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Introduction

The change in appearance and properties of substances upon applying various stimuli is a well-known phenomenon. For example, probably the most important substance on earth, water, is known to exist in three forms or *phases*: solid (ice), liquid (water), and gas (water vapor), depending on the temperature applied. Although ubiquitous, the transition processes between these phases are generally complex. In this book, we deal with (some of) the chemical physics of substances and their phase transitions.

As we need many concepts to deal with these transitions and the transition processes inevitably refer to the phases themselves, the book is divided into three parts. By and large, in the first part we deal with the theoretical tools needed and in the second part with the phases themselves, while in the third part we discuss the transitions. As many basic concepts and assumptions are used throughout, we briefly review them in this chapter. First, the concepts of matter, energy, and charge and their conservation laws are introduced, followed by some considerations about macroscopic and microscopic descriptions. Thereafter, the essential differences between solids, liquids, and gases are outlined, followed by a description of the approach to the various topics dealt with in this book. The final section deals with the units and notations used.

1.1 Constituents of Matter

We first briefly review the constituents of matter as far as they are relevant to our topic. For that, we accept its discrete nature. Basically, the history boils down to the fact that matter was considered, by chemists from the 1780s and later by physicists as well, to consist of a set of immutable and indestructible *elements* that could be divided into *metals*, *nonmetals*, and *gases*. The elements were supposed to have constant properties, such as mass, and consisted of *atoms* that got labels like H (hydrogen), O (oxygen), C (carbon), N (nitrogen), and which were systematically organized in the *periodic table of elements*. Elements can bond to other elements, resulting in *compounds* that were classified as *salt* (combining a metal with a nonmetal), *acid* (combining hydrogen with a nonmetal), and *base* (combining water with a metal), while the particular combination of elements in the substance was (is) addressed as the *composition*. The smallest entity that behaves chemically like the whole is a *molecule*. Molecules have a relatively simple, fixed ratio of atoms, as in H_2O (water). In other cases, the

stoichiometry, that is, the ratio(s) of the number of elements in a compound, varies considerably. The largest variation is found in compounds where there is a small energy difference between the various defect states, often transition metal oxides; for example, for TiO_x the range is $0.92 < x < 1.26$ [1]. It appeared somewhat later that some elements that are gaseous at room temperature are also compounds and are actually mostly diatomic molecules, for example, H_2, O_2, and N_2.

All these results were made possible by the (reproducible) *preparation* and *isolation*, often followed by *purification*, of substances, whereafter the study of their *physical properties* (response to stimuli that do not change the composition) and *chemical properties* (response to stimuli that do change the composition) became possible. One of the most important early results is the discovery that at constant temperature and pressure, certain amounts of the gaseous elements, labeled *mole*, contain the same number of molecules, a number known as the *number of Avogadro*.

Nowadays, all elementary entities are often counted in moles. The *molecular weight* of a substance translates this amount into kilograms of the substance.

As is well known in the meantime, atoms appear not to be indestructible but to be composed of other particles that together determine the properties of atoms. These are the *nuclei*, composite particles containing singly positively charged *protons* and neutral *neutrons*, collectively denoted as *nucleons*, and singly negatively charged *electrons*, which all three were for some time considered elementary particles. Still, later, it appeared that these particles were composed of a zoo of (still more) elementary particles. For our field of interest, employing energies relevant to life and terrestrial phenomena, foremost atoms, electrons, and protons are relevant. Adding an electron to an atom (with the related energy characteristic, the *electron affinity*) or removing an electron from an atom (with the related energy characteristic, the *ionization potential*) results in a charged atom called an *ion*. The numbers of protons and neutrons in the nucleus determine the *mass* of the nucleus, while the number of protons determines its *charge*. For a neutral atom, that charge is compensated by an equal number of electrons. The number of neutrons varies for most elements while having the same number of protons; each variety is called an *isotope*. For example, the isotope deuterium (D) of hydrogen (H) has one proton and one neutron, while H has one proton. Neutrons play a relatively minor role, but still, via their effect on mass, they can influence some properties of elements and molecules significantly (Table 1.1).

Table 1.1 Some properties of normal water (H_2O) and heavy water (D_2O).

	ρ (g cm^{-3}) at 25 °C	T_{mel} (°C)	T_n (°C)	γ (mN m^{-1}) at 25 °C	ρ_{max} at °C	η (mPa s) at 25 °C	$\Delta_{fus}H$ (cal mol^{-1})	$\Delta_{vap}H$ (cal mol^{-1})
H_2O	1.00	0.00	100.00	72.75	4.0	10.09	1436	10 480
D_2O	1.1079	3.82	101.42	67.8	11.6	12.6	1510	10 740

ρ, density; T_{mel}, melting point; T_n, boiling point; γ, surface tension; ρ_{max}, maximum density; η, viscosity; $\Delta_{fus}H$, enthalpy of fusion; $\Delta_{vap}H$, enthalpy of vaporization.
Source: Adapted from Prutton and Maron [2].

1.2   Matter and Energy: Interaction and Change

Let us now turn to the three conservation laws that appear to be fundamental: *conservation of mass, energy*, *and charge*. In this section, we deal first with energy, while in Section 1.3, we discuss mass and charge.

Surprisingly (or may be, not), the definition of energy is treated as a stepchild in many treatments of physical phenomena. The usual way to introduce energy is to refer to the kinetic energy (KE) of particles in mechanics, introduce thereafter the potential energy (PE), and show that their sum, that is, energy,[1] is conserved, and from there on more or less assume that energy conservation is always the case, including effects of heat, radiation, and so forth. It sounds a bit like this drink is brown and sold in bottles, and there are many competitors on the market. All true, but not really defining the drink. Using the abovementioned process of describing energy avoids the real question: What *is* energy?

Only recently a serious attempt was made by Hecht [4] as a result of a longer running activity to provide a real definition. As there is not much point in rephrasing what is a clear exposition, we will largely use his words ("…" for exact quotes, '…' for approximate quotes). In this connection, we will frequently need the concept of a *particle*, a not necessarily microscopic entity with mass m (to be discussed later) and an inaccessible internal structure that can move in space with velocity v. Such a particle is located at one point in space at one time, that is, it is considered small as compared to the total system considered.

The point of departure is that "on a very basic level, there is matter, interaction and change." "*Matter is that which interacts and, as a result, manifests observable physical properties that are amenable to being measured*." Matter interacts via equal and oppositely directed forces (interaction pairs): "there is no such thing as a single force. If matter did not interact, it could not be known and could not be said to exist. All matter interacts in one way or another, either via long-range or short-range forces. *Force is the agent of all observable physical change*. Nothing determinable happens without the action of force."

So, physical change occurs because of interactions. "*Energy is a measure of the capacity of matter interacting with matter to effectuate physical change. It is the conserved scalar measure of the extent of change that has already occurred, and/or change that can yet occur*." Thus, while force is that which changes the state of a system, 'energy is a measure of the extent of that change, whether it has already happened or is yet to happen. Energy is associated with all matter that exists and is a measure of the change resulting from matter interacting with matter; it is not an entity in and of itself, independent of matter.' "If matter did not interact, energy in all its manifestations would vanish and the concept would be meaningless." 'Due to the symmetrical nature of interactions, a change in one entity is accompanied by an energy-equivalent change in the entity with which it interacts.' "Accordingly, we have the principle of *Conservation of Energy*: *the total energy associated with any system can be accounted for at all times*."

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1 Initially I intended to insert here brief remarks about the history of the concept of energy, but refrained from that, not for not being a professional historian, but mainly because a short story probably will do injustice to players in this game: Young, Joule, the brothers William and James Thomson, Mayer, Clausius, von Helmholtz, Mach, Planck, and a few more scientists and, not to forget, engineers like father and son Lazare and Sadi Carnot, Clapeyron, Rankine, Gouy, Stodola, and Zeuner [3].

As an example, consider a stretched spring that has a quantity of energy stored (via internal interactions) by an applied force that is the agent of change. The spring in its energized state, characterized by the amount of energy stored, has the capacity to effectuate in the future a variety of changes, and "the energy stored is a measure of the ability of the spring to produce change (internally and externally) via the action of the forces it can exert."

1.3 Mass and Charge

We now have to turn to the concepts of mass and charge, and for that, we will have to use one or two results from special relativity theory. We use the formulation in which the mass m is considered speed independent (for a brief review, see Appendix B). For a single free particle, the energy $E = \gamma mc^2$, where $\gamma = (1 - v^2/c^2)^{-1/2}$ with $v = (\boldsymbol{v} \cdot \boldsymbol{v})^{1/2}$ the speed of the particle and c is the speed of light. So, when $v = 0$, $\gamma = 1$ and the energy becomes the *energy of rest* $E_0 = mc^2$. The difference between E and E_0 is the *energy of motion* or the organized KE ϑ of the particle moving as a whole and given by $\vartheta = \gamma mc^2 - mc^2$. Introducing the momentum $\boldsymbol{p} = \gamma m\boldsymbol{v}$ leads to $E = [c^2p^2 - (mc^2)^2]^{1/2} \cong mc^2 + p^2/2m$, and in its approximate form, apart from the constant mc^2, in agreement with the classical result. For a composite body containing many particles with total mass M, the object's total energy, measured in its center-of-mass frame (where it is motionless), is the rest energy $E_0 = Mc^2$. It encompasses the individual rest energies, kinetic energies, and potential energies of all the interacting particles that constitute the object. Note therefore that, as $E_0 = Mc^2$, $M \neq \Sigma_j m_j$ and the mass of a composite object as a whole change with its energy content.

Although seldom formally defined, mass is often considered to be a quantity of matter, generally simply assumed to be synonymous with the "amount of material," a measure presumably having to do with the type and number of particles constituting the material object. In view of the results of the theory of special relativity, this interpretation no longer holds. Another often-used definition is in terms of inertia. Using $\vartheta = \gamma mc^2 - mc^2$, we see that as v goes to c, γ approaches infinity and ϑ of an object possessing mass approaches infinity. Hence, it will take an infinite amount of energy for such an object to be propelled up to c, which is the maximum velocity. The well-known Michelson–Morley and Kennedy–Thorndike experiments confirmed that the speed of light is constant within 3×10^{-5}. More recently, Brecher [5] showed from observations of regularly pulsating X-ray sources in binary star systems that the speed of light is independent of the velocity of the source within 2×10^{-9}. Comparing frequencies of a cryogenic sapphire oscillator and a hydrogen maser (Figure 1.1a), Wolf et al. [6] confirmed that Lorentz transformations are obeyed with an overall uncertainty of $\leq 8 \times 10^{-7}$, again indicating a constant c. Bertozzi [7] showed similarly that c is the maximum speed for electrons (Figure 1.1b). Apparently, energy is the determinant of inertia so that mass cannot be defined in terms of inertia. Finally, there is the interpretation that mass produces gravity and is a measure thereof. In special relativity theory, both m and c are constants, and thus mc^2 as well. As $E = \gamma mc^2$, mass is derived from energy, and mass (and momentum) cannot be defined in terms of gravity.

So, then, what *is* mass? It seems that energy is a more fundamental concept than mass. After all, everything that has mass always has energy, but not everything that has energy always has mass (e.g. a photon). Considering $E_0 = Mc^2$, we learned that "*the mass of a*
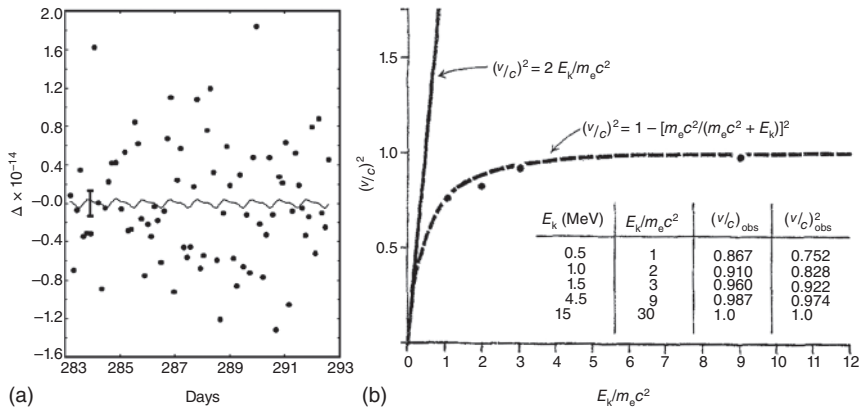
Figure 1.1 Relativity. (a) Constant relative frequency difference Δ between an oscillator and maser indicating that Lorentz transformations are obeyed with an uncertainty of $\leq 8 \times 10^{-7}$. Source: Adapted from Wolf et al. [6]. (b) The quantity v^2/c^2 versus $E_k/m_e c^2$ for various kinetic energies E_k for an electron with mass m_e showing the limiting velocity c [7].

composite system is a property of its matter, the internal motions thereof, and the interactions therein." The mass of any composite entity seems to represent an account of the entity's history: "*The mass of any system at rest is a measure of the amount of energy that went into creating that object as it exists at that moment.*" If a system cannot exist at rest, that is, at $p = 0$, that system has no mass.

Traditionally, PE is the energy said to be stored as a result of a configurational change in a system of interacting parts. PE Φ is a tremendously useful bookkeeping device, but it is not a quantity possessing measurable physicality. Only changes in Φ are defined, and these are defined as the work done on a system by conservative forces. Such work is measurable as it is being done. However, once work is done, it no longer exists and is no longer measurable. So, PE is not an empirical quantity as it is not itself amenable to measurement.

A composite system (at rest) possesses (excess) energy when it can undergo spontaneous change. To return to our example, a stretched spring is said to contain elastic energy; when released, it can experience self-initiated change. If a physical property of a system of interacting parts undergoes a change (temperature, volume, etc.), that property can be associated with a resulting difference in energy. Because the interaction energy, that is, the PE, is associated with the system's internal energy, it is conceptually subsumed into the rest energy E_0. Because $E_0 = Mc^2$, whenever the conceptual quantity known as the PE of a system increases or decreases, the mass of that system actually, sometimes measurably, increases or decreases.

The change in PE is thus a convenient way to keep track of the energy stored via interactions within a system, but which is actually stored as mass: $\Delta m = \Delta\Phi/c^2$, which is at least in principle, if not always in practice, measurable. One atomic mass unit (Da) corresponds to 931.494 MeV/c^2. As an example, consider ^{56}Fe, with 91.8%, the most abundant isotope of Fe, containing 26 protons with mass $m_p = 1.007\,276$ Da, 30 neutrons with mass $m_n = 1.008\,665$ Da, and 26 electrons with mass $m_e = 0.000\,548\,6$ Da. The actual mass of a nucleus M of atomic number Z and mass number A is given by

$$M = Zm_p + (A - Z)m_n - \delta m$$

where M is less than the mass of the sum of the parts by the *mass defect* δm, corresponding to a *binding energy* $c^2 \delta m$: the minimum energy that must be added to the system to dissociate it, to relocate its constituent parts, at rest and far from each other. For ^{56}Fe, we thus have $26 \times m_p + 30 \times m_n + 26 \times m_e = 56.4634$ Da, while its actual mass is 55.9349 Da. Hence, $\delta m = 0.5285$ Da $= 492.3$ MeV/c^2 or $\delta m/M = 0.92\%$ or $\delta m/(A+Z) = 8.8$ MeV/c^2 per nucleon [8]. For most of physics and chemistry, however, δm is much smaller. Consider, for example, the ^{1}H atom containing one proton and one electron, for which $\delta m = 1.461 \times 10^{-8}$ Da or $c^2 \delta m = 13.61$ eV.

Thus, a change in the PE of a system of interacting objects corresponds to a change in mass, which is, in principle, measurable. However, for energies relevant to life and terrestrial phenomena, the mass deficit δm is normally immeasurably small, but the corresponding energy $c^2 \delta m$ can be measured, and we accept conservation of mass (which is thus not exactly true) and introduce PE to satisfy conservation of energy (which is always exactly true).

Summarizing so far, there is matter interacting via forces that effectuate all change, and that interaction produces observable change. As a result of this interaction, a material system possesses a quantity of energy. Energy is the capacity of a system, acted upon by forces, to experience a specific amount of change, change that has already been imparted to it, or change that it can impart to itself and/or to its environment in the future. Work, heat, and electromagnetic radiation correspond to energy in transit and are means of transferring energy from one system to another.

Like mass, charge is velocity independent. This is shown by considering the H_2 molecule. Such a molecule contains two protons and two electrons. As the electrons move around the protons, they move on average faster than the protons. If a velocity dependence of charges is present, this would lead to an effective charge on the molecule. King [9–11] has shown that within one-part of 10^{20}, the charges of electrons and protons in H_2 are equal. Similar experiments for He, also containing two protons (and two neutrons), but with the protons moving much faster than in H_2 as they are contained in the nucleus, yielded the same result. Hence, these (and other) molecules are neutral, and charge is exactly conserved in special relativity theory and therefore in classical theory.

1.4 Macroscopic and Microscopic Approaches

Although a molecular image of matter nowadays seems to prevail, a *macroscopic description* is rather useful, in science as well as in technology. In the nineteenth century, the debate over whether atoms or molecules exist was still ongoing, and in such a case, one way to make progress is to avoid the issue. The macroscopic approach led to two related branches of science. The first extended particle mechanics to continuous media and is called *continuum mechanics*. The second considered the relationship between work and heat and led to the discipline we now call *thermodynamics*. At present, these two branches are often treated in a highly coupled way called *thermomechanics* [12]. For thermodynamics, the description is given in macroscopic or thermodynamic variables (pressure, volume, temperature, electric field, etc.), which [13]

- are few in number,
- involve no special assumptions concerning the structure of matter,

- are suggested more or less directly by our sensory perceptions, and
- can, in general, be directly measured.

The result is one of the most secure, if not the most secure, parts of science.

Somewhat parallel, a more mechanistic description based on rather simplified models of atoms and molecules, for example, as hard spheres, developed. In this *microscopic description*,

- assumptions are made concerning the structure of matter, for example, the existence of molecules is assumed;
- many quantities must be specified, whereas
- these quantities specified are not suggested by our sense perceptions; and
- they generally cannot be measured directly.

In this picture the few directly measurable properties that constitute the macroscopic description are in reality averages over a period of time of a large number of microscopic characteristics. Both approaches have their pros and cons, but both are useful, albeit typically for rather different types of problems.

1.5 Gases, Liquids, and Solids

Let us now survey the differences and similarities between gases, liquids, and solids, and the associated energetics. Starting with solids, two classes of solids can be distinguished: crystalline and amorphous materials. As is well known, the basic feature of crystalline solids is order. *Crystalline* solids can be further divided into single-crystalline or polycrystalline materials, in both of which a regularly ordered structure exists at the atomic scale (Figure 1.2a). This structure is maintained, at least in principle, throughout the whole material in a *single-crystalline* material, whereas in a *polycrystalline* material, regions of different crystallographic orientations exist. These regions are referred to as *grains*, and the boundaries between them are *grain boundaries*. Studies using X-ray diffraction have clearly revealed the long-range atomic order in these materials. In *amorphous* solids, there is no long-range order (Figure 1.2b), although the local coordination of a specific molecule[2] in the amorphous state may not be that different from the coordination of the same type of molecule in the corresponding crystalline state (if it exists). A *glass* is any thermodynamically nonequilibrium (amorphous or crystalline) solid where a state of order or disorder is frozen in, corresponding to an equilibrium state, which is possible for a higher temperature or any other value of the external parameters. Such a definition thus includes, for example, frozen-in disordered crystals.

From the observation that the structure of a solid is, in essence, maintained with increasing temperature up to the melting point,[3] it follows that the PE U_{pot} is more important than the KE U_{kin} because a high value for the PE more or less immobilizes the molecules in space. Therefore, we have

$$U_{pot} \gg U_{kin} \text{ for solids}$$

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2 Although we denote the basic entities as molecules for convenience, the term is generally also supposed to include free atoms and ions as well, whenever appropriate.

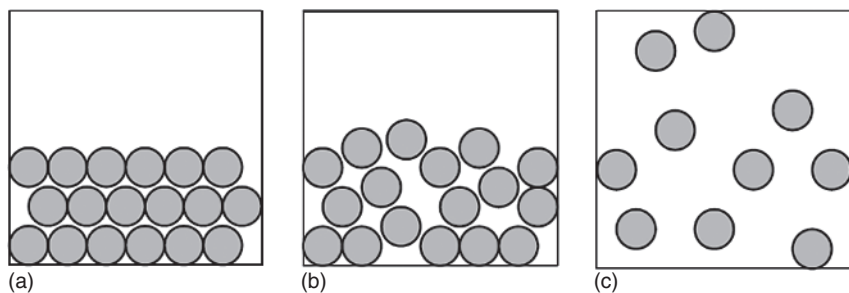3 We "forget" here for convenience of phase transformations (Section 1.6).

Figure 1.2 Schematic of structure and coordination of (a) a (crystalline) solid, (b) a liquid or amorphous solid, and (c) a gas. While solids and liquids have comparable values of density ρ, thermal expansion coefficient α, and compressibility κ, liquids and gases have more comparable values of viscosity η, shear modulus G, and diffusion coefficient D.

This makes a regular spatial array of molecules the most suitable *reference configuration* for modeling a crystalline solid. This regularity can be described globally by the concept of *lattices* (long-range order) and locally by a well-defined *coordination number* (short-range order). Other aspects, such as the KE of the molecules or defects in the regularity of the structure, can be considered to first order as perturbations of this regularity. This implies that relatively simple models for particular features of the solid state – that is, models that ignore many details – can already describe the physical phenomena of solids reasonably well.

For gases, the molecules move through space almost independently of each other, as evidenced by the wide applicability of the perfect gas law $PV = nRT$, with the pressure P, the volume V, the number of moles n, the gas constant R, and the temperature T. Here, order is nearly absent, and the reference configuration can be described as random (Figure 1.2c). This is exactly the reverse of the situation for a solid. Thus, we conclude that the PE is small as compared with the KE, and we have

$$U_{\text{pot}} \ll U_{\text{kin}} \text{ for gases}$$

The influence of intermolecular interactions can be considered first order as a perturbation, leading to some coordination of molecules with each other, so that also for gases, relatively simple models can provide a good clue for understanding.

Liquids do have some properties akin to those of solids and some other properties more like those of gases; that is, they have a *dual nature*. For example, their thermodynamic properties like density ρ, thermal expansivity α, and compressibility κ are typically not too different from those of the corresponding solid. As a rule of thumb, the specific volume increases by only 5–15% upon melting (water is a well-known exception). On the other hand, fluids (liquids and gases) have fluidity in common, although a liquid has a meniscus, whereas a gas has no such thing, and the viscosity η of liquids is higher than that of gases. This indicates that the movement of molecules in fluids is relatively easy when compared to solids, as also reflected by similar values of the shear modulus G – commonly assumed to be (near) zero – and diffusion coefficient D for liquids and gases. As might be expected, the situation for liquids with respect to energy is somewhere in the middle, and both the PE and the KE play an important role. Therefore, we have

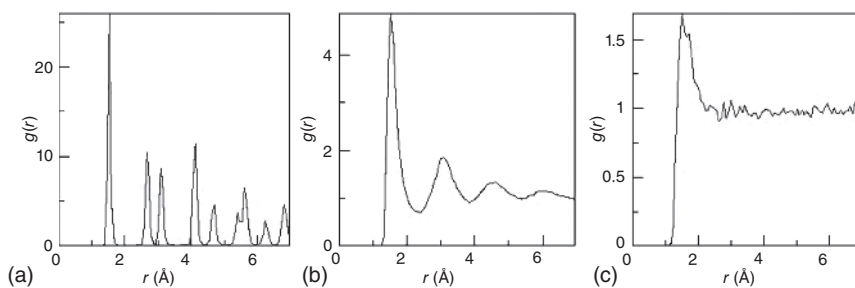$$U_{\text{pot}} \approx U_{\text{kin}} \text{ for liquids}$$

Figure 1.3 The pair correlation function $g(r)$. (a) A solid with a regular array of molecules leading to long-range order and well-defined coordination shells. (b) A liquid with similar density as the solid but having a random dense packing of molecules, leading only to short-range order in which the coordination number is of prime relevance. (c) A gas with a random packing of molecules and some rather limited ordering due to weak mutual attraction and exclusive volume of the molecules.

This implies that neither an ordered nor a fully disordered configuration is present in a liquid. The choice of a reference configuration becomes accordingly (much) more troublesome. Although long-range order is absent, short-range order is present, and the concept of coordination number is still valuable for liquids. However, because of the approximately equal importance of U_{pot} and U_{kin}, relatively simple models of liquids are usually less reliable than those for either solids or gases.

To summarize, while the dominant feature of a solid is order and that of a gas is disorder, the liquid is somewhere in between, both in structural and energetic aspects. In Figure 1.3, their static structure is illustrated by the *pair correlation function* $g(r)$, which describes the probability to find a molecule at a distance r from a reference molecule at the origin, scaled so that its average value is unity. For crystalline solids, only at discrete distances are other molecules present, whereas for gases, the probability of finding another molecule rapidly becomes constant with increasing r. For liquids, the situation is intermediate, as evidenced by some structure in $g(r)$ for small r and the limiting behavior of $g(r) = 1$ for large r. The coordination number is, however, similar to the coordination number in the corresponding solid.

For future reference, we note that often a threefold classification of fluids is made:

- *Simple fluids* are fluids of (more or less) spherical molecules such as Ar, CH_4, and N_2 for which angular dependence of the interaction potential is (almost) absent.
- *Normal fluids* are fluids without a specific interaction such as hydrogen bonding. Examples are C_6H_6, CCl_4, and cyclo-C_6H_{12}.
- *Complex fluids* if these specific interactions are present. Examples are H_2O, NH_3, and CH_3COOH.

Justification 1.1 *Kinetic Versus Potential Energy* Let us consider the magnitude of U_{kin} and U_{pot} a bit more quantitatively, and use from thermodynamics that $(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P$ with $U = U_{kin} + U_{pot}$ the (internal) energy. As for a perfect gas $PV_m = RT$ (with $V_m = V/n$) and $U = U_{kin} = 3RT/2$, we have for a perfect gas $(\partial U/\partial V)_T = 0$. For a van der Waals (vdW) fluid (Section 8.2), using the fact that the limit of the vdW energy for $V \to \infty$ approaches the energy for the perfect gas, one obtains, by integrating

Table 1.2 Argon thermodynamic essentials.

State	T (K)	V_m (l mol^{-1})	U_{pot} (kJ mol^{-1})	U_{kin} (kJ mol^{-1})	U (kJ mol^{-1})
Gas	273	22.4	−0.006 16	3.41	3.40
Vapor at T_n	87.3	6.79	−0.0203	1.09	1.07
Fluid at T_{cri}	151	0.0746	−1.85	1.88	0.0325
Liquid at T_n	87.3	0.0287	−4.81	1.09	−3.72
Solid at T_n	87.3	0.0248	−8.40	1.09	−7.31

Source: Adapted from Pryde [14] and Rice [15].

$(\partial U/\partial V)_T$, $U = U_{pot} + U_{kin} = -a/V_m + 3RT/2$, where a is one of the vdW constants, so that $U_{pot} = -a/V_m$ and $U_{kin} = 3RT/2$. Table 1.2 shows the magnitudes of U_{pot} and U_{kin} as calculated from the vdW equation for Ar in various states, where $a = 138.1$ J mol^{-1}. The change from $|U_{pot}| > U_{kin}$ for the solid and liquid at the normal boiling temperature T_n via $|U_{pot}| \cong U_{kin}$ for the fluid at the critical temperature T_{cri} to $|U_{pot}| < U_{kin}$ for the gas at any temperature is evident. The experimental value for U_{pot} for the liquid state at T_n is $U_{pot} = -5.84$ kJ mol^{-1}.

In the course of history, it also became clear that most substances can manifest themselves, given appropriate conditions, as gas, liquid, and solid, and this phase behavior is schematically shown in Figure 1.4. At sufficiently low temperature and sufficiently high pressure, a vapor (V) condenses to a liquid (L) or a solid (S), and this leads to the coexistence of vapor and liquid (V–L coexistence line), vapor and solid (V–S coexistence line), or liquid and solid (L–S coexistence line). Although, as far as is known, the fusion (L–S) curve continues to exist with increasing temperature,[4] the vaporization (V–L) curve ends at the *critical temperature* T_{cri} or critical point (CP). Above the CP, condensation is impossible, and the vapor is often addressed as gas (G). Moreover, above the critical isotherm, the difference between liquids and gases ceases to exist. Along the line A–CP (Figure 1.4), the liquid is in equilibrium with (an infinitesimal amount of) gas, while along the line B–CP the vapor is in equilibrium with (an infinitesimal amount of) liquid. These lines are conveniently addressed as *saturation lines*. Another special point is the *triple point* (TP, T_{tri}), the intersection of the V–L/V–S and L–S coexistence lines, where the vapor, liquid, and solid phases are in equilibrium. Although the typical values for $P(T_{tri})$ are $\approx 10^{-3}$ bar, those for $P(T_{cri})$ are ≈ 50 bar, but both show a wide range: for example, $P(T_{tri})$ for CO_2 is 5.2 bar and for neo-pentane $\cong 10^{-7}$ bar, and $P(T_{cri})$ for He is 2.3 bar and for Hg $\cong 1510$ bar. The TP is more sensitive to intermolecular interactions than the CP. To illustrate this, consider the isomers *n*-octane and 2,2,3,3-tetramethylbutane with T_{cri} of 569 and 568 K, but with T_{tri} of 216 and 374 K, respectively. The *normal melting point*, T_{mel}, that is, the melting temperature at 1 bar, is generally only marginally different from T_{tri}, for example, for water, $T_{tri} = 0.01\,°C$ (at 0.0061 bar) and $T_{mel} = 0\,°C$ (at 1 bar). Often pseudo-spherical molecules

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4 For the most extensively investigated liquid, Ar, no change in the character of the solid–liquid transition is observed up to $P = 12$ kbar at $T = 330$ K [17].
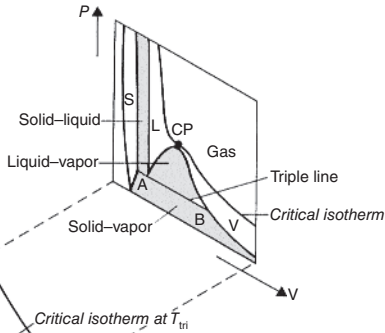
Figure 1.4 Phase relationships for a simple fluid between the solid (S), liquid (L), and vapor (V) phases. The triple point (TP) and critical point (CP) are indicated. As in the figure, some authors use the word "gas" for above-critical and "vapor" for below-critical conditions. Source: Finn [16]/Taylor & Francis.

have an unusually high melting point; for example, for adamantane ($C_{10}H_{16}$), $T_{mel} = 543$ K and for C_2Cl_6, $T_{mel} = 456$ K. Finally, we have the *normal boiling point* T_n, that is, the boiling temperature at 1 bar.

1.6 What to Expect?

As said, we will deal in Part 2 with solids, liquids, and gases and (some of) their properties as such, before entering the arena of transitions in Part 3. But first, to be self-contained as far as possible and using the metaphor of Poincaré as introduced in the Preface, we review in Part 1 the "tools" we need. We discuss in Chapter 2 *classical particle mechanics* (PM) and in Chapter 3 *quantum mechanics* (QM). Both disciplines are based on the discrete (or molecular) nature of substances, that is, on a mechanistic, *microscopic picture*. As an application of this picture, we discuss *intermolecular interactions* in Chapter 4. But before this microscopic picture was fully accepted, a purely phenomenological, *macroscopic picture* already emerged from engineering considerations, ignoring largely, if you are a purist completely, microscopic considerations. Not taking thermal effects into account (apart from the temperature dependence of properties), the approach is normally called *continuum mechanics* (CM) and a brief introduction is given in Chapter 5. Incorporating thermal phenomena led to a field nowadays known as *macroscopic* (or *phenomenological* or *classical*) *thermodynamics* (MT), which is reviewed in Chapter 6, including its extension to *linear irreversible thermodynamics*. Often, an integrated approach to classical and statistical thermodynamics is advocated [18, 19]. In this book, we review thermodynamics as an individual discipline, while its merger with *microscopic* or *statistical thermodynamics* (ST) appears naturally in Chapter 7.

In Part 2, we discuss the "bricks": the salient aspects of gases, liquids, and solids. In Chapter 8, we overview the macroscopic description of *gases* as given by the various equations of state and outline the microscopic description as embodied in the kinetic theory of gases and the virial approach. For *liquids*, we introduce in Chapter 9 the various approaches used in general, after which we mainly follow a structural approach. There are at least three distinguishable types of *solids* – inorganic, metallic, and polymeric materials – which we describe in Chapter 10. The importance of *interfaces* – the "cement" – warrants a separate discussion (Chapter 11).

In Part 3, we turn to the "house": the transitions and transformations between phases. Here, we distinguish between *phase transitions* (the change from one phase to another) and *phase transformations* (the structural change within one phase), the latter obviously being most important for solids. We also distinguish between continuous and discontinuous phase transitions. In Chapter 12, we discuss *general aspects. Discontinuous phase transitions* are divided into transformations between gases and liquids (Chapter 13) and between liquids and solids (Chapter 14). In Chapter 15, we deal with *continuous phase transitions*, the description of which is an example of an intimate mixture between molecular and mesoscopic arguments. Two phase transformations are discussed: one in the liquid state, for *liquid crystals* (Chapter 16), and one in the solid state, for *ferroelectrics* (Chapter 17), followed by the *glass transition* (Chapter 18). Finally, Chapter 19 deals with *irreversibility* and the *return to equilibrium*. The appendices provide elements of mathematics, special relativity theory, the lattice gas model, electrostatics, and probability, as well as some physical property data and answers to selected problems.

Overall, the focus in Parts 2 and 3 is on structure and thermodynamic aspects. As not all physical properties can be discussed, we opted to deal with dielectric behavior for all three phases to provide some continuity. For the basics, in Part 1, an axiomatic approach is followed. Generally, we refrain from discussing experimental methods and focus on the underlying theoretical concepts. Problems are mostly limited to the somewhat more complex types, ignoring the "plug-in" types. Each chapter contains specific references and a section titled "Further Reading," referring to a small set of recommended relevant books, that are referred to by author(s) and year.

1.7   Units and Notation

To avoid unnecessary semantic discussions, one better agrees on the meaning of the basic concepts used. This is the purpose of Sections 1.1–1.4. It is also expedient to know what to expect, and this is what is described in Section 1.6. Of course, one also must be able to measure properties quantitatively, and for that, a system of units for quantities is required. Restricting ourselves here to the Système International (SI), there are seven *base units*. The relevant ones for our purpose are for length (*meter*, m), for mass (*kilogram*, kg), for time (*second*, s), for temperature (*kelvin*, K or °C where $t/°C = T/K - 273.15$), and for amount of substance (*mole*, mol). Originally, standards were defined for these units, but since 2019, all base units are defined in terms of fundamental (physical) constants. *Derived units* are defined in terms of base units. Some important derived units for our considerations are the unit for force, the *newton* (N) defined as $N = kg\,m\,s^{-2}$, the unit for pressure, the *pascal* (Pa) defined as $Pa = N\,m^{-2}$, and the unit for energy, the *joule* (J) defined as $J = N\,m$. A brief

description of SI units, physical constants, and conversion factors is given in the front matter. This is not to say that other units will not be used, as these are frequently used in the literature. For a short or extensive review of measurement, see Ref. [20] or [21]. For the use of preferred units and symbols in the physical sciences, we refer to [22].

There remains the matter of notation, for which the conventions used should be clear. We use in (macroscopic and microscopic) thermodynamic discussions for summations over entities like molecules and states, a lowercase Latin index, say i or j, and for a summation over chemical components generally (but not always) a lowercase Greek index, say α or β. Furthermore, a superscript * is used for a pure compound, for example, the partial volume V_α^* of component α, and a superscript ° for a reference state, for example, the pressure $P°$, conventionally taken as 1 bar.

With respect to mathematical notation, scalars are addressed via an italic letter, say a, and vectors by an italic bold face letter, say $\boldsymbol{a}$ (direct notation) with components a_i (index notation). Column matrices are also labeled by, say a_i, or by a roman bold face letter, say $\mathbf{a}$ (matrix notation). Similarly, matrices are addressed by an italic letter with two subscripts, say A_{ij}, or by $\mathbf{A}$. The column $\mathbf{a}$ is used as a shorthand for a collective of N quantities, that is, $\mathbf{a} = \mathbf{a}_1\mathbf{a}_2...\mathbf{a}_N$. For example, for N molecules each with coordinates $\boldsymbol{r}_i$, where $\boldsymbol{r}_i = (x_i, y_i, z_i)$, we denote the coordinates collectively by $\mathbf{r} = \boldsymbol{r}_1\boldsymbol{r}_2...\boldsymbol{r}_N = x_1y_1z_1x_2y_2z_2...x_Ny_Nz_N$, or in a multidimensional integral, we write $\int d\mathbf{r}$, where $d\mathbf{r} = d\boldsymbol{r}_1 d\boldsymbol{r}_2...d\boldsymbol{r}_N = dx_1dy_1dz_1dx_2dy_2dz_2...dx_Ndy_Ndz_N$. Denoting the set b_i by $\mathbf{b}$ and the set a_i by $\mathbf{a}$, we can therefore write $c = \Sigma_i b_i a_i = \mathbf{b}^T\mathbf{a}$, using the transpose $\mathbf{b}^T$ of $\mathbf{b}$. This allows us to write the derivatives of a function $f(a_i)$ given by $b_i = \partial f/\partial a_i$ collectively as $\mathbf{b} = \partial f/\partial \mathbf{a}$ or of a set of functions $f_i(a_j)$ given by $B_{ij} = \partial f_i/\partial a_j$ as $\mathbf{B} = \partial \mathbf{f}/\partial \mathbf{a}$. We, therefore, distinguish between a vector $\boldsymbol{a}$ and its matrix representation $\mathbf{a}$. For a function, the notation $y = y(\mathbf{x})$ is often used, but if clarity is required, we use $y = f(\mathbf{x})$. The inner product c of two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ is in direct notation $c = \boldsymbol{ab}(= \Sigma_i b_i a_i)$ and in matrix notation $c = \mathbf{a}^T\mathbf{b}$. As we try to be pragmatic, we use direct, index, and matrix notations, whenever convenient. Generally, direct and matrix notations are the most compact, but in case of possible confusion, index notation, which is unambiguous, is given. Finally, for a reminder of some mathematics, we refer to Appendix A and to the front matter for a summary of the notation used.

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Further Reading

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Eyring, H., Henderson, D., and Jost, W. (ed.) (1971). *Physical Chemistry, an Advanced Treatise*, Vol. I–XI. New York: Academic Press. This set of books contains many useful parts for all aspects of physical chemistry, despite being somewhat dated.

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