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Klaus D. Sattler

Mercury: From Atoms to Solids

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Elke Pahl, Peter Schwerdtfeger
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3.1 Introduction

Elemental mercury is the only metal that is liquid at room temperature (melting temperature \( T_m = -38.83^\circ C \)); the only other low melting metal is gallium (\( T_m = 29.76^\circ C \)) [1]. This has been known since ancient times and is reflected in the Greek name *Hydrargyrum* meaning “watery silver” and the Latin *Argentum vivum* meaning “quick silver.” It is speculated that its low melting point is due to relativistic effects [2–4], which energetically lowers the 6s band substantially [5], thus making mercury a very hard atom with a static dipole polarizability of only \( \alpha_0 = 5.025(50) \text{ Å}^3 \) [6,7]. It is clear that such strong and pronounced relativistic effects for the 6s shell [5], which are close to the relativistic 6s maximum of gold [4,8], makes mercury rather unique in chemical and physical properties among the other Group 12 metals zinc and cadmium. Some of the physical and chemical properties of the Group 12 elements are compared in Table 3.1, and in many of these properties we see anomalies that, most likely, are caused by relativistic effects. For the next Group 12 element (below Hg) with nuclear charge \( Z = 112 \) (Copernicium, Cn), even larger relativistic effects are predicted [9–11], and the dipole polarizability of this element is now the lowest of all the Group 12 elements (\( \alpha_0(112) = 3.8 \text{Å}^3 \)) [12].

Mercury occurs in many natural materials including coal, gas, and oil in small quantities; it is estimated that by burning fossil fuels about 2400 tons per year of mercury are released into the atmosphere [13]. Thus, the contamination of the atmosphere and the bioaccumulation of it, especially in fish, present large-scale problems. Since oxidized mercury is easier removed than mercury in its elemental form, the search for efficient and regenerable oxidation catalysts like noble metals is important [14,15]. For humans, mercury is toxic and leads to damage to the nervous tissue, kidneys, and liver. It is therefore important that mercury be handled with care, which is the main reason why mercury is not the metal of choice in the study and design of new nanomaterials. In fact, most of the nanoscience research here concentrates on the development of sensors for the detection of small amounts of mercury [16].

Mercury is, however, an interesting element to be studied by theoreticians, as mercury clusters range from van der Waals bonded to more covalent systems, before finally reaching the metallic state at larger cluster size [17]. The dissociation energies (\( D_e \)) therefore vary widely from about 0.05 eV for the dimer [18] to 0.67 eV (cohesive energy \( E_{coh} \)) for the bulk metal. For an ideal Lennard-Jones system, we have the simple relation \( E_{coh} = 8.61D_e \) [19], which is obeyed for either the face-centered cubic fcc or the hexagonal close-packed hcp solid. Instead, \( E_{coh} = 13.4D_e \), i.e., mercury does not behave like an ideal Lennard-Jones system. It is therefore a challenge to simulate mercury in the gas, liquid, or the solid phase.

The first appearance of the 6s–6p gap closure to the metallic state at a specific cluster size is still a matter of intense debate [20,21]. Early measurements by Rademann gave an estimated band gap closure for Hg\(_n\) at \( n \approx 70 \) [22,23], Singh obtained \( n \approx 80 \) [24,25], Pastor et al. \( n \approx 135 \) [26–28], and a recent photoelectron study on negatively charged mercury clusters by Busani et al. gave \( n = 400 \pm 30 \) [29–31]. In liquid mercury, the single 6s–6p gap opens at a density of \( \rho = 8.8 \text{ g cm}^{-3} \) (the density of liquid mercury under standard conditions is \( 13.59 \text{ g cm}^{-3} \)) [32]. This agrees with experiment where a gradual transition from metallic to semiconducting and insulating properties has been observed at elevated temperatures and pressures [33]. An interesting comparison is to superheavy element 112; due to a very strong relativistic 7s stabilization element 112 never becomes metallic as recent solid-state calculations show [10].

There is also a very large contraction of the Hg–Hg equilibrium bond length \( r_e \) when going from the van der Waals bonded dimer (\( r_e = 3.69 \text{ Å} \)) [18] to the solid state (\( r_e = 3.01 \text{ Å} \)) [1], which is not found in the rare gas elements. Such large differences indicate
the importance of many-body forces beyond the two-body force such as the two-body Lennard-Jones potential [34]. This clearly distinguishes mercury from rare gas interactions, which are reasonably well described by two-body forces only [19]. Further, there is no bonding interaction at the Hartree–Fock level starting from a Dirac–Coulomb Hamiltonian including Breit interactions in the low-frequency limit [39,40]. They reproduce experimental ionization potentials and electronic excitations [1,41] within a few 100 cm⁻¹. In fact, such calculations are now so precise that quantum electrodynamic effects have to be taken into account to produce results of experimental accuracy [42]. Figure 3.1 shows ionization potentials and static dipole polarizabilities for all group 12 metals. It is clear that relativistic effects in such properties are large and cannot be neglected anymore. The relativistic increase in the ionization potential and the subsequent decrease in the polarizability has led to the conclusion, that both Hg and element 112 are chemically inert [9]. The (indirect) relativistic expansion of the core 5d orbitals also leads to a larger 5d/6s mixing [5]. Finally, spin–orbit coupling splits both the 5d and 6p levels in Hg. The splitting between the 5p⁰/5p² states of neutral Hg is 0.79 eV, while the 3D_{5/2}/3D_{3/2} splitting in Hg⁺ is 1.86 eV [41]. The 6p₁/₂ spin–orbit stabilization will reduce the 6s/6p band and therefore shift the onset of metallicity to smaller Hg clusters. Further, in a mercury vapor lamp the UV light produced at 253.7 nm comes from the spin-forbidden ⁵P₁ → ³S₀ transition, which becomes allowed in the spin–orbit coupled case [45].

### 3.2 The Mercury Atom

We briefly mention both, theoretical and experimental work on the Hg atom, mainly to discuss the importance of relativistic effects necessary to understand the physical properties of the Hg clusters. The most accurate calculations for Hg come from Kaldor’s group using Fock-space coupled-cluster theory starting from a Dirac–Coulomb Hamiltonian including Breit interactions in the low-frequency limit [39,40]. They reproduce experimental ionization potentials and electronic excitations [1,41] within a few 100 cm⁻¹. In fact, such calculations are now so precise that quantum electrodynamic effects have to be taken into account to produce results of experimental accuracy [42]. Figure 3.1 shows ionization potentials and static dipole polarizabilities for all group 12 metals. It is clear that relativistic effects in such properties are large and cannot be neglected anymore. The relativistic increase in the ionization potential and the subsequent decrease in the polarizability has led to the conclusion, that both Hg and element 112 are chemically inert [9]. The (indirect) relativistic expansion of the core 5d orbitals also leads to a larger 5d/6s mixing [5]. Finally, spin–orbit coupling splits both the 5d and 6p levels in Hg. The splitting between the 5p⁰/5p² states of neutral Hg is 0.79 eV, while the 3D_{5/2}/3D_{3/2} splitting in Hg⁺ is 1.86 eV [41]. The 6p₁/₂ spin–orbit stabilization will reduce the 6s/6p band and therefore shift the onset of metallicity to smaller Hg clusters. Further, in a mercury vapor lamp the UV light produced at 253.7 nm comes from the spin-forbidden ⁵P₁ → ³S₀ transition, which becomes allowed in the spin–orbit coupled case [45].

![FIGURE 3.1](image)

**FIGURE 3.1** A comparison between experimental (or relativistic coupled cluster) ionization potentials and static dipole polarizabilities for the group 12 metals with (R) and without (NR) relativistic effects. Experimental values for Zn, Cd, and Hg are taken from Refs. [1,6,43,44], relativistic coupled-cluster calculations come from Refs. [12,39].

### Table 3.1: A Comparison of Chemical and Physical Properties of the Group 12 Elements

<table>
<thead>
<tr>
<th>Property</th>
<th>Zn</th>
<th>Cd</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>I₁ (eV)</td>
<td>9.394</td>
<td>8.994</td>
<td>10.438</td>
</tr>
<tr>
<td>I₂ (eV)</td>
<td>17.96</td>
<td>16.908</td>
<td>18.757</td>
</tr>
<tr>
<td>I₃ (eV)</td>
<td>3.63</td>
<td>4.08</td>
<td>4.48</td>
</tr>
<tr>
<td>αₐ (Å)</td>
<td>5.75</td>
<td>7.36</td>
<td>5.02</td>
</tr>
<tr>
<td>Tᵥ (°C)</td>
<td>419.53</td>
<td>321.07</td>
<td>38.83</td>
</tr>
<tr>
<td>Tᵣ (°C)</td>
<td>907</td>
<td>767</td>
<td>356.62</td>
</tr>
<tr>
<td>λ (W m⁻¹ K⁻¹)</td>
<td>0.85</td>
<td>0.517</td>
<td>3.95</td>
</tr>
<tr>
<td>ρ (10⁻⁸ Ω m)</td>
<td>5.9</td>
<td>7.6</td>
<td>95.78</td>
</tr>
<tr>
<td>M</td>
<td>0.38</td>
<td>0.38</td>
<td>1.0</td>
</tr>
<tr>
<td>B (GPa)</td>
<td>70</td>
<td>42</td>
<td>25</td>
</tr>
</tbody>
</table>

**Notes:** I₁ and I₂ are the first and second ionization potentials of the atom; I₃ is the work function of the bulk; αₐ is the static electric dipole polarizability; Tᵥ and Tᵣ are the melting and boiling points; Tᵣ is the superconducting transition temperature; λ is the thermal conductivity; ρ is the specific resistance; M the electron–phonon coupling constant; B the bulk modulus, and for the bulk structures; hcp refers to hexagonal closed packing, rhomb to rhombohedral. Results are taken from Ref. [1].
3.3 Mercury Clusters

It is obvious that any theoretical method able to accurately describe Hg clusters from small to large sizes has to reproduce experimental values reasonably well for the smallest cluster, the dimer Hg₂, as well as for the solid metal. For Hg₂, accurate experimental results are scarce. Table 3.2 shows a comparison between different theoretical results with experiment. As the interaction between two Hg atoms in Hg₂ is of van der Waals (dispersive) type with possibly a rather small dissociation energy of 400 cm⁻¹ [46], it is currently not easy to obtain accurate values from both theory or experiment. Currently, the most precise calculations come from Peterson [47] using a small-core relativistic pseudopotential for Hg, including spin–orbit corrections and extrapolating to the basis set limit using correlation consistent basis sets at the coupled-cluster level of theory. Relativistic effects are important, as they decrease the bond distance by about 0.2 Å, and slightly lower the dissociation energy [18,37,48]. Table 3.2 clearly shows the huge stabilization effect on removing an electron out of the antibonding orbital in Hg₂, i.e., the dissociation energy increases by a factor of 29 when going from Hg₂ to Hg₂⁺. This rather large effect will diminish with increasing cluster size toward the solid state. Excited states of Hg₂ and Hg₂⁺ were also studied in the past by both experimental [51–53,55,58–60] and theoretical methods [61–64]. Also, some excited states of Hg₂ are found to be more stable due to the excitation of an electron out of the antibonding orbital; the dissociation energy increases up to a factor of 25 and the bond length is strongly reduced to about 3 Å, the distance found in solid Hg (see Ref. [63] and references therein). We note here that the importance of relativistic effects in optical transitions in Hg-containing alloys was already discussed in 1972 by Kisiel and Lee [65].

The study of large mercury clusters to, for example, probe the convergence toward the bulk is a nontrivial task for both theoreticians and experimentalists. As calculations show, for the simple mercury dimer as well as for the solid state, relativistic effects have to be included [24,37,48]. For larger clusters, the computer time becomes prohibitively large for all electron methods at the many-body expansion of the interaction potential does not converge smoothly. The relativistic pseudopotential approximation (also called effective core potential method) is used, which has been proven to be very accurate compared to all electron calculations if care is taken for the proper choice of the core and in the adjustment procedure [66]. While the inclusion of scalar relativistic effects is more or less straightforward, spin–orbit effects, electron correlation, and the basis set superposition error present a much larger problem [18,47,67]. Theoretical studies of clusters have therefore been limited to rather small cluster sizes, where the extrapolation to the bulk limit is questionable. Nevertheless, a number of interesting computational studies on mercury clusters have appeared in the past decade.

Dolg and coworkers have studied small neutral and charged mercury clusters [49,68]. An ELF (electron localization function) analysis showed predominantly van der Waals type bonding for Hgₙ (n ≤ 4) [68]. They also investigated the size dependence of ionization potentials, electron affinities, and binding energies with increasing cluster size up to Hg₇ and found significant covalent bonding character for these clusters. For medium-sized clusters, Dolg and coworkers suggested a hybrid model consisting of a pairwise additive dispersion potential proportional to R⁻⁶ together with a two-valence electron relativistic pseudopotential. The latter is a so-called large-core pseudopotential which includes core-polarization effects describing dynamic correlation from the 5d core of Hg, and finally core–core repulsion effects between the Hg atoms [69]. This hybrid model is a good approximation for Hgₙ as comparison with more accurate coupled-cluster calculations using a small-core pseudopotential, which does not include the 5d electrons as core electrons, for Hg show [69]. A simulated annealing procedure confirmed the Lennard-Jones behavior of these structures with icosahedral structures for Hg₁₃ and Hg₅₅ [69]. However, in a later paper they used a genetic algorithm procedure when searching for the global minima and found very unusual structures from Hg₂ to Hg₇, which deviate substantially from the compact Lennard-Jones like shapes [70,71], which for small- to medium-sized closed atom-shell clusters are Mackay icosahedra [72]. As two-body interactions favor compact structures due to maximizing the number of interacting pairs, this result would imply that the many-body expansion of the interaction potential does not converge smoothly. This was indeed found in a recent paper by

### Table 3.2 Spectroscopic Properties for the Hg₂ 1Σ₉⁺ and Hg₂⁺ 3Σ₉⁺ Ground States from Experimental and Theoretical Work

| Molecule | Method | rₑ | D₀ | ωₑ | ωₑxₑ | I.P. | Refs.
|----------|--------|----|----|----|------|------|------
| Hg₂⁺     | Theo.  | 3.687 | 0.048 | 19.8 | 0.23 | 8.85/9.60   | [47,49] |
|          | Exp.   | 3.69 ± 0.01 | 0.047 ± 0.002 | 19.6 ± 0.3 | 0.26 ± 0.05 | 9.0–9.5     | [23,50–55] |
| Hg₂⁺     | Theo.  | 2.74 | 1.40 | 112 | —    | 14.5²⁺     | [49,56] |
|          | Exp.   | —    | 1.6 ± 0.2 | —  | —    | —           | [57] |

**Notes:** The equilibrium bond distance rₑ is given in Å, the dissociation energy D₀ in eV (zero-point vibrational energy correction included), the harmonic vibrational frequency ωₑ, and the anharmonicity correction ωₑxₑ in cm⁻¹, and the ionization potential I.P. in eV.

* Adiabatic I.P.
* Vertical I.P.
* Own unpublished results at the MP2 level of theory. The local minimum of metastable Hg₂⁺ was taken as a reference. The vertical I.P. is only slightly different to the adiabatic value.
Moyano et al. [35]. However, more recent accurate coupled-cluster calculations show that, beside the importance of such many-body effects, the mercury clusters do follow the usual growth pattern of compact cluster structures [73], which contradicts the original results [70,71].

Moyano et al. used two-body and effective three-body interactions between the mercury atoms in a simulated annealing approach to obtain global minimum structures for larger mercury clusters up to Hg40 [35]. Again these clusters show rather compact structures similar to the Lennard-Jones structures with magic cluster numbers of 6, 13, 19, 23, 26, and 29 atoms, in agreement with diatomic-in-molecules (DIM) calculations by Kitamura [74]. These values also coincide with the mass distribution of mercury–cesium cluster ions observed by Ito et al. [75]. The calculations of Moyano et al. also reveal a fast convergence of the polarizability toward the bulk limit in contrast to the singlet–triplet gap or the ionization potential. However, the cluster sizes were far too small to accurately predict the onset of metalliclicity.

It is now evident that it remains a challenge to accurately describe electronic properties for global minimum structures for larger mercury clusters, and, what is required at finite temperatures, to perform molecular dynamic simulations to obtain properties, which can be compared to the experiment. Nevertheless, a number of theoretical studies appeared in the past dealing with neutral or charged mercury clusters in ground and excited electronic states [56,76–78]. Hg6 is the smallest cluster which can bind an extra electron (electron affinity of 0.13 eV at the coupled-cluster, CCSD(T), level of theory) [77]. Gaston et al. studied the photoabsorption spectra of cationic mercury clusters [56]. The experimental photoabsorption spectra of singly charged cationic mercury clusters Hg6+ carried out by Haberland and coworkers show a sharp change in behavior at cluster size n = 6 [60,79]. It has been interpreted as the onset of a plasmon-like resonance in the 6s–6p transition. Both, relativistic density functional theory DFT and wavefunction-based methods revealed that the onset of a plasmon-like resonance corresponds to a structural change from linear to three-dimensional cluster isomers, i.e., a change from single electron–hole excitations in small linear clusters to plasmon-like collective transitions for the larger three-dimensional clusters [56].

Medium- to large-sized mercury clusters have been studied extensively in the past by experimental methods [20–23,26–31, 80–84], mainly to answer the question at what cluster size the transition from van der Waals to metallic bonding occurs [26]. An excellent review on cluster size effects and the extrapolation to the bulk for metallic clusters is given by Johnston [21]. Here we mention the most recent work of Busani et al. [29]. They measured photoelectron spectra of the mass-resolved negatively charged mercury clusters up to Hg26−. Upon photoexcitation, the 6p electron can be detached leaving the resulting neutral cluster in its electronic ground state. Alternatively, electrons can be detached from the 6s band of the mercury cluster leaving the resulting neutral cluster in an “electron–hole pair” excited state. The difference between both results is a direct measure for the HOMO–LUMO (6s–6p) gap in the photoelectron spectrum of the negatively charged cluster, which approximately provides the excitation band gap for the corresponding neutral cluster. Large changes in the structure of mercury clusters due to the excess electron are not expected at larger cluster size as the charge will be smeared out. Extrapolation to higher cluster sizes indicates a band gap closure at the size range of n = 400 ± 30, a considerably larger value than previously reported (see Section 3.1) [29].

Bescós et al. studied time-resolved ultrafast multiphoton ionization and fragmentation dynamics of mercury clusters Hg2n (n ≤ 110) with femtosecond pulses [81]. At laser intensities of 1014 W cm−2, they observed singly, doubly, and triply charged mercury clusters. Ionization potentials and electron excitation energies for mercury clusters up to Hg40 were determined by photoelectron and UV/vis-photoabsorption spectroscopy by Rademann et al. [22,23,84]. Their estimate for the onset of the metallic phase is at much smaller cluster size compared to Busani et al. [29]. Blanc et al. looked at the stability of triply charged mercury clusters, Hg3n [82]. They found Hg603+ to be stable with respect to fragmentation into Hg502+ and Hg50+ (n + m = 60), but not Hg60+.

3.4 Liquid Mercury and the Mercury Surface

Along with the lowest melting point Tm = −38.83°C = 234.32 K [1] of all metals, assumed but not yet proven to be due to large relativistic effects lowering the 6s band substantially [2–5], mercury also shows the lowest critical temperature of all metals. Accepted experimental values for the liquid–gas critical point are a critical temperature Tc = 1751 K at a critical density ρc = 5.8 g cm−3 and a critical pressure pc = 1673 bar [85,86]. These values are experimentally accessible, mercury presents an ideal system to investigate liquid properties close to the critical region. Therefore, over the last decades, extensive research on the experimental as well as on the theoretical side of the liquid–vapor coexistence curve up to the critical region has been taken place. Most of the studies focus on the interesting region of the metal to nonmetal (M–NM) transition which occurs when fluid mercury is expanded close to the critical values. At ambient conditions, the density of liquid Hg is 13.6 g cm−3; the M–NM transition takes place at densities around 9 g cm−3 (see, e.g., the review on experimental evidence in Ref. [87] and theoretical calculations in Refs. [32,88]). In recent years, development in experimental techniques, especially the use of x-ray scattering methods based on third-generation synchrotron sources, as well as on the theoretical side (particularly in computational simulations) allowed for an improved understanding of the underlying mechanism of this M–NM transition (see, e.g., Refs. [89–97]) as well as for a better understanding of liquid metal surfaces where the existence of surface-induced atomic layering in liquid mercury was established [98,99]. New developments include the use of liquid Hg as a novel substrate for the deposition of Langmuir monolayers of organic substances [100–103] and the investigation of geometrically confined liquid Hg in nanopores [104–108] or carbon nanotubes [109,110]. Of interest are also the study of...
the liquid mercury–water interface [111–113] due to its importance in electrochemical cells and the adsorption of Hg on metal surfaces [114] in connection with the search for Hg oxidation catalysts.

Despite the fundamental, unsolved question, why mercury is liquid at ambient conditions, to our knowledge, there has only been one molecular dynamics study by Sumi et al. [115] trying to determine the melting temperature. They found a melting point of 232 K in accidentally good agreement with experiment, regarding the facts that their study relied on an ab initio potential curve of Hg, which considerably exceeds the bond length of the Hg dimer by 0.6 Å and that many-body effects were totally neglected. In later work, they used a scaled version of their potential in order to match the bond length better allowing them to reproduce experimental data at the M–NM transition region, but they did not calculate the melting point anew [116]. A promising ansatz to get information about the melting temperature is the cluster approach: Here, the melting temperature of nanoclusters, with several complete shells of atoms around a central atom therefore showing an enhanced stability, are extracted out of MC simulations and are extrapolated to the bulk value. This has recently been shown to be successful for neon and argon [117] where bulk melting points could be determined with high accuracy in a pure ab initio treatment. Of course, for Hg, great care of the treatment of the interparticle potential has to be taken, since the many-body expansion is known to fail (see below).

All computer simulations like molecular dynamics or Monte Carlo methods for liquids need, of course, information about the electron distribution of the system. The electronic distribution can either be modeled by a form of density functional theory (for liquid Hg, see, e.g., Refs. [32,118]) or by modeling or approximating directly the potential energy [119]. In most computational simulations of liquid Hg, the latter ansatz is chosen and the interparticle potential $V_{\text{int}}$ is divided into pairwise $V^{(2)}$ and higher terms:

$$V_{\text{int}} = \sum_n V^{(n)} = \sum_{i<j} V^{(2)}(r_{ij}) + \sum_{i<j<k} V^{(3)}(r_{ij},r_{ik},r_{jk}) + \cdots \quad (3.1)$$

The sums run over all particles in the simulation cell or up to a chosen cutoff distance and $r_{ij}$ is the interparticle distance. Unfortunately, already the three-body terms are becoming quickly too expensive and, for Hg, the expansion is known to be not converging [35,73]. As a result, recent molecular dynamics simulations on liquid metallic mercury using a Lennard-Jones potential curve by Schwerdtfeger et al. [18] (see also a recent parameterization of Tang and Toennies [130]). The effective potentials include the many-body effects in an approximate way and are dependent on the temperature. Effective pair potentials have been constructed in a number of different ways and applied with good success to a variety of the structure and properties of liquid mercury in wide ranges of temperatures and pressures. These works used the link between pair potentials and the pair distribution function, which itself is related by Fourier transform to the experimentally determined static structure factor. Either one starts with guesses for the potential that is refined using experimental data [124,125] or a guessed initial configuration is refined using the experimental structure data like in the reverse Monte Carlo method [121,122,126,131]. The effective two-body potentials are characterized by a steeply rising repulsive branch at short interatomic distances and a relatively weak oscillating branch at larger distances. Effective three-body potentials were constructed by introducing a semiempirical $C_6(T)/r^6$ term fitted to experimental data [127,128] or through quantum-chemical calculations of cohesive energies for selected geometries of clusters and bulk crystals yielding effective many-body potentials that depend on the coordination number and the nearest-neighbor distance [96,97].

In Figure 3.2, the gas–liquid coexistence curve close to the critical region is depicted, showing the onset of the M–NM transition in the liquid region at densities around 9 g cm$^{-3}$ corresponding to a temperature of about 1670 K at the gas–liquid coexistence line. First indications for the M–NM transition were found by Franck and Hensel [132]. Different mechanisms for the transition have been proposed, which can be roughly divided into a homogeneous expansion mechanism (dating back to the pseudogap model proposed by Mott [133–135]), where the nearest-neighbor distance is gradually increasing while the coordination number is constant, and a heterogeneous expansion mechanism [88,136] making a decrease in the average coordination of the Hg atoms in the liquid with an (almost) constant next-nearest-neighbor distance responsible for the transition. After extensive experimental and theoretical investigations, the heterogeneous mechanism first proposed by Mattheis and Warren [136] and in the Franz model [88] is now the accepted

![FIGURE 3.2 Gas–liquid coexistence curve and selected isochors at densities of 10, 9, 5, and 1 g cm$^{-3}$. The solid lines are theoretical data from Ref. [98]; the dashed lines refer to experimental data (Refs. [87,138]). The filled diamonds show the experimental and theoretical critical points. The shaded area presents the nonmetallic liquid region.](image-url)
one and was refined in the last years due to experimental (see work of Hensel [86,87,137] and references therein as well as newer experimental work in Refs. [91,92,138]) and theoretical [32,96,97,121–123,126,129] progress. Exact measurements of the static structure factor and calculations of its Fourier transform, the pair distribution function $g(r)$ (which gives the relative probability of an atom having a neighbor at distance $r$) proved a clear decrease in the average coordination number while the first peak of $g(r)$ and thus the nearest-neighbor distance remains almost constant. In more detail: Below the M–NM transition, the local structure of liquid Hg is assumed to be similar to the crystal structure of $\alpha$-Hg (going back to the early experimental work by Kaplow et al. [139]): There are six hexagonally arranged atoms at 3.5 Å (close to the van der Waals dimer distance) around a central atom and six atoms at 3.0 Å (corresponding to the metallic distance in the solid) in an upper as well as lower plane three by three (see Figure 3.3). Around the M-NM transition, atoms at the shorter distances were shown to be selectively taken away causing the transition to the nonmetallic phase [91,96,97,126,129].

New experiments of the dynamic structure factor that allow the study of dynamical properties of expanded fluid Hg by using inelastic x-ray scattering have shed new light on the M–NM transition [93,94], and suggest that the transition is not a gradual one but a first-order transition at which a new style of fluctuations between metallic and nonmetallic domains appears [94]. Thermodynamically, and thus in all experiments measuring static properties, the discontinuous density jumps in the first-order transition are obscured by strong thermal agitation and structural disorder and feign a gradual transition. Earlier indications for a first-order transition was given in a theoretical investigation of the volume dependence of the pair distribution function $g(r)$ (which gives the relative probability of a fluid mercury: While moving differently locked up in a cage formed by their nearest neighbors [142]. This behavior was confirmed by recent molecular dynamics simulation by González et al. [143].

Experimental progress also allowed to study the crystal structure and properties of liquid Hg under geometrical confinement by embedding Hg into nanoporous matrices like porous glass, synthetic opals, or zeolites [104–108]. Even a 1D confinement can be realized by filling carbon nanotubes with Hg, which is achieved as a result of electrowetting [109]. Large interest in these nanostructured composites stems from the fact that fundamental questions of condensed matter physics related to finite-size effects can be addressed as well as applications in nanoelectronics and nano-fluidics are to be expected. Experiments on Hg in porous glasses and other nanoporous materials have shown that the crystal structure of bulk Hg ($\alpha$-Hg) is identical to that of confined Hg [104], whereas the melting/freezing temperatures are shifted toward lower temperatures and the transitions are broadened in comparison to bulk Hg [105,106]. These trends are enhanced with decreasing pore size [107]. These effects caused by the finite size are in analogy to the observed behavior in clusters where one also finds decreasing melting temperatures and line broadening with decreasing cluster size (see, e.g., Ref. [117]). Also the Knight shift and thus the electronic susceptibility was shown to decrease with decreasing pore size [108]. For the carbon nanotubes similar effects are predicted by a molecular dynamics simulations [110].

In this study, an ordering of the Hg atoms near the walls of the nanotubes and density oscillations, which extend several atomic diameters into the bulk, are suggested, even resulting in a close-packed cylindrical shell structure for the smallest nanotubes.

Metallic liquids exhibit a complex surface structure in which the atoms are stratified parallel to the liquid–vapor interface persisting into the bulk for a few atomic diameters and leading to density oscillations along the surface normal. This phenomenon of surface layering has been predicted theoretically [144], but could not be proven unambiguously in experiments [145] until experimental improvement due to access to third-generation x-ray sources finally allowed to resolve these oscillations, first in Hg [98,146] and Ga [147]. In Hg, the layering was found to have a spacing of 2.72 Å and a decay length of less than 5 Å. Surface layering seems to be a more universal property of liquid surfaces in general [148–152] but the reasons behind are not yet clearly identified; possibilities include surface tension, geometrical confinement effects due to the necessarily rapid decay of the density at the liquid–vapor interface [152] and a low ratio of melting and critical temperature $T_m/T_c$ [148–151].

Another interface of great interest due to its importance in electrochemical cells is the one between liquid Hg and water. This interface was studied by molecular dynamics simulations with pure water [111] as well as in the presence of alkali cations

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**FIGURE 3.3** Rhombohedral lattice of Hg showing the 12 next-nearest neighbors: 6 mercury atoms are arranged in a hexagon around the central atom with a distance of 3.5 Å while the other 6 atoms are located closer to the central atom with a distance of 3.0 Å above and below the plane three by three.

High-resolution inelastic neutron scattering measurements of the dynamic structure factor were also performed at room temperature in order to investigate the microscopic dynamics of liquid mercury [140–142]. It was shown that the so-called cage diffusion plays a dominant role in the collective dynamics of liquid mercury: While moving diffusively, particles find themselves

Experimental progress also allowed to study the crystal structure and properties of liquid Hg under geometrical confinement by embedding Hg into nanoporous matrices like porous glass, synthetic opals, or zeolites [104–108]. Even a 1D confinement can be realized by filling carbon nanotubes with Hg, which is achieved as a result of electrowetting [109]. Large interest in these nanostructured composites stems from the fact that fundamental questions of condensed matter physics related to finite-size effects can be addressed as well as applications in nanoelectronics and nano-fluidics are to be expected. Experiments on Hg in porous glasses and other nanoporous materials have shown that the crystal structure of bulk Hg ($\alpha$-Hg) is identical to that of confined Hg [104], whereas the melting/freezing temperatures are shifted toward lower temperatures and the transitions are broadened in comparison to bulk Hg [105,106]. These trends are enhanced with decreasing pore size [107]. These effects caused by the finite size are in analogy to the observed behavior in clusters where one also finds decreasing melting temperatures and line broadening with decreasing cluster size (see, e.g., Ref. [117]). Also the Knight shift and thus the electronic susceptibility was shown to decrease with decreasing pore size [108]. For the carbon nanotubes similar effects are predicted by a molecular dynamics simulations [110].

In this study, an ordering of the Hg atoms near the walls of the nanotubes and density oscillations, which extend several atomic diameters into the bulk, are suggested, even resulting in a close-packed cylindrical shell structure for the smallest nanotubes.

Metallic liquids exhibit a complex surface structure in which the atoms are stratified parallel to the liquid–vapor interface persisting into the bulk for a few atomic diameters and leading to density oscillations along the surface normal. This phenomenon of surface layering has been predicted theoretically [144], but could not be proven unambiguously in experiments [145] until experimental improvement due to access to third-generation x-ray sources finally allowed to resolve these oscillations, first in Hg [98,146] and Ga [147]. In Hg, the layering was found to have a spacing of 2.72 Å and a decay length of less than 5 Å. Surface layering seems to be a more universal property of liquid surfaces in general [148–152] but the reasons behind are not yet clearly identified; possibilities include surface tension, geometrical confinement effects due to the necessarily rapid decay of the density at the liquid–vapor interface [152] and a low ratio of melting and critical temperature $T_m/T_c$ [148–151].

Another interface of great interest due to its importance in electrochemical cells is the one between liquid Hg and water. This interface was studied by molecular dynamics simulations with pure water [111] as well as in the presence of alkali cations
(see Refs. [112,113] and references therein). In analogy with the just discussed surface layering at the liquid mercury–vapor interface, one finds comparable far-ranging density oscillations in the mercury phase as well as a change in the water density profile up to distances of about 10 Å. The mobility of the adsorbed water is equally restricted parallel and perpendicular to the interface. The bulk densities are, however, almost identical to the pure liquids [111]. When alkali cations are present, it was shown, that the ions are adsorbed within the first layer of mercury losing part of their hydration shell and becoming less mobile. Otherwise, the structure of the hydration shell as well as of the mercury surface are not much changed in its main features [112,113].

Yet another example for the importance of liquid mercury interfaces is the use of liquid Hg as a novel substrate for the deposition of Langmuir monolayers of organic molecules like alkylthiols, fatty acids, and alkanes [100,103]. Langmuir monolayers are studied as models of 2D matter and as a route to nanoelectronics and molecular electronics [153]. In contrast to the use of solid metals or of water as substrates, liquid mercury shows no steps or structural defects at the surface and the surface is atomically smooth due to the high surface tension and lack a long-range order of its own, but strong chemical bonds to the functional groups exist. Thus, new structures for the organic monolayers on liquid Hg have been found in synchrotron x-ray scattering experiments, especially until then unknown layers of surface-parallel molecules [101–103]. When the coverage is increased, one finds phase transitions to ordered phases of molecules with surface-normal orientation [101,103].

As already mentioned in the introduction, huge amounts of Hg are released into the atmosphere by combustion of fossil fuels. The removal of Hg in power plants is therefore an important issue. Since oxidized Hg can be removed quite efficiently, the search for oxidation catalysts is of great interest with the noble metals being regarded as hopeful candidates. Thus, a fundamental understanding of the adsorption of Hg to these metal surfaces is important. It was shown in experimental studies [154,155] as well as in theoretical studies [114,156] that Hg atoms adsorb quite strongly to the metal surfaces. In a recent DFT study [114], Steckel calculated binding energies for adsorption of mercury at Ag, Au, Cu, Ni, Pt, and Pd surfaces (on the 001 and the 111 face) for different amounts of coverage finding binding energies of up to about 1 eV per atom for Pt and Pd. The calculated values should provide a lower estimate to the actual values due to the used (GGA) density functionals, which is also confirmed by comparison with available experimental data (see Refs. [154,155] and references therein). The adsorbed Hg atoms are found in the fourfold or threefold follow positions of the 001 or 111 faces, respectively. This is in contrast to recent findings of Sarpe-Tudoran et al. [156] who found the bridge position as the most stable one.

### 3.5 Solid Mercury

Mercury freezes at \( T_m = -38.83^\circ C \) adopting a rhombohedral crystal structure with lattice constants of \( a = 3.005 \text{ Å} \) and an angle of \( \alpha = 70.53^\circ \) [1]. The lattice has three equal crystallographic axes inclined to each other at the angle \( \alpha \) (an angle of \( \alpha = 60^\circ \) corresponds to a face-centered cubic [fcc] lattice). Thus, Hg deviates from the hexagonal close-packed (hcp) structure found for the lighter group IIB metals zinc and cadmium. The unusual structure is another anomaly of Hg caused by relativistic effects. This was recently shown unambiguously by Gaston et al. [38]. Until recently, not only the lattice constants, but also the cohesive energy \( E_{coh} \) and the bulk modulus could be calculated with increasing accuracy of up to about 1.5% of the experimental data [36,38,73,157,158]. On exerting pressure, one finds a multitude of high-pressure phases for Hg. Besides the rhombohedral \( \alpha \)-Hg, a tetragonal \( \beta \)-phase, an orthorhombic \( \gamma \)-phase, and finally a hcp lattice structure for \( \delta \)-Hg have been discovered [159,160].

Already in the 1960s the general features of the density of states (DOS) and the band structure of Hg were known by experiment giving detailed information on the Fermi surface by measuring the de Haas–van Alphen effect [161] as well as by calculations [162,163]: At the Fermi energy \( E_F \), one finds a broad \( sp \) band (width about 10 eV), which mixes at its low-energy part with the narrow \( d \) band. This mixing is possible due to indirect relativistic effects. The strong relativistic contraction of the \( s \) bands [24,136,162,164] causes the interatomic Hg–Hg spacing in the solid [38], which in turn leads to an energy increase of the \( d \) bands. Just above \( E_F \), a structure-induced minimum in the DOS separates the \( sp \) band from empty states of predominantly \( p \) character. The band structure was also calculated by Deng et al., emphasizing the existence of flat and steep bands at the Fermi level, what they used as a possible explanation for the superconductivity of Hg observed below 4 K [165]: The pairing of electrons occurs in the flat bands, whose position relative to \( E_F \) is periodically changed by lattice distortions (phonons). When the top of the band lies above \( E_F \), the electron pairs are scattered into the steeper bands, whereas when the band maximum lies beyond \( E_F \), the bands are filled up out of the electron reservoir of the steep bands. At the critical temperature, the pairs become stable and a superconducting state results [165].

The rhombohedral lattice structure of \( \alpha \)-Hg in contrast to the hcp structures found for zinc and cadmium was studied intensely over the last decades. It was shown early on that the fcc structure is unstable with respect to a rhombohedral distortion and metastable with respect to a tetragonal distortion of the body-centered cubic (bcc) lattice [163], which was confirmed in later studies by Singh within a DFT framework including the energetically relatively high-lying \( d \)-electrons explicitly as valence electrons [24,164] and by Kresse and Hafner, who calculated the total energy of Hg as function of a rhombohedral or tetragonal distortion of an fcc or bcc lattice, respectively [32]. Nevertheless, theoretical predictions of the Hg structure that give accurate values for the lattice parameters or the cohesive energy remain a challenge. Whereas a pure mean-field (Hartree–Fock) treatment yields no binding at all [35,36], density functional approaches fail badly when attempting to optimize the lattice structure of Hg or getting sensible values for the cohesive energy. Depending on the underlying functionals, one gets anything from strong overbinding to severe underbinding.
An alternative approach was developed in the last years in the form of a wavefunction-based correlation treatment [36, 38, 157, 158] using the incremental scheme dating back to Stoll [166]. In this approach, the cohesive energy is split into the mean-field (Hartree–Fock) part, calculated for the infinite solid system, and the correlation energy \( E_{\text{corr}} \) computed with the following many-body expansion using the wavefunction-based coupled-cluster approach:

\[
E_{\text{corr}} = \sum_i \varepsilon_i + \sum_{i<j} \varepsilon_{ij} + \sum_{i<j<k} \varepsilon_{ijk} + \cdots
\]  

(3.2)

\( E_{\text{corr}} \) is expanded in one-body increments \( \varepsilon_i \), two-body increments \( \varepsilon_{ij} \), and so on and the sums extend over groups of localized orbitals. The energy increments are calculated for finite embedded clusters, which mimic the environment found in the solid. Details of this embedding are crucial and have been discussed in detail in Ref. [158]. While Hartree–Fock and the one-body increments of the correlation energy lead to no binding at all, the main contributions to the binding were shown to come from the two-body increments, half of that originating from core–valence correlation of the \( d \)-shell. Three-body increments are required and account for about 10% of the correlation energy [36, 38]. Very high accuracy could be achieved by that treatment yielding lattice constants of \( a = 2.96 \text{ Å} \) and \( \alpha = 69.5^\circ \), a cohesive energy of \( E_{\text{coh}} = -0.649 \text{ eV} \), and a bulk modulus \( B = 0.360 \text{ Mbar} \) [38], compared to the experimental values \( a = 3.005 \text{ Å} \), \( \alpha = 70.53^\circ \), \( E_{\text{coh}} = -0.67 \text{ eV} \) [1], and \( B = 0.382 \text{ Mbar} \) [164].

Solid mercury exists in at least four different phases if subjected to pressure. At ambient pressure, Hg is liquid at room temperature, showing a local structure of \( \alpha \)-Hg [139] with six hexagonally arranged atoms at 3.5 Å around a central atom and six atoms at 3.0 Å in an upper as well as lower plane three by three (See Figure 3.3). At \( T_{\text{m}} = 234 \text{ K} \), Hg solidifies in this rhombohedral \( \alpha \)-Hg structure and may exhibit a tetragonal phase at lower temperatures (below \( T = 77 \text{ K} \)), but only if this phase is formed at high pressures. This transition to the \( \beta \)-phase was already discovered very early by Bridgman [167] and a high potential barrier for the transformation from \( \alpha \) to \( \beta \)-Hg was made responsible for the fact that \( \alpha \)-Hg remains metastable at temperatures below 77 K [168]. Interestingly, also the \( \beta \)-phase becomes a superconductor at slightly lower temperatures, at \( T_c = 3.94 \text{ K} \) compared to 4.15 K for \( \alpha \)-Hg [169]. At room temperature, mercury becomes solid at a pressure of \( p = 12 \text{ kbar} \) crystallizing in the \( \alpha \)-form. Further increase of the pressure leads to the body-centered tetragonal \( \beta \)-phase at \( p = 37 \text{ kbar} \), the orthorhombic \( \gamma \)-phase at \( p = 120 \text{ kbar} \) [170], and finally, at 370 kbar, Hg transforms into a hcp structure named \( \delta \)-Hg [159, 160]. In contrast to this observed polymorphism, Zn and Cd stay in the hcp structure over the whole pressure range [159].

### 3.6 Conclusions

The electronic configuration of Hg is \([\text{Xe}] 4f^{14}5d^{10}6s^2\) with closed \( 5d \) and \( 6s \) shells. Due to large relativistic \( 6s \) contraction, the energy of the \( 6s \) orbitals/bands is lowered significantly leading to large changes in almost all properties observed, from the Hg atom over the clusters to the liquid or solid bulk phase. This sets Hg apart from its lighter homologues zinc and cadmium, with mercury behaving sometimes more like a rare gas. This causes anomalies in almost all atomic properties, like the small electric dipole polarizability or the high ionization potential, in the weak van der Waals binding of the Hg dimer, over to the complicated binding behavior in the clusters, to finally the rhombohedral crystal structure of the solid and low melting and gas–liquid critical temperatures. The unusual high superconducting transition temperature, which led Kamerlingh Onnes to the discovery of this phenomenon, is, most likely, also a manifestation of relativistic effects. The theoretical description of the interaction between Hg atoms is complicated by the necessity of a proper relativistic treatment, and by the need to explicitly consider the \( 5d \) electrons as valence electrons, as the corresponding orbitals/bands are energetically elevated by indirect relativistic effects mixing into the \( 6s \) orbitals/bands. Furthermore, the many-body decomposition of the interaction potential between Hg atoms is not converging smoothly, i.e., a simple treatment in terms of two-body and perhaps three-body potential terms is not adequate in contrast to the rare gas elements.

Nevertheless, progress was made in the last years, giving detailed explanations for the \( M \)–\( NM \) transition in liquid Hg, and allowing the calculation of lattice parameters and the cohesion energy of solid Hg with high accuracy. Still, a number of fundamental problems remain unsolved, the most prominent are certainly the questions, why Hg is liquid at room temperature, or what causes the high superconducting transition temperature of 4 K.

Beside these fundamental questions, experimental as well as theoretical progress has opened up new exciting fields of research with possible application in different areas of nanoscience. Examples are the use of liquid mercury as a novel substrate for Langmuir monolayers of organic molecules and the investigations of liquid/solid Hg embedded in porous nano-matrices or carbon nanotubes. These fields are still at their initial stages and need a detailed understanding of the fundamental properties of Hg from the dimer over the clusters to the bulk.

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