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A quantum statistical treatment of the metal–non-metal and liquid–vapour transitions in mercury

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Abstract. A quantum statistical approach for a charged particle system is used to give a unified treatment of the metal–non-metal and liquid–vapour transitions in mercury. The equation of state, which can be derived using the Green function method, is interpreted in terms of free charged particles and bound states, the energies of which are shifted due to the interaction with the medium. The numerical results suggest that the degree of ionization noticeably influences the liquid–vapour phase transition in mercury. Theoretical results for the liquid–vapour coexistence curve and the density dependence of the ionization energy are compared with experimental data.

Mercury has the lowest known critical temperature (1751 K) of any fluid metal. It is therefore not surprising that it has proven to be the most extensively investigated substance for the study of the interrelations of the metal–non-metal transition and the liquid–vapour phase transition [1, 2]. Precise measurements of the electrical [3], optical [4], and thermophysical [5] properties including the exact location of the critical point ($T_c = 1751$ K, $p_c = 1673$ bar, and $\rho_c = 5.8$ g cm⁻³) are available for fluid mercury over the whole liquid–vapour coexistence range. The data clearly demonstrate that radical changes in the electronic states occur from phase to phase. For example, far below the critical point, the liquid phase is highly conducting but the coexisting vapour phase is not. Nearer to the liquid–vapour critical point, where the distinctions between the coexisting phases vanish, electrical conductivity, thermoelectric, Knight shift [6], and optical data of mercury show that non-metallic behaviour is present in both phases. The metal–non-metal transition appears to occur at a density higher than that of the critical point and is generally located at 9 g cm⁻³.

The existence of the electronic transition makes the problem of describing the liquid–vapour transitions theoretically more difficult for mercury than for simple non-metallic fluids such as argon. Generally, it can be said that the two limiting cases of the dense liquid metal and the low-density vapour phase are reasonably well understood. However, the connection between these limits through the critical region of the phase diagram has been described only with highly simplified models [7, 8]. A complete and satisfactory solution of the problem requires the simultaneous calculation of the electronic structure and the phase behaviour over wide ranges of pressure and temperature starting from realistic atomic properties of mercury. A unified treatment has to include both limiting cases, van der Waals and metallic bonding, and their interplay as a function of density.

There have been some attempts at a unified treatment of the electronic and thermodynamic phase transition in alkali metals [9, 10], which are based upon a quantum statistical approach. Simple models such as an ideal mixture of quantum gases or a fermion liquid of quasiparticles are not sufficient to describe strongly correlated systems where effects such as the Mott transition from localized, bound electrons to itinerant, free electrons are of importance. A more fundamental approach has been given within a quantum statistical approach to charged particle systems [11]. Physical properties are related to thermodynamic Green functions, which are treated by perturbation theory. A representation by Feynman diagrams can be used to identify different many-particle effects within the perturbative series expansion.

We will treat here the equation of state $n = n(T, \mu)$ which relates the particle density n to the temperature T and the chemical potential μ . As a thermodynamic potential, the pressure $p(T, \mu) = \int_0^\mu d\mu' n(T, \mu')$ and further thermodynamic quantities can be derived from that equation of state. Furthermore, stability against phase separation requires $(\partial\mu/\partial n)_T \geq 0$. If this stability condition is violated, a Maxwell construction can be used to determine the phase transition region.

On the other hand, we have

$$n(T, \mu) = \frac{1}{\Omega} \sum_p \int \frac{d\omega}{\pi} f(\omega) \text{Im} G(p, \omega - i0) \quad (1)$$

where Ω denotes the volume of the system and p stands for the momentum and possible internal quantum numbers of the single-particle states (spin). $f(\omega)$ is the (fermionic or bosonic) distribution function containing the temperature and the respective chemical potential. The single-particle Green function G is related to the self-energy $\Sigma(p, \omega)$ for which a cluster decomposition [11] can be given. In this way, the density n is split into contributions of single-particle states, bound states, and scattering states. Compared with the isolated few-body system, the single-particle and bound state properties are modified due to the interaction with the medium. In particular, the quasiparticle energies and bound state energies are shifted.

This Green function approach has been applied [11] to strongly coupled Coulomb systems such as hydrogen, the alkali elements, and the rare gases, but also to the electron-hole plasma in excited semiconductors. A systematic treatment has been developed, which is able to describe the low-density case, where we have a non-metallic gas or a partially ionized plasma, as well as the high-density case, where we have a degenerate liquid of quasiparticles. Extended work has been done to investigate the degree of ionization, possible plasma phase transitions, and optical and transport properties in these materials. In particular, highly sophisticated approximations have been used to find the critical data of Cs and other alkali vapours [9], which are in reasonable agreement with experimental values. A simpler approach to the phase transitions in the alkali fluids has been given recently [10], dropping the modifications of the single-particle and bound state energies due to the interaction with the medium.

Our microscopic approach starts from a charge neutral system consisting of electrons, density $2n$, and mercury ions Hg^{2+} , density n . Potentials are assumed between these constituents, which, in principle, can be deduced from a more elementary description of the system. The evaluation of the Green function for the electrons and the Hg^{2+} ions, respectively, has been performed by standard methods using a diagram representation [9, 11]. A cluster decomposition for the self-energy $\Sigma(p, \omega)$ allows us to account for the formation of bound states such as neutral Hg atoms and Hg^+ ions. As already mentioned above, the

total density can be decomposed into a contribution of free particles and the contributions of bound and scattering states. The contribution of scattering states is partially taken into account by introducing the quasiparticle picture; further contributions are neglected here. With respect to the variety of bound states, we restrict ourselves to the ground states of Hg^+ and atomic Hg, neglecting excited states or further possible constituents such as Hg^- , Hg_2 , or Hg_2^+ . The Green function approach allows to introduce formally new chemical potentials μ^α , $\{\alpha\} = \{2+, +, 0, e\}$, corresponding to the different components in the system, $\{\text{Hg}^{2+}, \text{Hg}^+, \text{Hg}, e^-\}$ (chemical picture). The relation

$$\mu^0 = \mu^+ + \mu^e = \mu^{2+} + 2\mu^e = \mu \tag{2}$$

expresses the chemical equilibrium of the respective chemical reactions, $\text{Hg} \rightleftharpoons \text{Hg}^+ + e^-$, and $\text{Hg}^+ \rightleftharpoons \text{Hg}^{2+} + e^-$. Now, the total density is decomposed into the partial densities n^α of the respective constituents in this chemical picture $n = n^0 + n^+ + n^{2+}$, $2n = n^e + n^+ + 2n^0$, where

$$n^\alpha = \frac{1}{\Omega} \sum_p f[E^\alpha(p) - \mu^\alpha] \tag{3}$$

contains the in-medium energies $E^\alpha(p)$.

For further evaluation, it is useful to introduce an ‘ideal’ part μ_{id}^α of the chemical potential according to the relations

$$n^0 = \frac{1}{\Lambda_0^3} e^{\beta(\mu_{\text{id}}^0 - E_0^0)} \quad n^+ = \frac{2}{\Lambda_0^3} e^{\beta(\mu_{\text{id}}^+ - E_0^+)} \quad n^{2+} = \frac{1}{\Lambda_0^3} e^{\beta\mu_{\text{id}}^{2+}} \quad n^e = \frac{2}{\Lambda_e^3} F_{1/2}[\beta\mu_{\text{id}}^e] \tag{4}$$

where $E_0^+ = -18.8$ eV and $E_0^0 = -29.2$ eV are the energies to bind one (Hg^+ , E_0^+) or two electrons (Hg , E_0^0) to the ion Hg^{2+} , respectively. $\Lambda_\alpha^2 = 2\pi\hbar^2/(m_\alpha k_B T)$ is the thermal wavelength, and $F_{1/2}$ denotes the Fermi integral; spin multiplicities are given explicitly.

Comparing (4) with (3), the excess parts

$$\Delta\mu^\alpha = \mu^\alpha - \mu_{\text{id}}^\alpha \tag{5}$$

are determined by the in-medium shifts of the energies $E^\alpha(p)$. Before specifying $\Delta\mu^\alpha$ as a function of the partial densities n^α due to the interactions with the various constituents, we give the solution of the equation of state $n(T, \mu)$.

We introduce effective binding energies which are density and temperature dependent according to $\Delta\mu^\alpha$:

$$E^+ = E_0^+ + \Delta\mu^+ - \Delta\mu^{2+} - \Delta\mu^e \quad E^0 = E_0^0 + \Delta\mu^0 - \Delta\mu^{2+} - 2\Delta\mu^e. \tag{6}$$

Utilizing the condition of chemical equilibrium (2) and eliminating the ideal parts of the chemical potentials, the partial densities are given by

$$n^{2+} = \frac{n^e}{2} \left(1 + e^{\beta(\mu_{\text{id}}^e - E^+)} \right)^{-1} \quad n^0 = n^{2+} e^{\beta(2\mu_{\text{id}}^e - E^0)}. \tag{7}$$

From the condition of charge neutrality follows the relation $n^+ = n^e - 2n^{2+}$. In this way, the partial densities n^{2+} , n^+ , n^0 are given in terms of μ_{id}^e or, solving the Fermi integral in

(4), by n^e . The equation of state is then obtained in parametric form according to $n(n^e, T)$ and, furthermore, we have

$$\mu(n^e, T) = k_B T \ln(n^{2+} \Lambda_0^3) + \Delta\mu^{2+} + 2\mu_{id}^e + 2\Delta\mu^e. \quad (8)$$

From the effective binding energies E^+ , E^0 (6) the ionization energies $I^+ = E^+ - E^0$ and $I^{2+} = E^{2+} - E^0$ (with $E^{2+} = \Delta\mu^{2+}$) are obtained, which are necessary to separate one or two electrons, respectively, from neutral Hg atoms. Due to the interaction parts of the chemical potentials $\Delta\mu^\alpha$, these ionization energies are functions of the density and temperature of the system. We will discuss these effective ionization energies in relation to the metal–non-metal transition.

With increasing density, the binding energies E^0 and E^+ go to zero. As a result, the corresponding bound states vanish—they are dissolved in the continuum of scattering states (Mott effect). The corresponding partial density no longer contributes to the total density above the Mott density. However, the physical properties change smoothly at the Mott density as proven by the Levinson theorem [12]. The jump in the bound state contribution is compensated by a corresponding jump in that of the scattering states [13, 14]. These discontinuities are avoided using the Planck–Larkin partition function [11]

$$n^\alpha \sim \Theta(I^\alpha) (e^{-\beta I^\alpha} - 1 + \beta I^\alpha) \quad (9)$$

where $\Theta(x)$ is the step function.

The main problem is the determination of the interaction parts to the chemical potentials as given by the partial densities in the medium

$$\Delta\mu^\alpha = \sum_\beta \Delta\mu^{\alpha\beta} \quad (10)$$

where $\Delta\mu^{\alpha\beta}$ denotes the contribution of the species β to the shift of species α . These interaction parts are derived in general form from microscopic treatments of the interparticle forces. A systematic quantum statistical approach can be given using the technique of Green functions [11, 15]. We give here only final expressions relevant for the system under consideration.

For the long-range Coulomb interactions between charged particles, we utilize convenient interpolation formulae [16]. These Padé formulae are derived on the basis of higher-order approximations for the free energy of systems of point charges in the low-density limit, for the degenerate electron gas, and the strongly coupled ion system. To describe mercury ions with various degrees of ionization, we have used the generalizations according to [17].

It is well known that the long-range Coulomb interaction leads to a plasma phase transition from a phase of low degree of ionization to a phase of high ionization (Mott transition). However, in order to obtain relevant results for mercury, we have to take into account short-range interactions, which are of special importance for ions and neutrals. In principle, these short-range interactions can be derived from an analysis of the cluster expansion of the self-energy [15]. We will use here a semi-empirical approach to these short-range terms.

The van der Waals interaction between neutrals ($\Delta\mu^{00}$) has been derived from the experimental second virial coefficient using a Lennard-Jones potential. Comparing with measurements in the low-density region [5], a parameter set $\varepsilon = 0.00652$, $\sigma = 5.07$ has been used [18] (we use Rydberg units in what follows, i.e. energies are given in Rydbergs,

1 Ryd = 13.6 eV, and distances in units of the Bohr radius, $a_B = 0.5291 \times 10^{-10}$ m). The hard-core contributions to the chemical potentials were treated by a Carnahan–Starling formula [19]

$$\mu_{CS} = k_B T \eta \frac{8 - 9\eta + 3\eta^2}{(1 - \eta)^3} \quad \eta^{\alpha\beta} = \frac{\pi}{6} n^\beta d_{\alpha\beta}^3. \quad (11)$$

For the hard-core diameters we have adopted the values $d_0 = 5.1$ in correspondence with the Lennard-Jones parameters, $d_+ = 4.5$ according to the reduction of the atomic wave functions in Hg^+ , and $d_{2+} = 2.04$ from the measured compressibility in the liquid state; $d_{\alpha\beta} = (d_\alpha + d_\beta)/2$. We mention that the results given below are not very sensitive with respect to the parameters d_+ , d_{2+} because of the low concentration of the respective species.

The electron–ion interaction is modified at short distances by the repulsion due to the Pauli principle with respect to the bound electrons. We have taken into account this contribution by the Wigner–Seitz method of an excluded volume, also determined by the hard-core radius.

The treatment of the interaction between charged particles and neutrals is very important. A screened polarization potential has been used, leading to a virial coefficient [15]

$$\Delta\mu_{PP}^{e0} = 4\pi\alpha n^0 \int_0^\infty r^2 \frac{(1 + \kappa r)^2}{(r^2 + r_0^2)^2} e^{-2\kappa r} dr. \quad (12)$$

The cut-off parameter $r_0 = 1.4$ was chosen in accordance with [20]. The screening length is given by

$$\kappa^2 = 2n \frac{e^2}{\varepsilon\varepsilon_0 k_B T} \quad \varepsilon\varepsilon_0 = (1 + 4\pi\alpha n^0)\varepsilon_0 \quad (13)$$

where ε is the dielectric function, and $\alpha = 34.4$ is the polarizability of a mercury atom. Using these contributions to $\Delta\mu^\alpha$, see also [17], we have found self-consistent solutions for the partial densities. The results for the relevant quantities are shown in figures 1–3.

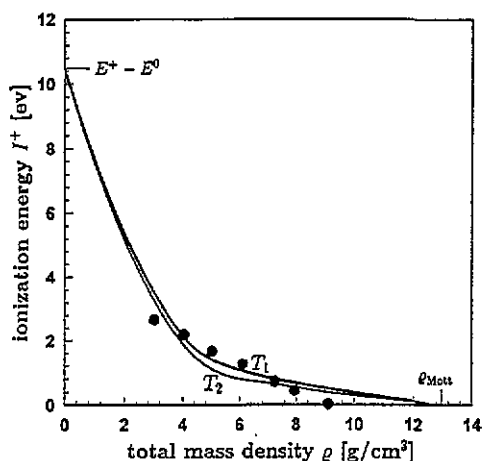


Figure 1. Ionization energies of mercury as a function of the mass density at temperatures $T_1 = 1260$ K, $T_2 = 1750$ K. Experimental data (solid circles) from [4].

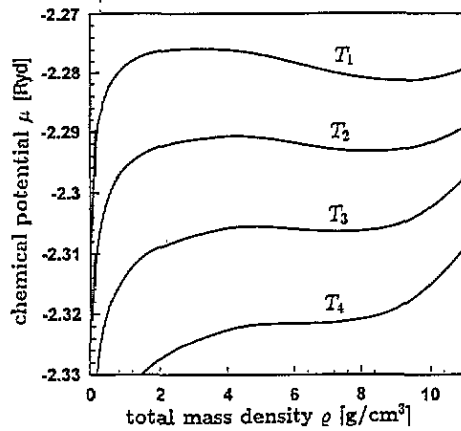


Figure 2. Isotherms of the chemical potential of mercury as a function of the mass density. The region of instability $(\partial\mu/\partial n)_T < 0$ has to be replaced by a Maxwell construction. Temperatures: $T_1 = 1260$ K; $T_2 = 1420$ K; $T_3 = 1580$ K; $T_4 = 1740$ K.

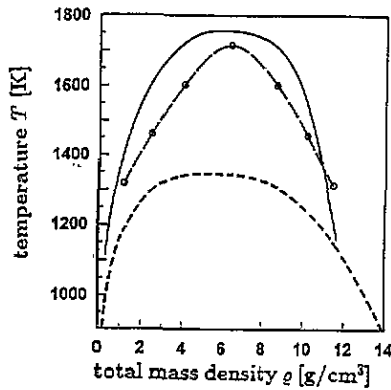


Figure 3. The coexistence curve of mercury. A comparison of the present results (long-dashed line) with the experimental coexistence curve [3] (solid line), and the coexistence curve of a pure atomic reference system without ionization (Lennard-Jones system, short-dashed line).

In figure 1, the ionization energy $I^+(n, T)$ is shown for different temperatures as a function of the total density n . Starting with the atomic ionization energy of 10.44 eV in the low-density limit, it decreases with density due to the polarizability of the medium as described by the polarization potential. Passing through zero indicates the Mott density $n_{\text{Mott}}(T)$ where the bound state disappears, and a transition to the doubly ionized state occurs. We have neglected the two excited states of neutral Hg at energies that are hardly populated at the relatively low temperatures considered here.

The density dependence of the calculated ionization energies can be contrasted with the experimental behaviour of the optical properties of fluid mercury [4, 21, 22]. Dense liquid mercury has a behaviour close to a metal showing Drude-like optical conductivity $\sigma(\omega)$ deriving from the free electrons. This gradually changes with density until by 9 g cm^{-3} $\sigma(\omega)$ is characteristic of materials with energy gaps. At even lower densities, down to about 3 g cm^{-3} in the vapour, optical absorption edges are observed from which effective

optical gaps (solid points in figure 1) can be determined. For still lower densities this is no longer possible because here the experimentally observed absorption edge is dominated by transitions to the broadened singlet and triplet states of the neutral mercury atom [23, 24]. The latter hampers the observation of the transitions to the continuum states. It should be emphasized here that the location of the Mott density as obtained from our Green function calculation, see figure 1, is sensitive with respect to the screening in the medium, and a more detailed treatment of dynamical screening may give a variation of the Mott density.

The composition of mercury is mainly determined by the lowering of the ionization energy discussed above. Up to the Mott density, the composition is governed by the contribution of neutral atoms. The contribution of the singly charged mercury ions is small, and the partial density of Hg^{2+} is negligible. Therefore, mercury vapour can be considered as a non-metallic dielectric system up to the Mott density. The reason for this behaviour is found from the ionization energy the value of which is large compared with the temperature. Above the Mott density, mercury becomes fully ionized.

Figure 2 shows the equation of state $n(\beta, \mu)$ for different temperatures as a function of density. The instability region $(\partial\mu/\partial n)_T < 0$ should be replaced by a Maxwell construction. It can be shown that the lowering of the ionization energy with increasing density destabilizes the system such that the liquid–vapour phase transition, which is already present in the atomic system, is shifted to higher temperatures. Considering different isotherms, the critical parameters $T_c = 1740$ K and $\rho_c = 6.2$ g cm⁻³ are found, which are in good agreement with the experimental values.

The coexistence curve is obtained from the Maxwell construction and shown in figure 3. The theoretical values are in reasonable agreement with the experimental results. However, the Mott density occurs at higher densities compared with the experimental data. This may be the reason for the deviations of the theoretical coexistence curve from the experimental one which are still to be seen. To demonstrate the importance of the ionization equilibrium to the form of the coexistence curve of mercury, we compare also with that of pure atomic mercury (Lennard-Jones system) without the possibility of ionization (short-dashed line). Agreement with the experimental values can only be stated in the limit of the dilute vapour where mercury is atomic. The deviations already become much more pronounced above 1 g cm⁻³ and, especially, the critical temperature is too low (~ 1330 K). Thus, the effect of the ionization equilibrium is a considerable increase of the critical temperature up to experimental values.

It should be pointed out that we have tried to give a first quantum statistical approach to mercury vapour near the phase transition region. We are interested in relevant interaction effects that govern the composition and the thermodynamic properties of this strongly coupled system. Of course, a microscopic approach to the short-range interaction terms is possible, avoiding the input of atomic parameters as used here. A more fundamental approach should start with the atomic orbitals of mercury for the derivation of those parameters. Such a general approach was derived in [25] for hydrogen and helium.

Furthermore, it is obvious that a detailed comparison between theory and experiment requires an extensive investigation of further many-particle effects in dense mercury vapour such as, for instance, dynamical screening, Pauli blocking, and wave function overlap, and the account of the contributions of scattering states.

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References

- [1] Hensel F 1990 *J. Phys.: Condens. Matter* **2** 33
- [2] Hensel F and Uchtmann H 1989 *Ann. Rev. Phys. Chem.* **40** 61
- [3] Götzlaff W, Schönherr G and Hensel F 1988 *Z. Phys. Chem., NF* **156** 219
- [4] Uchtmann H, Brusius U, Yao M and Hensel F 1988 *Z. Phys. Chem., NF* **156** 151
- [5] Götzlaff W 1989 *Doctoral Thesis* Philipps-Universität Marburg
- [6] Warren W W and Hensel F 1982 *Phys. Rev. B* **26** 5980
- [7] Alekseev V A and Iakubov I T 1983 *Phys. Rep.* **96** 1
- [8] Hernandez J P 1985 *Phys. Rev. A* **31** 932
- [9] Redmer R and Röpke G 1989 *Plasma Phys.* **29** 343
- [10] Chacón E, Hernandez J P and Tarazona P 1993 *J. Phys.: Condens. Matter* **5** 1753
- [11] Kraeft W-D, Kremp D, Ebeling W and Röpke G 1986 *Quantum Statistics of Charged Particle Systems* (Berlin: Akademie)
- [12] Bollé D 1979 *Ann. Phys., NY* **121** 131
- [13] Zimmermann R and Stolz H 1985 *Phys. Status Solidi b* **131** 151
- [14] Rogers F J 1986 *Astrophys. J.* **310** 723
- [15] Redmer R, Röpke G and Zimmermann R 1987 *J. Phys. B: At. Mol. Phys.* **20** 4069
- [16] Ebeling W, Förster A, Richert W and Hess H 1988 *Physica A* **150** 159
- [17] Förster A 1991 *Doctoral Thesis* Humboldt Universität zu Berlin
- [18] Röpke G, Nagel S and Redmer R *Z. Phys. Chem., NF* submitted
- [19] Carnahan N F and Starling K E 1969 *J. Chem. Phys.* **51** 632
- [20] Goldberger M L and Watson K M 1965 *Collision Theory* (New York: Wiley) p 853
- [21] Ikezi H, Schwarzenegger K, Somins A L, Passner A L and McCall S L 1978 *Phys. Rev. B* **18** 2494
- [22] Hefner W, Schmutzler R W and Hensel F 1980 *J. Physique Coll.* **41** C862
- [23] Bhatt R N and Rice T M 1979 *Phys. Rev. B* **20** 466
- [24] Uchtmann H, Popielawski J and Hensel F 1981 *Ber. Bunsenges. Phys. Chem.* **85** 555
- [25] Nagel S, Stein H, Leike I, Redmer R and Röpke G 1992 *J. Phys. B: At. Mol. Opt. Phys.* **25** 613