Predicting the gas-liquid transition of mercury from interatomic many-body interaction

Hikaru Kitamura
Department of Physics, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan
E-mail: kitamura@scphys.kyoto-u.ac.jp

Abstract. A new cross-hierarchical equation of state for expanded fluid mercury is developed by combining quantum-chemical analysis of interatomic interactions and soft-sphere fluid variational approach. The theory incorporates ab initio diatomic potential energy curves and an additional many-body potential describing the associative interaction of an atom with its neighbouring atoms forming a local temporary cluster. The experimental gas-liquid coexistence curves are accurately reproduced without introducing empirical adjustable parameters. The gas-liquid transition is dominated by the many-body interaction, which becomes strongly attractive as the average coordination number increases and the local electronic states change from nonmetallic to metallic.

1. Introduction
Fluid metals undergo metal-nonmetal (M-NM) and gas-liquid (G-L) transitions when expanded at high temperatures and pressures [1]. The phase diagrams and thermodynamic properties of mercury, a representative fluid metal, have been accurately measured through intensive experimental studies during these 40 years (for a review, see [1]), whereas first-principles microscopic theories accounting for those phase transitions have not been established yet. In this paper, we present an equation of state for expanded fluid mercury that can predict the G-L coexistence curve accurately on the basis of the quantum-mechanical interatomic interactions [2,3]. We shall thereby show that the G-L transition is controlled essentially by the attractive many-body interaction associated with temporary cluster formation in the fluid.

2. Theory
2.1 Many-body interaction
It has been known [4] that the binding energy of two Hg atoms in the ground $6s^2\, ^1S_0$ state amounts to 0.043 eV; the corresponding equilibrium bond length is $7.06\, a_B$, with $a_B$ denoting the Bohr radius. It is clear that such a weak attractive force cannot account for the observed G-L critical temperature, $T_c = 0.151$ eV, of fluid mercury. When many Hg atoms aggregate to form a cluster, however, the strength of each bond is enhanced and the bond length decreases, due to the configuration mixing between the ground and excited ($6s6p$) electronic states [5-7]. Consequently, the potential energy function $V(r_1, \cdots, r_N)$ of an $N$-atom system cannot be written simply in terms of the diatomic potential $V_{\text{dimer}}(r)$, but an additional contribution arises from the many-body potential $V_{mb}(r_1, \cdots, r_N)$; that is,
where \( r_i \) denotes the positional vector of the \( i \)th atom.

Figure 1 illustrates the values of \( V_{mb}(z, r_{nn})/N \) computed for various configurations of clusters and bulk crystalline solids, each characterized by the coordination number \( z \) and the nearest-neighbor distance \( r_{nn} \). We find that the many-body interaction is attractive (\( V_{mb} < 0 \)); its magnitude is enhanced significantly due to a large 6s-6p mixing as the number of nearest-neighbor atoms increases. Although a crude linear interpolation has been adopted in the regime \( 4.3 \leq z \leq 8 \), we note that a similar abrupt change in the cohesive energy has been detected in Hg\(_N\) clusters for \( 30 < N < 100 \) [8].

\[ V(r_i, \cdots, r_N) = \frac{1}{2} \sum_{i \neq j}^N V_{dime}(|r_i - r_j|) + V_{mb}(r_i, \cdots, r_N), \quad (1) \]

2.2 Equation of state

In the bulk fluid, \( z \) and \( r_{nn} \) can be regarded as fluctuating variables so that their instantaneous values differ from atom to atom; hence, the potential \( V_{mb}(z, r_{nn})/N \) should be averaged over all possible atomic configurations to obtain thermodynamic quantities. In the fluid variational theory, only the correlation functions for the reference hard-sphere (HS) fluid are needed to perform the statistical averages [2,3]. For given atomic number density \( n \) and temperature \( T \), the Helmholtz free energy \( f \) per atom in units of \( k_B T \) may thus be formulated as [2,3]

\[
f(n, T; \eta) = f_{HS}(\eta) + \frac{n}{2k_B T} \int_0^\infty dr 4\pi r^2 V_{dime}(r) g_{HS}(r) + f_0(\eta) \\
+ \sum_{z=1}^{z_{max}} p_{HS}(z) \left[ \int_{r_{min}}^{r_{max}} dr_{nn} H_{HS}(r_{nn}) \frac{V_{mb}(z, r_{nn})}{Nk_B T} \right] \left[ \int_{r_{min}}^{r_{max}} dr_{nn} H_{HS}(r_{nn}) \right]^{-1}. \quad (2)
\]

Here, \( \eta = \pi n \sigma^3/6 \) is the packing fraction with \( \sigma \) denoting the HS diameter, \( f_{HS}(\eta) \) refers to the free energy of the HS fluid in the Carnahan-Stirling approximation, \( g_{HS}(r) \) represents the radial-distribution function of the HS fluid [10], and \( f_0(\eta) \) is the soft-sphere correction. Within the excluded-volume approximation, \( p_{HS}(z) \) may take on the form [2,3] \( p_{HS}(z) = 12!/[z!(12-z)!] \eta(1-\eta)^{12-z} \), the radius \( r_{max} \) of the first-coordination shell has been set as \( r_{max} = 1.176 \sigma \) by imposing a constraint that the maximum value of \( z \) should be 12. The average coordination number is then given as \( \langle z \rangle = 12 \eta \). The distribution function \( H_{HS}(r_{nn}) \) has been evaluated with the aid of the conditional pair-distribution function for the HS fluids [11]. The variational parameter \( \sigma \) in equation (2) is optimized so as to minimize \( f \).
3. Results and discussion

The G-L coexistence curve computed with equation (2) is shown in figure 2. It can be seen that the present result reproduces the experimental data [1] fairly well. The critical density, temperature, and pressure are predicted as $\rho_c=5.82 \text{ g cm}^{-3}$, $T_c = 1774 \text{ K}$, and $P_c = 1.97 \text{ kbar}$, which agree well with the corresponding experimental values $[1]$, $\rho_c(\text{exp}) = 5.8 \text{ g cm}^{-3}$, $T_c(\text{exp}) = 1751 \text{ K}$, and $P_c(\text{exp}) = 1.67 \text{ kbar}$. A large difference between the coexistence curves with and without $V_{mb}$ clearly demonstrates the significance of the many-body interaction. It has been shown $[2,3]$ that the optimized HS diameter is virtually constant, $\sigma \approx 5.6a_0$, along the coexistence curve.

![Figure 2. Gas-liquid coexistence curves. The full result obtained from equation (2) is shown by the thick solid curve, with the dot indicating the critical point; the dotted curve depicts the average of the gas and liquid densities. The dashed curve represents the coexistence curve obtained by setting $V_{mb}=0$ in equation (2). The experimental coexistence curve [1] is indicated by the dot-dashed curve. The thin solid curves represent the contours of constant average coordination number, $\langle z \rangle=1, 3$ and 5.](image)

Table 1 lists the values of the pressure for selected combinations of mass densities and temperatures. We find that our theory reproduces the experimental data $[1,12]$ accurately below the critical density, but overestimates the pressure in the density range of 9-11 g cm$^{-3}$, where the M-NM transition is expected.

| $\rho_m$ (g/cm$^3$) | 3 | 5 | 7 | 9 | 10.7 | 12 |
|---------------------|---|---|---|---|------|----|
| T (K)               | 1812 | 1802 | 1782 | 1722 | 1353 | 922 |
| $P$ (kbar)          | 1 | 2 | 2 | 3 | 1 |
| $P_{\text{exp}}$(kbar)$[1,12]$ | 1 | 1 | 1 | 1 | 0.4 | 0.1 |

Figure 3 displays the internal pressure, $P_i = (\partial U / \partial V)_T$, the isothermal volume derivative of the internal energy, computed along the coexistence curve. Since $U$ is dominated by the cohesive energy, $P_i$ depends mainly on the density. We find that $P_i$ exhibits a maximum at about 11 g cm$^{-3}$; this trend is qualitatively consistent with the measurements by Yao and Endo $[13]$ and those by Postill et al. $[14]$.

It can be seen in figures 2, 3 and table 1 that the discrepancies between the theoretical and experimental equations of state are largest for $\rho_m=9-11$ g cm$^{-3}$; in this density range, it would be necessary to consider the possibility of heterophase fluctuations $[15]$ associated with the M-NM transition, which might be dismissed in this work.

Table 1. Comparison of theoretical ($P$) and experimental ($P_{\text{exp}}$) pressures.
We remark finally that, in the case of alkali metals such as K, Rb and Cs, the dimer in the ground $\Sigma_g$ state is tightly bound while the remaining many-body interaction indicates a weakening of the bond due to the electron delocalization [16]. Strong tendency toward dimer formation should be carefully treated to interpret the recent structural data on expanded fluid Rb by Matsuda et al [17].

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