Equation of state for expanded fluid mercury: Variational theory with many-body interaction

Hikaru Kitamura
Department of Physics, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

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A variational associating fluid theory is proposed to describe equations of state for expanded fluid mercury. The theory is based on the soft-sphere variational theory, incorporating an ab initio diatomic potential and an attractive many-body potential; the latter is evaluated with quantum chemical methods and expressed as a function of the local atomic coordination number and the nearest-neighbor distance. The resultant equation of state can reproduce the observed gas-liquid coexistence curve with good accuracy, without introducing phenomenological effective pair potentials. Various thermodynamic quantities such as pressure, isochoric thermal pressure coefficient, adiabatic sound velocity, and specific heat are calculated over a wide density-temperature range and compared with available experimental data. © 2007 American Institute of Physics. [DOI: 10.1063/1.2712443]

I. INTRODUCTION

Expanded fluid metals undergo liquid-gas and metal-nonmetal (M-NM) transitions at high temperatures and high pressures.1 Mercury, whose gas-liquid critical temperature is the lowest (Tc=1751 K) among all the fluid metals, has so far been most intensively studied; a number of experimental data on thermodynamic, structural, transport, and optical properties are currently available over a wide range of densities and temperatures.1–4

Despite of the progress in experimental studies, theoretical models for the equation of state and gas-liquid coexistence curve of mercury have not been established yet, due mainly to the difficulty in describing phase transitions accompanying a drastic change in chemical bonding; the low-density gas phase is dominated by weak van der Waals forces between 6s2 closed-shell atoms, whereas the dense liquid phase is characterized by strong metal congestion with overlapping 6s-6p bands. At elevated temperatures near Tc, M-NM transition occurs within the liquid phase at around 9 g/cm3, which was detected through measurements of the optical excitation gap and the Knight shift.1,4

The interplay between the atomic density fluctuation and change in local electronic states brings about interatomic many-body interaction, which is attractive and plays a crucial role in the phase transition.5 A cooperative attractive interaction would enhance the possibility of temporary cluster formation, i.e., association effect,6 which significantly affects the optical absorption spectra in dense mercury vapor.3,7 In principle, atomic motions in the presence of many-body interaction could be simulated with the molecular dynamics method combined with the density-functional electronic-structure calculations,8 but the construction of phase diagrams and extensive equation-of-state data for fluid mercury has not yet been accomplished through such simulations.

On the other hand, the accurate determination of interatomic interactions in diatomic molecules and small clusters has been achieved, owing to recent progress in ab initio quantum-chemical methods9,10 and spectroscopic studies.11 It has been revealed that the repulsive part of the potential energy curve of Hg2 in the ground state is unusually soft as compared to other rare-gas atoms.11 The origin of the soft repulsion has been ascribed to the admixture of 6s and 6p states at short ranges, which also contributes to the increment of binding energies in clusters.12 The outcome of those quantum-chemical analyses would provide a basis for the construction of a theory which facilitates first-principles predictions of fluid phase diagrams.

In this paper, we propose a new equation of state for the expanded fluid mercury which we refer to as the variational associating fluid theory. The theory can treat microscopic interatomic interactions, mesoscopic clustering (association) effect, and macroscopic phase transitions in a coherent fashion, making it possible to predict various thermodynamic quantities without introducing phenomenological state-dependent potentials. The development of such first-principles theory would be indispensable for estimating phase diagrams of other liquid metals whose critical points are not easily accessible through experiments.

In Sec. II, we construct interatomic many-body potentials through quantum-chemical calculations. Free energies are then formulated in Sec. III on the basis of the soft-sphere variational theory. Numerical results on the gas-liquid coexistence curves and various thermodynamic quantities are presented and compared with experimental data in Sec. IV. Concluding remarks and future issues are given in Sec. V.

II. MANY-BODY POTENTIAL

We consider a system composed of N mercury atoms with positional vectors {ri} (i=1, ..., N). The total potential energy function \( V(r_1, ..., r_N) \) can generally be decomposed
into a pairwise summation of suitably chosen binary potentials and the remaining many-body contribution, that is,

$$V(r_1,\ldots,r_N) = \frac{1}{2} \sum_{i,j=1}^{N} V_{\text{dimer}}(|r_i - r_j|) + V_{\text{mb}}(r_1,\ldots,r_N).$$  \( (1) \)

Specifically, we take \( V_{\text{dimer}}(r) \) as a diatomic potential energy curve of Hg\(_2\) in the ground state correlating to Hg(6\(^1\)S) + Hg(6\(^1\)S) asymptote.\(^9\) We adopt the analytic formula by Schwertfeger et al.\(^9\) based on spin-orbit corrected scalar relativistic coupled cluster calculations using large uncontracted (11s10p9d4f/3g2h) basis set (cc-ULB+SO scheme), which reads

$$V_{\text{dimer}}(r) = \lambda_E \sum_{j=1}^{9} \frac{a_{2j}}{\alpha_{B}(\lambda_r)^{2j}},$$  \( (2) \)

with \( \lambda_E = 1.11, \lambda_r = 1.0143, a_0 = -1.123 860 \times 10^5, a_6 = -1.095 406 \times 10^5, a_{10} = 1.138 508 \times 10^7, a_{12} = -4.533 23 \times 10^8, a_{14} = 9.225 373 \times 10^7, a_{15} = -9.403 784 \times 10^{10}, \) and \( a_{18} = 3.801 021 \times 10^{11}. \) This potential takes on a minimum value of \( V_{\text{dimer}}(r) = -0.043 \text{ eV at } r = 7.06a_B, \) with \( a_B \) denoting the Bohr radius.

The basic idea of this work is to evaluate the many-body potential \( V_{\text{mb}}(r_1,\ldots,r_N) \) explicitly for particular geometries of clusters and crystalline solids, and to express \( V_{\text{mb}}(r_1,\ldots,r_N)/N \) as a function of \( z \) (mean coordination number) and \( r_{\text{mn}} \) (nearest-neighbor distance); these are the two relevant parameters controlling the M-NM transition.\(^13\) For this purpose, we have carried out spin-orbit diatomics-in-molecules (DIM) calculations\(^12\) to evaluate \( V_{\text{mb}}(z,r_{\text{mn}})/N \) for small Hg\(_m\) clusters with the geometries illustrated in Fig. 1: Hg\(_3\) (D\(_{3h}\)), Hg\(_4\) (T\(_d\)), Hg\(_5\) (D\(_{3h}\)), and Hg\(_7\) (D\(_{5h}\)). These geometries may be characterized by \( z = 2, 3, 3.60, \) and 4.29, respectively. We have also assumed motionless so that the distance \( r_{\text{mn}} \) of all the nearest-neighbor bonds within a cluster has been changed simultaneously. Numerical calculations have thereby been performed in the range of \( 5.3 \leq r_{\text{mn}}/a_B \leq 6.5. \) In this range, mercury clusters remain nonmetallic, with a finite energy gap between the ground and first-excited energy levels.\(^12\)

We have likewise evaluated \( V_{\text{mb}}(z,r_{\text{mn}})/N \) for face-centered cubic (fcc) \( (z=12) \) and body-centered cubic (bcc) \( (z=8) \) structures of bulk solid. These crystalline structures are considered to be metallic, judging from the overlap of \( 6s \) and \( 6p \) bands in the density of states calculated by Matthiess and Warren Jr.\(^14\) We thus regard the system as a mixture of ions with net charge number \( Z = 2 \) and conduction electrons with number density \( n_e = Zn. \) The accurate evaluation of the cohesive energies for solid mercury requires careful treatment of the relativistic effect,\(^15\) electrons in the \( 5d \) band.\(^15\)

![FIG. 1. Cluster geometries adopted in the DIM calculations.](image1)

and electron correlation.\(^16\) Simple nearly free electron treatment with local pseudopotentials is not applicable to liquid mercury, but Chekmarev et al.\(^17\) showed that addition of empirical corrections leads to considerable improvement of the theory so that reliable predictions of liquid structures and cohesive energies can be achieved at the ambient condition. By following their approach, the cohesive energy per atom may be expressed in a following form:

$$V = \frac{3}{N} \sum_{i=1}^{N} \Phi_{\text{eff}}(s_i,r_{\text{mn}}) + U_{\text{mon}}(n).$$  \( (3) \)

where \( \Phi_{\text{eff}}(r) \) describes the density-dependent effective pair potential between ions and \( U_{\text{mon}}(n) \) is the energy independent of the ionic structure. Expressions for \( \Phi_{\text{eff}}(r) \) and \( U_{\text{mon}}(n) \) are presented in the Appendix. The summation in Eq. (3) describes the interaction of a reference ion with surrounding \( N_i \) ions in the \( i \)th nearest-neighbor shell located at a distance \( s_i r_{\text{mn}} \) away from the reference ion. The parameter values for fcc lattice \( (z=12) \) are \( s_1 = 1, s_2 = \sqrt{2}, N_1 = 12, N_2 = 6, \) and \( n = \sqrt{2} r_{\text{mn}} \) for bcc lattice \( (z=8) \) are \( s_1 = 1, s_2 = 2/\sqrt{3}, N_1 = 8, N_2 = 6, \) and \( n = 3/\sqrt{4} r_{\text{mn}} \). The summation has been truncated at \( i = 2, \) and the contributions from more distant neighbors \( (i > 3) \) have safely been neglected. By subtracting the diatomic contribution from Eq. (3), we obtain

$$\frac{V_{\text{mb}}(z,r_{\text{mn}})}{N} = \frac{V}{N} - \frac{1}{N} \sum_{i=1}^{N} V_{\text{dimer}}(s_i r_{\text{mn}}).$$  \( (4) \)

Numerical values of \( V_{\text{mb}}(z,r_{\text{mn}})/N \) so computed are displayed in Fig. 2. We find that the many-body interaction is attractive \( (V_{\text{mb}} < 0) \) and its magnitude increases as \( r_{\text{mn}} \) decreases and/or \( z \) increases. The microscopic origin of the interaction is attributed to the admixture of excited 6p state onto the ground 6s state in the electronic wave functions when many atoms aggregate instantaneously.\(^12\) We observe that the magnitude of \( V_{\text{mb}}(z,r_{\text{mn}})/N \) is remarkably large in the metallic regime \( z > 8, \) which means that the short-range repulsive core of the effective interatomic potential in the metallic state is considerably smaller than that in the isolated dimer or small nonmetallic clusters. Such distinctly different behavior of the cohesive energies in the metallic and nonme-

![FIG. 2. Many-body potential per atom for various values of \( r_{\text{mn}}. \) The dots represent the computed data; the solid curves indicate their linear interpolations.](image2)
The ac-
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reference system to mimic the interatomic correlation in fluid
sphere or soft-sphere fluid would serve as an appropriate

theory, where correlation functions for the soft-sphere fluid
are replaced by those for the hard-sphere fluid, and the soft-
crossover from nonmetallic to metallic branch in the range
N≈15–100, which may correspond to z=7–9 if the cluster
geometry is icosahedral and z=5–8 if it is tetrahedral.19 We
have no convincing theoretical data for V_{mb}(z, r_{mn})/N in the
intermediate-z range where M-NM transition occurs. In this
work, we have linearly interpolated the data at z=4.29 and
z=8 as shown by the solid curves in Fig. 2. Though this is a
crude treatment of the M-NM transition, we shall see later
that the overall feature of the resultant gas-liquid coexistence
curve is consistent with experimental observations. The
accurate determination of V_{mb}(z, r_{mn})/N for the entire range of z
is deferred to a future study. For each z (z=1,2,12), we have
thus expressed V_{mb}(z, r_{mn})/N as a smooth function of
r_{mn}, as exhibited in Fig. 3.

III. EQUATION OF STATE

In this section, we formulate the equation of state for fluid mercury by extending the conventional fluid variational
theory of simple fluids20,21 to the cases of nonsimple fluids.5 In
so doing, the attractive many-body potentials shown in
Fig. 3 are taken into consideration. Unlike typical associating
fluids such as water,22 the directional dependence of intermolecular interactions may play a minor role in the case of fluid
mercury, because both the van der Waals interactions in the
gas phase and metallic bonding in the liquid phase are essen-
tially isotropic. Accordingly, we expect that either a hard-
sphere or soft-sphere fluid would serve as an appropriate
reference system to mimic the interatomic correlation in fluid
mercury.

Ross21 proposed an approximate soft-sphere variational
theory, where correlation functions for the soft-sphere fluid
are replaced by those for the hard-sphere fluid, and the soft-
core effect is incorporated through an additional empirical
correction term in the free energy. We adopt his theory and
take the inverse sixth power potential as a reference,23 with
the recognition that the repulsive part of V_{dimer}(r) is rather
soft due to the induction effect and approximately

\begin{align*}
  f(n, T; \sigma) = f_{id} - e_s^{\text{HS}} + \frac{n}{2k_B T} \int_0^\infty dr 4\pi r^2 V_{dimer}(r) g_{\text{HS}}(r) \\
  + \left( \frac{V_{mb}(z, r_{mn})}{Nk_BT} \right)_{\text{HS}} + f_6.
\end{align*}

Here,

\begin{align*}
  f_{id} &= \ln \left( \frac{2\pi\hbar^2}{Mk_BT} \right)^{3/2} n - 1
\end{align*}

represents the ideal-gas free energy with M=3.331
×10^{-22} \text{ g}\) denoting the mass of a Hg atom. The quantities
with subscript “HS” are evaluated for the hard-sphere fluid
with core diameter \(\sigma\). The excess entropy is evaluated in the
Carnahan-Stirling approximation,20

\begin{align*}
  S_{\text{HS}}^x = - \frac{4 - 3 \eta}{(1 - \eta)^2},
\end{align*}

with \(\eta = \pi n \sigma^3 / 6\) designating the packing fraction. The last
term on the right-hand side of Eq. (5),

\begin{align*}
  f_6 &= -0.932 71 \eta - 0.495 05 \eta^2 - 2.129 24 \eta^3 \\
  &\quad + 0.500 30 \eta^4,
\end{align*}

represents the soft-sphere correction obtained by Young and
Rogers.23 The radial distribution function \(g_{\text{HS}}(r)\) for the
hard-sphere fluid is available in parametrized form by Trokhym-
chuk et al.24

The coordination number \(z\) of an atom in the fluid may
be defined as the number of nearest-neighbor atoms
contained within a sphere of suitably chosen volume \(\nu=(4\pi \sigma^3 / 3)\) encompassing that atom. The instantaneous
value of \(z\) differs from atom to atom due to structural disor-
der. In light of the observations in Figs. 2 and 3, we expect
that an atom with larger \(z\) and/or smaller \(r_{mn}\) may experience
a stronger attractive force than that with smaller \(z\) and/or larger \(r_{mn}\). Accordingly, we take a statistical average of the quantity \(V_{mb}(z, r_{mn})/N\) over all possible realizations of \(z\) and
\(r_{mn}\). Strictly speaking, the average should be taken for the
reference soft-sphere system, but since it is difficult to get
probability distribution functions of \(z\) and \(r_{mn}\), we replace them by the hard-sphere counterparts for
simplicity. We also treat \(z\) and \(r_{mn}\) as statistically independent
variables, neglecting their mutual correlations. We thus
evaluate the term \(\langle \cdots \rangle_{\text{HS}}\) in Eq. (5) as

\begin{align*}
  \left\langle \frac{V_{mb}(z, r_{mn})}{Nk_BT} \right\rangle_{\text{HS}} &= \sum_{z=1}^{z_{\text{max}}} \rho_{\text{HS}}(z) \frac{\int_{r_{mn}}^\infty dr\pi r^2 H_{\text{HS}}(r) V_{mb}(z, r_{mn})/Nk_BT}{\int_{r_{mn}}^\infty dr H_{\text{HS}}(r)}. 
\end{align*}

Here, \(\rho_{\text{HS}}(z)\) is the distribution function of \(z\) for the hard-
sphere fluid. Through simple geometrical considerations
within the excluded-volume approximation,5 we arrive at an
expression as follows:
\[ p_{HS}(z) = \frac{p_{HS}(0)(nv - \eta)(nv - 2\eta) \cdots (nv - z\eta)}{z!} (1 - \eta)^2 \]

for \(1 \leq z \leq z_{max}, \quad (10)\)

and \(p_{HS}(0)\) is determined from the normalization \(\sum_{z=0}^{\infty} p_{HS}(z) = 1\). In this work, we take the maximum value of \(z\) as \(z_{max} = 12\) (corresponding to the fcc lattice), and \(v\) is chosen as \(v = (z_{max} + 1)\pi\sigma^3/6\), leading to \(r_{max} = (z_{max} + 1)\pi\sigma^2/2 = 1.176\sigma\). In this case, we can prove that \(p_{HS}(0) = (1 - \eta)^{z_{max}}\), and average coordination number is given by

\[ \langle z \rangle = \sum_{z=0}^{\infty} z p_{HS}(z) = z_{max} \eta, \quad (11)\]

which is proportional to the packing fraction.

The distribution function \(H_{\text{HS}}(z)\) represents the probability of finding a nearest-neighbor particle at distance \(r_{mn}\) from the reference particle. The properties of this function were discussed in detail by Torquato.\(^{26}\) He obtained an analytic expression for \(H_{\text{HS}}(z)\) in terms of a dimensionless distance \(z = r_{mn}/\sigma\) as

\[ \sigma H_{\text{hs}}(r_{mn}) = 24\eta(a_0x^2 + a_1x + a_2)\exp[-\eta(8a_0(x^3 - 1)
+ 12a_1(x^2 - 1) + 24a_2(x - 1))], \quad (12)\]

with

\[ a_0 = 1 + 4g(\sigma), \quad a_1 = \frac{3\eta - 4}{2(1 - \eta)} + 2(1 - 3\eta)g(\sigma), \]
\[ a_2 = \frac{2 - \eta}{2(1 - \eta)} + (2\eta - 1)g(\sigma), \quad g(\sigma) = \frac{1 - \eta^2}{(1 - \eta)^3}. \]

We note that \(H_{\text{HS}}(r_{mn})\) is a decreasing function of \(r_{mn}\) with a peak at \(r_{mn} = \sigma\), the peak becomes sharper as \(\eta\) increases. Our treatment of cooperative interaction represented by Eq. (9) is analogous to the associating fluid model of liquid water by Truskett et al.,\(^{22}\) except for the anisotropic interaction in the latter.

For given \(n\) and \(T\), the total free energy \(f(n, T, \sigma)\) of Eq. (5) is minimized with respect to the variational parameter \(\sigma\) as \(\partial f(n, T, \sigma)/\partial \sigma|_{n,T} = 0\). The pressure \(P\), entropy \(S\), internal energy \(U\), and Gibbs free energy \(G\) are then calculated in a standard way as \(p = P/nk_B T = n(\partial f/\partial n)|_T\), \(s = S/Nk_B\), \(\sigma = -[\partial f(T)/\partial T]|_n\), \(u = U/Nk_B T = f + s\), and \(G/Nk_B = f + p\), respectively; the derivatives in these formulas should be evaluated under the constraint that \(f\) be minimized with respect to \(\sigma\). We remark that both Eqs. (10) and (12) depend on \(n\) so that their density derivatives also contribute to the pressure.

**IV. NUMERICAL RESULTS**

**A. Gas-liquid coexistence curves**

At sufficiently low temperatures, the derivative \(\partial P/\partial n|_T\) can take on a negative value, indicating the onset of the first-order gas-liquid transition. The saturation densities in the gas and liquid phases, \(n_{gas}\) and \(n_{liq}\), are obtained in accordance with the conditions of two-phase equilibrium: \(P(n_{gas}, T) = P(n_{liq}, T)\) and \(G(n_{gas}, T) = G(n_{liq}, T)\). The gas-liquid coexistence curves so obtained are displayed in Fig. 4.

**FIG. 4.** Gas-liquid coexistence curve on the mass density-temperature plane. The thick solid curve corresponds to the present result; the dashed curve represents the experimental data (Refs. 1 and 3). The mean density \(\rho_m\) in this work is plotted by the dotted curve; the corresponding experimental data (Refs. 1 and 26) are shown by dots. The thin solid curves depict the contours of constant mean coordination numbers.

\[ (\rho_m - T)\text{diagram; }\rho_m = Mn \text{ and in Fig. 5 (}\text{T-P diagram). It can be seen that our coexistence curves reproduce the experimental data}\(^{13,26}\) reasonably well. The critical density, temperature, and pressure are predicted to be \(\rho_c = 5.82\ \text{g/cm}^3\), \(T_c = 1774\ \text{K}\), and \(P_c = 1.97\ \text{kbars}\), which are in good agreement with the corresponding experimental values: \(\rho_c(\text{exp}) = 5.8\ \text{g/cm}^3\), \(T_c(\text{exp}) = 1751\ \text{K}\), and \(P_c(\text{exp}) = 1.67\ \text{kbars}\). At the melting point \((T = 234\ \text{K} \text{ and } P = 1\ \text{bar})\), our theory yields \(\rho_{liq} = Mn_{liq} = 14.02\ \text{g/cm}^3\), \(S/Nk_B = 6.0\), and \(U/N = -0.056\ \text{Ry/atom}\), which compare with the corresponding experimental values: \(\rho_{liq}(\text{exp}) = 13.65\ \text{g/cm}^3\), \(S(\text{exp})/Nk_B = 8.3\), and \(U(\text{exp})/N = -0.034\ \text{Ry/atom}\).

In Fig. 4, we also plot the average of gas and liquid densities \(\rho_d = (n_{gas} + n_{liq})/2\). Experimental data\(^{1,26}\) reveal that \(d\rho_d/dT < 0\) for sufficiently low temperatures and in the vicinity of the critical point, whereas \(d\rho_d/dT > 0\) in the range of \(T = 1400 - 1700\ \text{K}\). It is remarkable that the present theory likewise predicts the behavior \(d\rho_d/dT > 0\) above 1500 K. 

**FIG. 5.** Gas-liquid coexistence curve on the temperature-pressure plane. The thick solid curve indicates the present result; the thick dashed curve refers to the experimental data (Refs. 1 and 3). The dots represent the corresponding critical points. Thin solid curves indicate isochores at respective densities, compared with experimental data (Refs. 1 and 3) (thin dashed curves).
$dp_d/dT$, which is absent in simple rare-gas fluids, is intimately related to the M-NM transition in the liquid phase. We suppose that the strong cohesive force associated with metallization tends to increase the values of $n_{\text{liq}}$ in that range.

The gas-liquid coexistence curve is determined through a delicate balance between the free energies in the two phases, and hence it is sensitive to the adopted theoretical model. When fluid mercury is treated as a partially ionized nonideal plasma, the resultant coexistence curve on the $\rho_m$-$T$ plane becomes too sharp, and the values of $n_{\text{liq}}$ are underestimated especially in the M-NM transition range. Plasma theories assume that the delocalized electrons extend uniformly over the entire space. Such assumption may not be appropriate in expanded fluid metals: Spatial distributions of electronic wave functions may be governed by the local atomic arrangement, as pointed out by Chacón et al. in their tight-binding models of fluid alkali metals. The present model significantly improves our previous plasma-theoretical treatment, but it should be noted in Fig. 4 that our coexistence curve still exhibits small deviation from the experimental data in the M-NM transition range at around 9 g/cm$^3$. We shall come to this point later in Sec. IV C.

**B. Structures**

The present theory cannot describe atomic structures of the real system, but qualitative arguments on the structures may be possible through the correlation functions of the reference hard-sphere fluid with optimized core diameters. We see in Fig. 6 that the optimized value of $\sigma$ along the coexistence curve remains virtually constant ($\sigma/a_B = 5.58-5.60$) over a wide density range $\rho_m = 2-12$ g/cm$^3$. It is notable that this value is close to the observed first peak position of the radial-distribution function, $5.67a_B$, which is likewise almost unchanged within the liquid phase as revealed by the x-ray diffraction experiments. By substituting the optimized $\sigma$ into Eq. (11), we find that the average coordination number is proportional to the density as $\langle z \rangle = 0.49\rho_m$ (g/cm$^3$) along the coexistence curve (Fig. 7). These features corroborate the picture of inhomogeneous expansion.

In Fig. 7, the distribution function $p_{\text{HS}}(z)$ is illustrated for three different points on the coexistence curve. In the low-density gas phase, the distribution has a sharp peak at $z=0$, indicating that the many-body interaction does not contribute appreciably to the equation of state. As the density increases, the position of the peak shifts toward large-$z$ side and the peak height becomes lower, in qualitative agreement with the results of the reverse Monte Carlo simulation by Arai and McGreevy. At the critical point, the three- and four-body interactions ($z=2$ and 3) are predicted to be dominant, but the fluctuation is so large that the atoms having larger $z$ also contribute to the cohesive energy. At the normal liquid density at 293 K, the peak is located at $z=7$ and hence the significant part of the distribution is contained in the metallic domain.

The contours of $\langle z \rangle = 3$ and 5 obtained from Eq. (11) are superposed on the phase diagram in Fig. 4. We find that $\langle z \rangle$ depends not only on $\rho_m$ but also on $T$. This is because the radius $r_{\text{max}}$ of the first coordination region depends on the optimum core diameter $\sigma$ and the latter becomes small as $T$ increases.

**C. Thermodynamic quantities**

Isochores at $\rho_m$ (g/cm$^3$) = 1, 5, 10, and 12 are plotted and compared with experimental data by Götzlaff (taken from Ref. 1) in Fig. 5. The present theory shows fairly good agreement with experiments at the lowest and highest densities, but tends to overestimate the pressure in the M-NM transition regime (10 g/cm$^3$). Pressure-density relations at constant temperatures (1723 and 1813 K) are likewise presented in Fig. 8. We find that the agreement between theory and experiment is good below the critical density, whereas our equation of state turns out too stiff in the liquid phase at around 9 g/cm$^3$.

We have also computed isochoric thermal pressure coefficient $\gamma_v = \langle \partial P/\partial T \rangle_v$, along the coexistence curve. As manifested in Fig. 9, the present theory agrees fairly well with the experimental results at low and high densities, but theoretical values are too large at intermediate densities of 9-12 g/cm$^3$, suggesting that the effective interatomic interaction is estimated to be too repulsive in this range.

The specific heats at constant volume ($C_v$) and constant pressure ($C_p$) are evaluated respectively as
The specific heat at constant volume $C_v$ and at constant pressure $C_p$ evaluated with Eq. (13) at $P=2$ kbars (solid curves). The black and white circles with an error bar depict experimental data by Levin and Schmutzler (Ref. 33).

The adiabatic sound velocity is defined and calculated as

$$c_s = \sqrt{\sqrt{\frac{\partial P}{\partial \rho_m}}_S} = \sqrt{\frac{1}{M} \left( \frac{\partial P}{\partial \rho_m} \right)_T + \frac{T}{n^2 C_v N} \frac{\gamma_v^2}{n^2}} \quad (14).$$

In Fig. 11, theoretical values of $c_s$ at $P=2$ kbars are presented and compared with the experimental measurements by Kohno and Yao. At densities higher than about 4 g/cm$^3$, our theory tends to overestimate the sound velocity, though a qualitative trend of the experimental data is reproduced. The deviation between theory and experiment is enlarged particularly in the M-NM transition range around $\rho_m=9$ g/cm$^3$. The experimental curve exhibits an inflection at $\rho_m=9$ g/cm$^3$, whereas our theoretical curve shows a rather smooth density dependence. The inflection was reproduced through the molecular dynamics simulation by Munejiri et al., who deduced an effective interatomic pair potential from measured static structure factors and claimed that change in the repulsive part of the potential causes the inflection.
V. CONCLUDING REMARKS

Previous theoretical analyses of thermodynamic properties in the expanded fluid mercury were limited to empirical modifications of the van der Waals equations or computer simulations using density- or temperature-dependent effective pair potentials adjusted to reproduce existing experimental data. These methods would not be successful if experimental data are not available in advance. In contrast, the variational associating fluid theory developed here is the first to predict thermodynamic quantities of fluid mercury by using quantum-chemical interatomic interactions as input, without resorting to empirical state-dependent pair potentials. A salient feature of the present scheme lies in its cross-hierarchical nature, bridging the gap between macroscopic thermodynamics and microscopic interatomic interactions by taking additional account of the mesoscopic association effects. Our theory is also advantageous from the practical point of view, in a sense that various thermodynamic quantities can be obtained over a wide density-temperature range without massive computations. Though the theory has been applied exclusively to mercury in this work, the formalism is quite general and would be applicable to other fluids after suitable modifications.

We have stressed the importance of the attractive many-body interaction among atoms, which becomes strong as the local coordination number (z) increases and the nearest-neighbor distance (r_{nn}) decreases. The statistical average of the potential has been carried out by taking into account fluctuations of z and r_{nn} in the reference hard-sphere fluids. As exposed in Figs. 2 and 3, the many-body potential in mercury is relatively weak in the nonmetallic, small-z regime, while it becomes substantially strong in the metallic, large-z regime. As the density increases, the atomic coordination increases and a strong cohesive force is produced, which plays a dominant role in the gas-liquid transition. Along the coexistence curve, we have found that the average coordination number is nearly proportional to the density while the optimized core diameter (and hence the distance of the closest approach) is virtually constant, supporting the invariance of the structuring process.

We have computed such thermodynamic quantities as isochoric thermal pressure coefficient and sound velocity, which show reasonable agreement with experimental data. The isochoric thermal pressure coefficient and sound velocity are essentially proportional to the density and vary with the coordination number in a way that the closest approach increases and the nearest-neighbor distance decreases. This theoretical prediction is in close agreement with experimental findings.

The structure-independent energy per ion may be evaluated as

\[
U_{\text{el}}(n) = \frac{ZF_{\text{eq}}}{N} + \frac{E_M}{N} - \frac{n}{2} \Phi(k = 0) + \frac{E_{\text{def}}}{N} + \frac{e^2}{a_B} \left( \frac{C_1}{r_s} + \frac{C_2}{r_e^2} \right).
\]

Here, F_{eq}/N_c denotes the free energy per electron of the homogeneous electron liquid, whose analytic expressions are available in the literature. The Hartree energy is defined as

\[
\Phi(k) = \frac{(Ze)^2}{r} + \frac{1}{2\pi^2} \int_0^{\infty} \frac{dk}{kr} \Phi_{\text{BS}}(k) \sin(kr).
\]

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APPENDIX: COHESIVE ENERGIES OF METALLIC SOLIDS

In the conventional local pseudopotential theory of nearly free-electron metals, the pair potential between ions is calculated as

\[
\Phi(r) = \frac{(Ze)^2}{r} + \frac{1}{2\pi^2} \int_0^{\infty} \frac{dk}{kr} \Phi_{\text{BS}}(k) \sin(kr).
\]

Here, V^p(r) refers to the Fourier transform of the bare electron-ion pseudopotential V^p(k), and \( e_r(k) \) designates the dielectric function of the homogeneous electron liquid at density n, where strong exchange and Coulomb correlations are incorporated through the static local-field correction G(k). Chekmarev et al. modified Eq. (A1) by adding the repulsive Born-Mayer potential of the form \( \Phi_{\text{BM}}(r) = A(e^2/a_B) \exp(-Br/a_B) \) to obtain the improved effective ion-ion interaction as

\[
\Phi_{\text{eff}}(r) = \Phi(r) + \Phi_{\text{BM}}(r).
\]

The coefficients A and B are adjusted so that the pair-distribution functions computed with Eq. (A3) agree with experimental data.

The structure-independent energy per ion may be evaluated as

\[
U_{\text{el}}(n) = \frac{ZF_{\text{eq}}}{N} + \frac{E_M}{N} - \frac{n}{2} \Phi(k = 0) + \frac{E_{\text{def}}}{N} + \frac{e^2}{a_B} \left( \frac{C_1}{r_s} + \frac{C_2}{r_e^2} \right).
\]
\[
\frac{E_{H}}{N} = n_{e} \int d\mathbf{r} \left[ V^\rho(r) + \frac{Ze^2}{r} \right].
\] (A5)

The self-part of the band-structure energy is calculated in accordance with Eq. (A2) as

\[
\frac{E_{\text{BS}}^{\text{self}}}{N} = \frac{1}{4 \pi^2} \int_{0}^{\infty} d\mathbf{k} k^2 \Phi_{\text{BS}}(k).
\] (A6)

The ionization potential \( I_p \) is an energy required to remove valence electrons from an isolated atom. The final term on the right-hand side of Eq. (A4) corresponds to the empirical correction which ensures mechanical stability and a correct value of the cohesive energy.\(^{17}\) Here, we have introduced the dimensionless electron-density parameter \( r_s = a_e/a_B \), with \( a_e = (3/4\pi n_e)^{1/3} \) denoting the Wigner-Seitz radius.\(^{40}\)

When the Ashcroft empty-core pseudopotential\(^{20}\) with the core radius \( R_c \) is adopted for \( V^\rho(r) \), we have \( \Phi(k=0) = 4\pi(Ze^2)(D_k + R_k^2) \). Here, \( D_k \) represents the long-range screening distance of the electrons defined as \( D_k = \lim_{k \to 0} \left[ 1/k^2 \Phi_{\text{BS}}(k) \right] = a_{B}^2 \left( \pi \lambda / 4 r_s \right) - \lambda^2 \lambda_0(r_3) \), with \( \lambda = (4/9 \pi) \)\(^{1/3} \); \( \lambda_0(r_3) = \lim_{k \to 0} [G(k) / (k/k_F)^2] \) is related to the long-wavelength limit of the local-field correction \( G(k) \), with \( k_F = \left( 3\pi^2 n_e \right)^{1/3} \) denoting the Fermi wave number.\(^{40}\) An analytic expression for \( G(k) \) was presented by Ichimaru and Utsumi.\(^{40,41}\)

In applying the above formalism to liquid mercury, we follow Chekmarev et al.\(^{17}\) and adopt \( R_c = 0.915a_B \), \( A = 200 \), and \( B = 2 \). The sum of the first and second ionization potentials for an isolated Hg atom amounts to \( I_p/k_B = 3.388 \times 10^5 \) K. In Eq. (A4), we have set \( C_1 = -0.197 \) and \( C_2 = 0.6 \) so that the observed cohesive energy of 0.67 eV/atom is reproduced for the fcc lattice (\( z = 12 \)); although the rhombohedral structure is slightly more stable than fcc in the ground state, the linear muffin-tin orbital (LMTO) calculation by Bose\(^{42}\) showed that the relative difference between the cohesive energies of these two lattice structures is as small as 2\%. Our theory predicts the optimum lattice constant of the fcc solid to be 6.07\( a_B \), in good agreement with the LMTO result,\(^{42}\) 6.04\( a_B \).

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