ln \mathscr{L}_y = d\lambda_x + d\lambda_y = -d\lambda_z = -d \ln \mathscr{L}_z. \tag{11.10}$$

With the tangential pressure $P_{\mathrm{t}} = P^{xx} = P^{yy}$ and the normal pressure $P_{\mathrm{n}} = P^{zz}$ from

$$P^{\ell\ell} = -\frac{1}{V} \left(\frac{\partial A}{\partial \ln \mathscr{L}_\ell} \right)_{\mathscr{L}_{k \neq \ell}, \mathbf{N}, T}, \tag{11.11}$$

cf. Eq. (9.7), the variation of the free energy during this transformation is obtained as

$$dA = -P^{xx} V d\lambda_x - P^{yy} V d\lambda_y - P^{zz} V d\lambda_z = -V (P_{\mathrm{n}} - P_{\mathrm{t}}) d\lambda_z. \tag{11.12}$$

Inserting Eq. (9.15) and $d\lambda_z = -d \ln s$, the surface tension can be computed as

$$\gamma = \frac{dA}{ds} = \frac{V (P_{\mathrm{n}} - P_{\mathrm{t}}) d \ln s}{s \, d \ln s} = \frac{\mathscr{L}_z}{2} \left\langle \frac{\Pi_{\mathrm{n}}(\mathbf{q})}{V} - \frac{\Pi_{\mathrm{t}}(\mathbf{q})}{V} \right\rangle_{NVT} = \frac{\langle \Pi_{\mathrm{n}}(\mathbf{q}) - \Pi_{\mathrm{t}}(\mathbf{q}) \rangle}{s}, \tag{11.13}$$

where Π_{n} and Π_{t} is the virial in normal and in tangential direction.

---

[12] The exact values of V' and V'' depend on the choice of dividing surface; accordingly, all extensive properties associated with the homogeneous reference systems and, hence, almost all excess properties of the interface depend on this choice. This has the disadvantage that most quantitative statements, at least at the microscopic level, need to be supplemented with a statement on how the dividing surface was defined. However, it also has the advantage that the dividing surface can be positioned such that a particular excess term becomes zero; e.g., the equimolar dividing surface, defined by $N^{\mathrm{E}} = 0$, is frequently used.

[13] Periodic boundary conditions are used in most cases; this results in an arrangement of the type *vapour — liquid — vapour* in the simulation volume which then contains two parallel vapour-liquid interfaces.

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