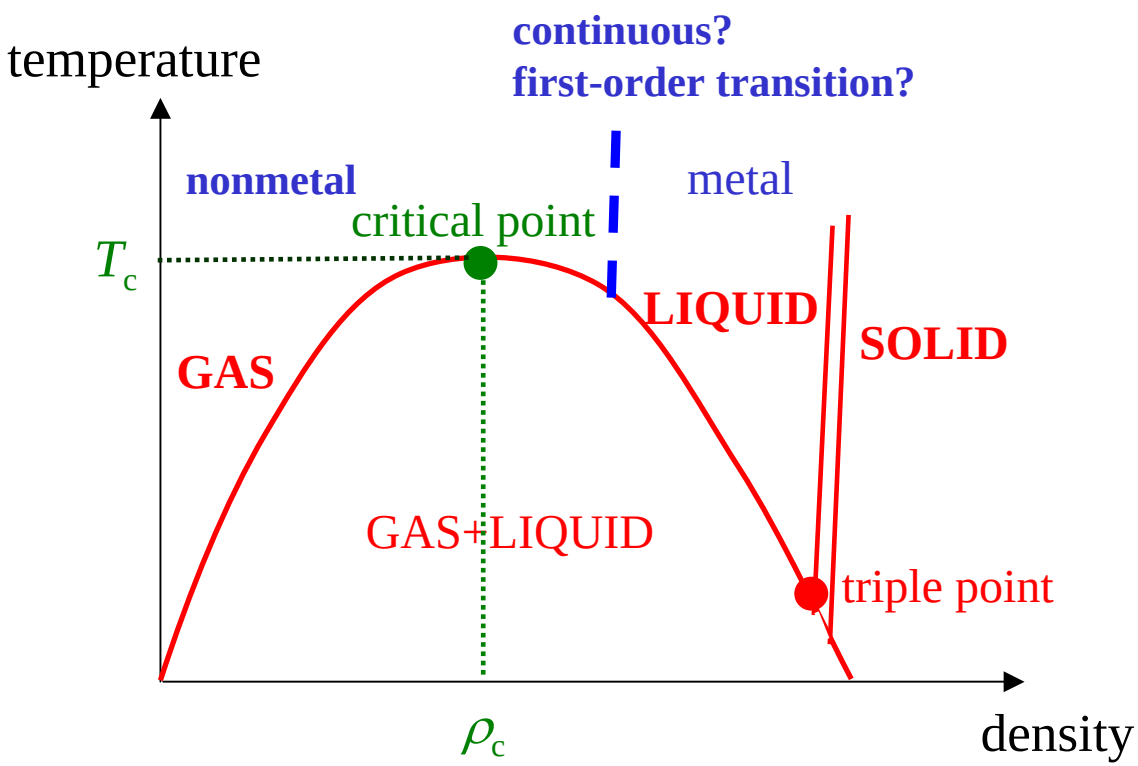
WDM school, January 14, 2008

Equation of State for Fluid Mercury Based on Interatomic Many-Body Interactions

Hikaru Kitamura

Department of Physics, Kyoto University

■ Schematic phase diagram of a metallic element



Gas-liquid transition accompanying ***change in the electronic states***

L. Landau & J. Zeldovich, Acta Physiochim. URSS **18**, 194 (1943)

F. Hensel & W.W. Warren, *Fluid Metals* (Princeton, 1999)

■Critical points of fluid metals

Hensel & Warren, *Fluid Metals* (Princeton, 1999)

elements	T_c (K)	P_c (bar)	ρ_c (g/cm^3)	
Mercury (Hg)	1751	1673	5.80	divalent
Cesium (Cs)	1924	92.5	0.38	monovalent (alkali)
Rubidium (Rb)	2017	124.5	0.29	
Potassium (K)	2178	148	0.18	
Sodium (Na)	2483	248	0.30	
……..				

Importance of mercury

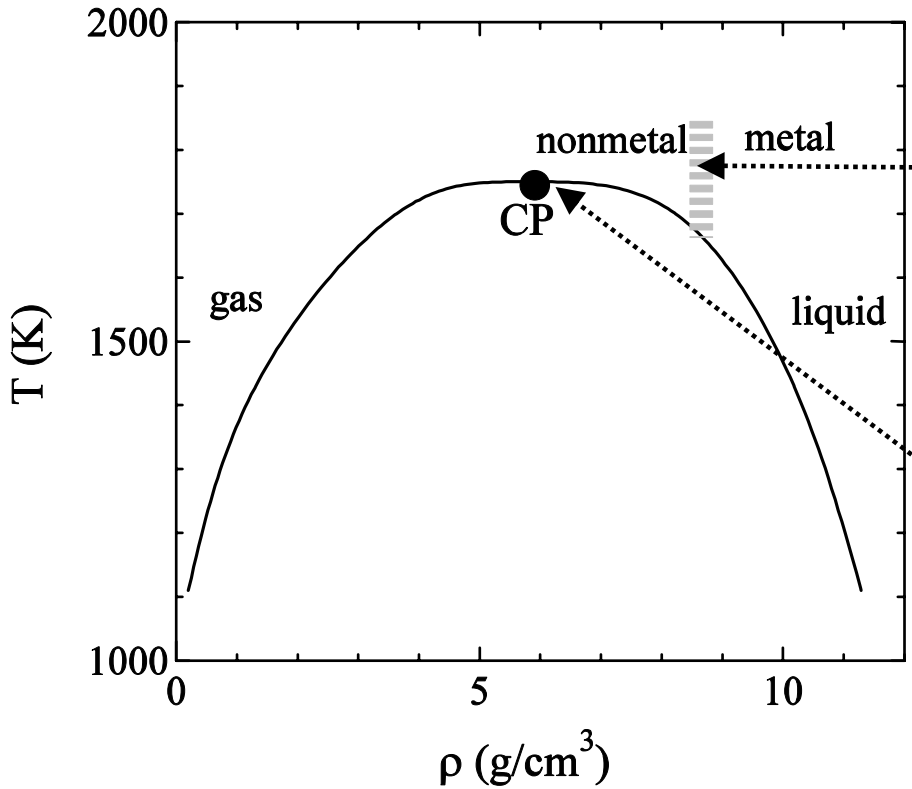
-- **lowest** critical temperature

-- critical point accessible through **static** experiments

-- **intensive** experimental investigations

■ Phase diagram of mercury

F. Hensel & W.W. Warren, Jr., *Fluid Metals* (Princeton, 1999)



Metal-nonmetal (M-NM) transition

$\rho \sim 9$ g/cm^3

- closure of s-p band gap
- weakly first order (?)

Gas-liquid critical point

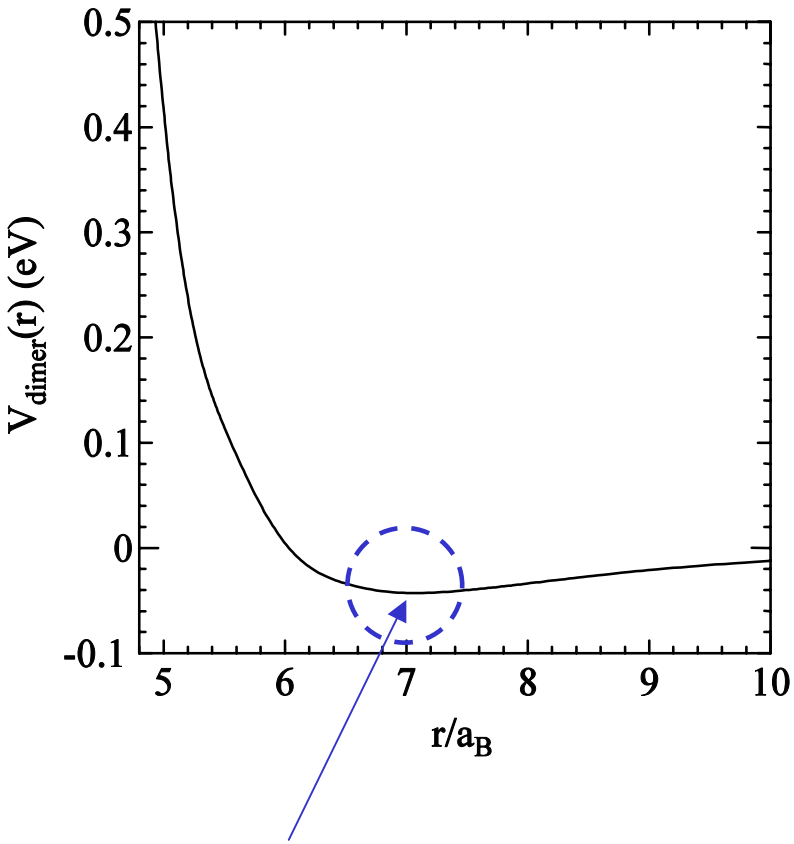
DC conductivity $\sim 1\ \Omega^{-1}\mathrm{cm}^{-1}$

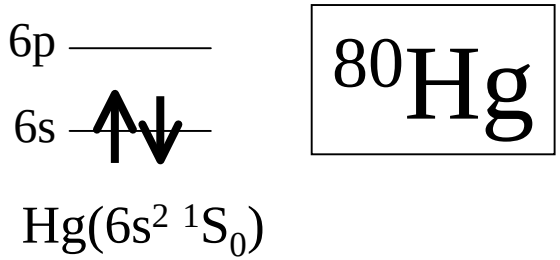
(cf. $10^4\ \Omega^{-1}\mathrm{cm}^{-1}$ in metallic state)

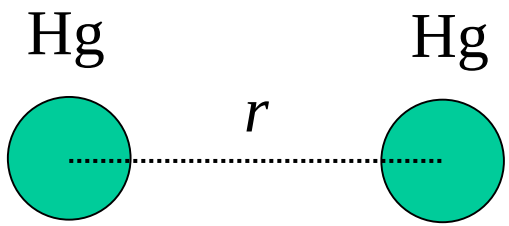
- Explain this phase behavior with microscopic interatomic interactions

■ *ab initio* diatomic potential $V_{\mathrm{dimer}}(r)$

Schwerdtfeger et al., J. Chem. Phys. **115**, 7401 (2001)







- equilibrium bond length = 7.06 a_B
- binding energy = **0.043 eV**

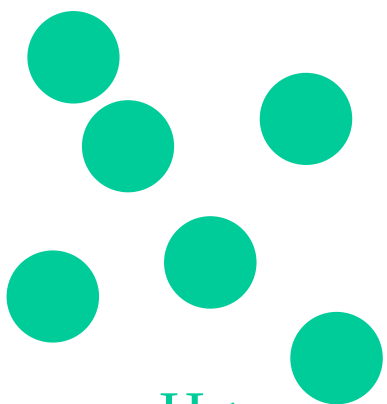
too weak to account for $\boldsymbol{T_c}$ **(= 0.151 eV)**

■ many-body interaction

total potential energy of Hg_N

$$V(\mathbf{r}_1,\cdots,\mathbf{r}_N)=\frac{1}{2}\sum_{i,j=1(i\neq j)}^{N} V_{\mathrm{dimer}}\left(\left|\mathbf{r}_i-\mathbf{r}_j\right|\right)+V_{\mathrm{mb}}(\mathbf{r}_1,\cdots,\mathbf{r}_N)$$

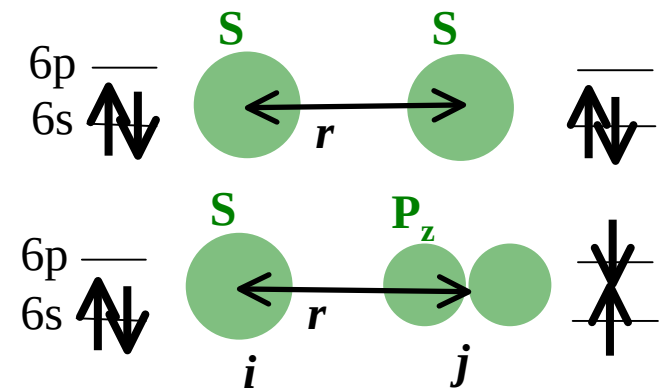
***many-body* potential due to 6*s*-6*p* mixing (attractive)**



Hg_N

6s-6p configuration mixing

dissociation limit $r \to \infty$



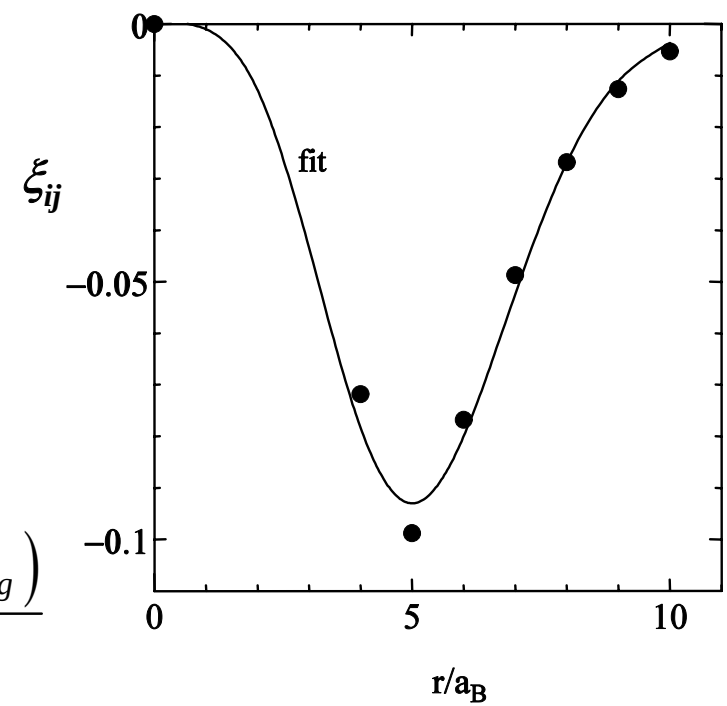
$$\begin{cases} \left| X\,{}^1\Sigma_g^{(0)} \right\rangle = \left| {}^1S \right\rangle \left| {}^1S \right\rangle & \textbf{ground state} \\ \left| {}^1\Sigma_g^{(0)} \right\rangle = \dfrac{1}{\sqrt{2}} \left(\left| {}^1S \right\rangle \left| {}^1P_z \right\rangle - \left| {}^1P_z \right\rangle \left| {}^1S \right\rangle \right) & \textbf{excited state} \end{cases}$$

$\downarrow$ mixing (r : finite)

$$\boxed{\left| X\,{}^1\Sigma_g \right\rangle = \frac{1}{\sqrt{1+\xi_{ij}^2}} \left| X\,{}^1\Sigma_g^{(0)} \right\rangle + \frac{\xi_{ij}}{\sqrt{1+\xi_{ij}^2}} \left| {}^1\Sigma_g^{(0)} \right\rangle}$$

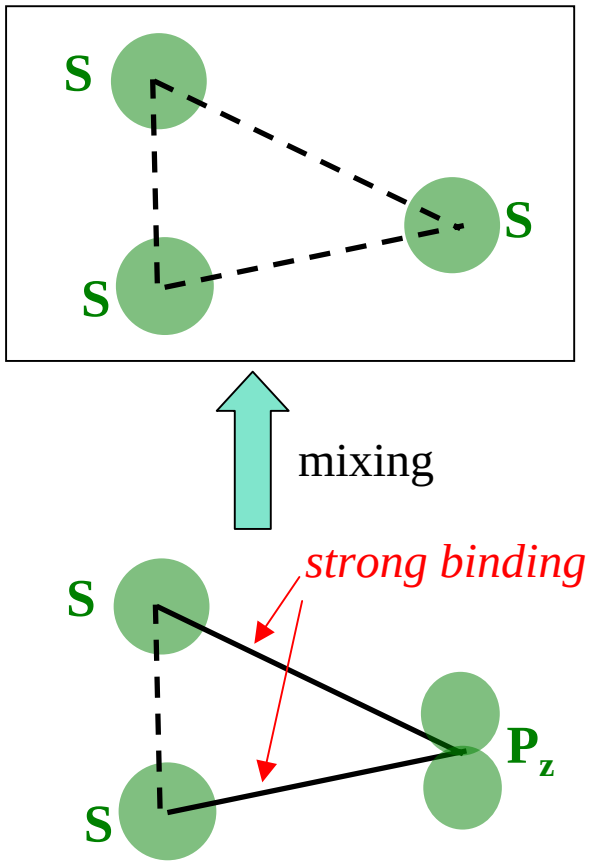
$$\left| {}^1\Sigma_g \right\rangle = \frac{-\xi_{ij}}{\sqrt{1+\xi_{ij}^2}} \left| X\,{}^1\Sigma_g^{(0)} \right\rangle + \frac{1}{\sqrt{1+\xi_{ij}^2}} \left| {}^1\Sigma_g^{(0)} \right\rangle$$

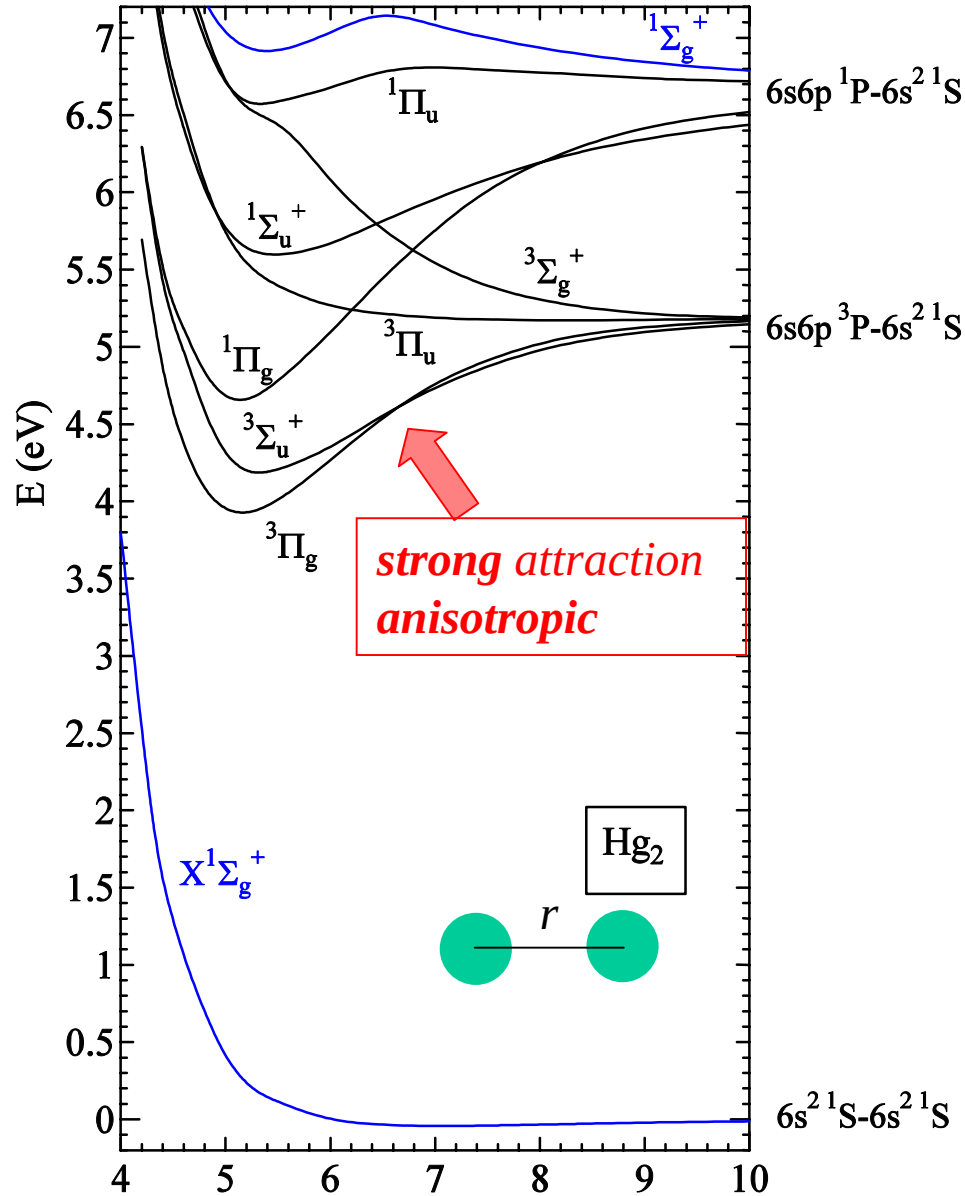
$$\xi_{ij} \cong -\frac{\left\langle X\,{}^1\Sigma_g^{(0)} \middle| \mathbf{H}^{(ij)} \middle| {}^1\Sigma_g^{(0)} \right\rangle - \left\langle X\,{}^1\Sigma_g^{(0)} \middle| {}^1\Sigma_g^{(0)} \right\rangle E\left(X\,{}^1\Sigma_g \right)}{E\left({}^1\Sigma_g \right) - E\left(X\,{}^1\Sigma_g \right)}$$



mixing parameter (function of r)

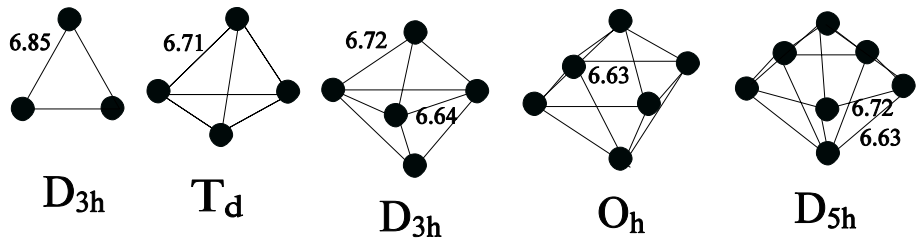
6*s*-6*p* *mixing* (continued)





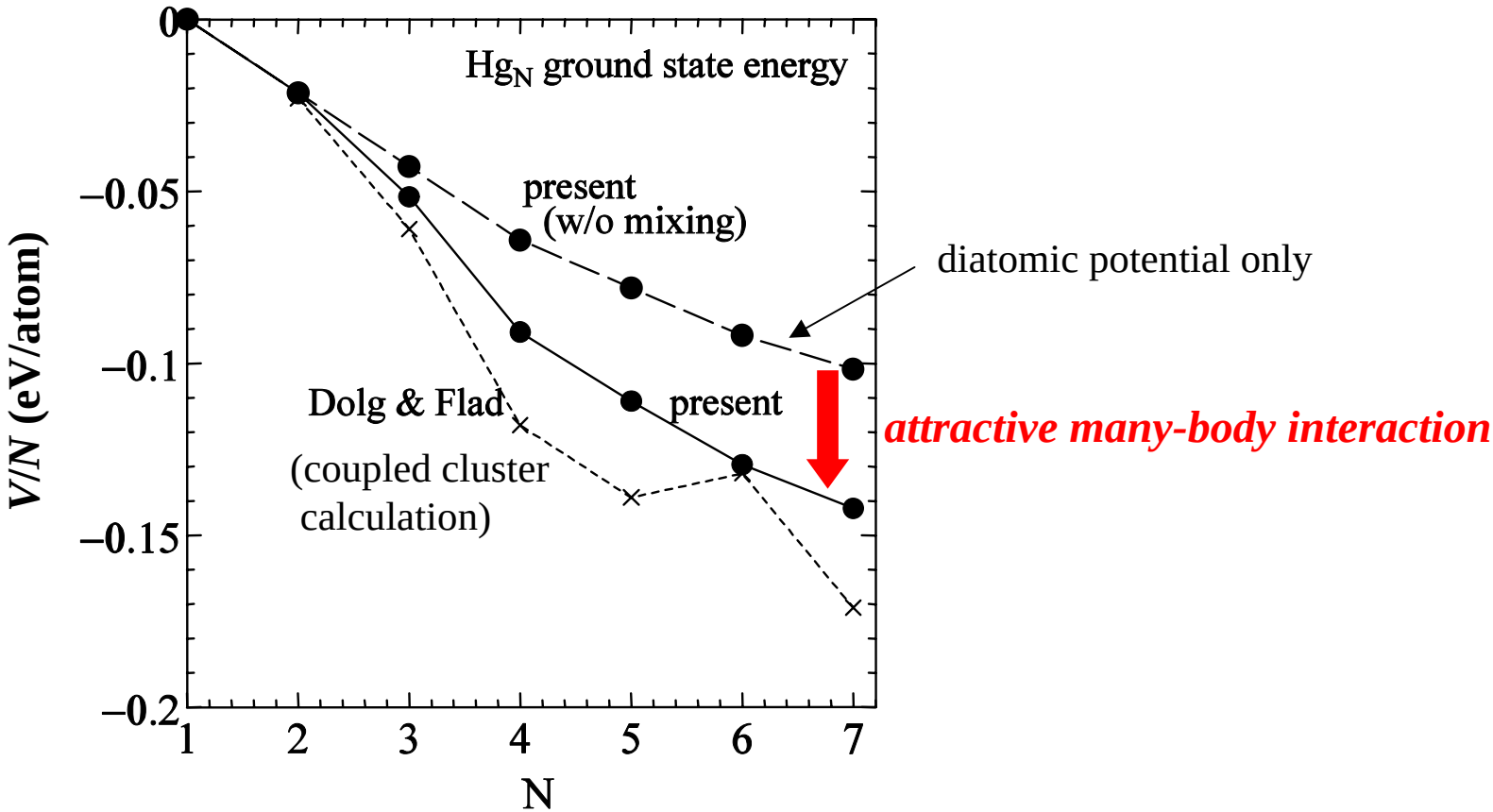
Czuchaj, Rebentrost, Stoll & Preuss,
Chem. Phys. **214**, 277 (1997)

many-body interaction: Hg_N clusters (nonmetallic)



Quantum-chemical calculation:
diatomics-in-molecules (DIM) method

H. K., Chem. Phys. Lett. **425**, 205 (2006)



many-body interaction: crystalline solids (metallic)

potential energy per atom

electron gas energy, etc.

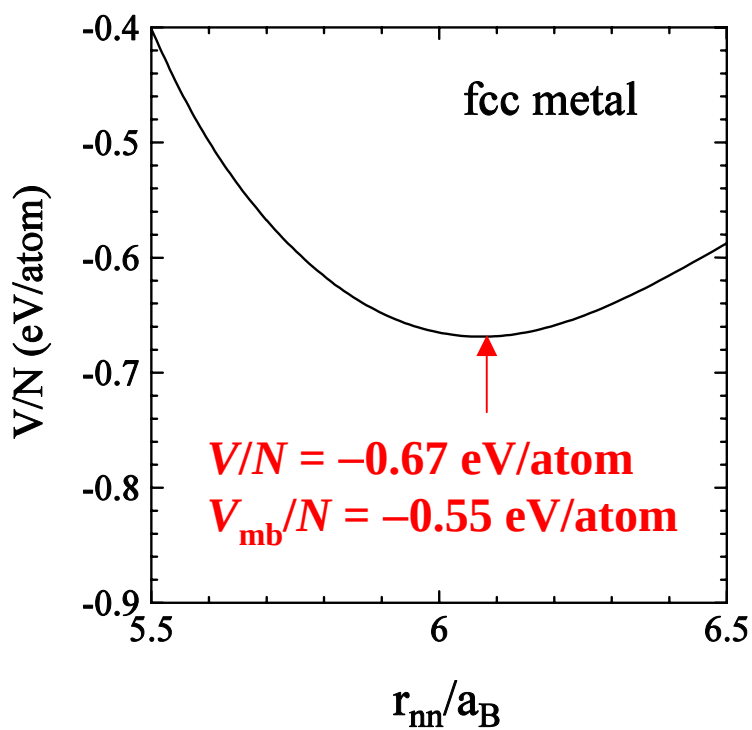
$$\frac{V}{N} = \frac{1}{2}\left[12\Phi_{\text{eff}}\left(r_{\text{nn}}\right) + 6\Phi_{\text{eff}}\left(\sqrt{2}r_{\text{nn}}\right)\right] + \frac{U_0(n)}{N}$$

1st neighbor **2nd neighbor**

core radius

$$\Phi_{\text{eff}}\left(r\right) = \frac{(Ze)^2}{r} + \frac{1}{2\pi^2}\int_0^\infty dk k^2 \frac{4\pi(Ze)^2}{k^2}\left[\frac{1}{\varepsilon_{\text{e}}(k)} - 1\right]\cos^2(kR_{\text{c}})\frac{\sin(kr)}{kr} + A\frac{e^2}{a_{\text{B}}}\exp\left(-B\frac{r}{a_{\text{B}}}\right)$$

electron screening

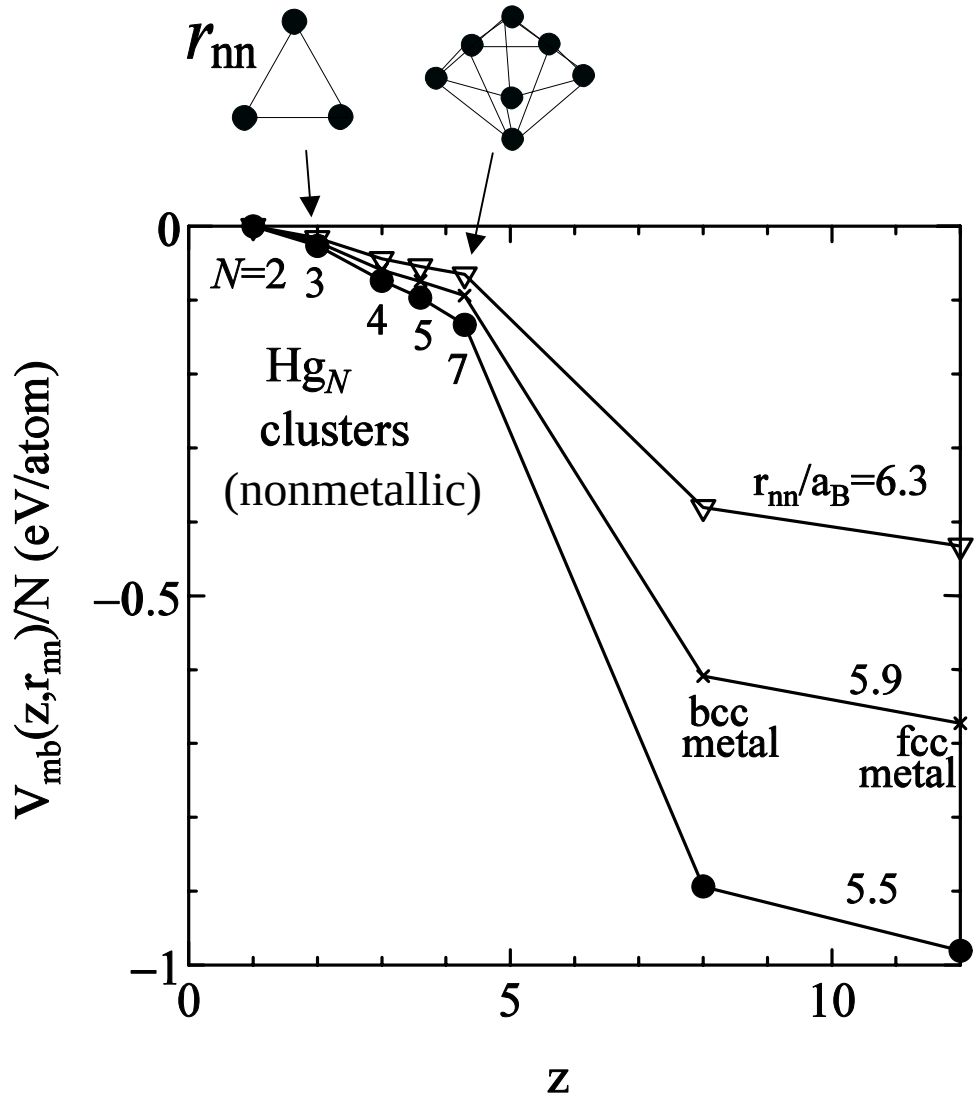


effective potential between Hg^{2+} ions (Z=2)

Chekmarev et al., Phys. Rev. E **59**, 479 (1999)

many-body potential: parametrization

H. K., J. Phys.: Condens. Matter **19**, 072102 (2007)



coordination number

nearest-neighbor distance

$$\frac{V_{mb}(z, r_{nn})}{N}$$

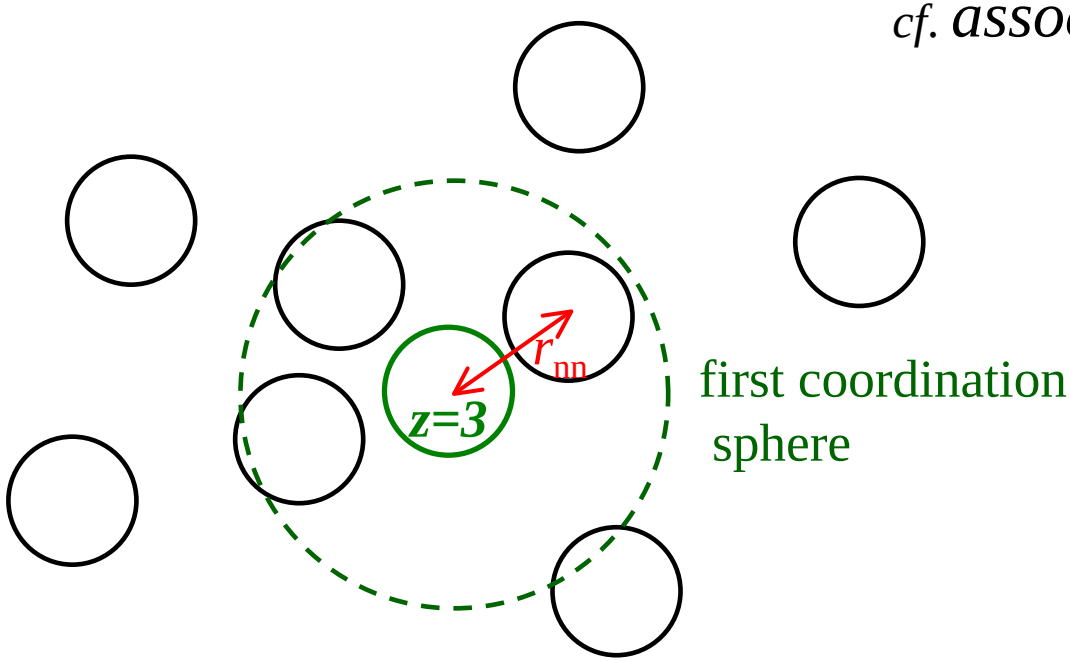
At higher temperatures,

$$\frac{V_{mb}(z, r_{nn}, T)}{N}$$

(thermal excitation of electrons)

■ temporary clustering in the fluid

cf. associating fluid theory



z, r_{nn}: fluctuating variables

■ Gibbs-Bogoliubov inequality

e.g., R.P. Feynman, *Statistical Mechanics* (Addison-Wesley, 1990)

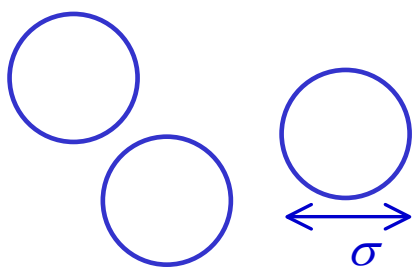
Helmholtz free energy

$$F \leq F_0 + \left\langle H - H_0 \right\rangle_0$$ variational theory

$$\left\langle \cdots \right\rangle_0 \equiv \frac{\mathrm{Tr}\left[(\cdots) \exp(-H_0 / k_\mathrm{B} T) \right]}{\mathrm{Tr}\left[\exp(-H_0 / k_\mathrm{B} T) \right]}$$

statistical average over the **<u>reference system '0'</u>**

hard-sphere (HS) reference system



Helmholtz free energy

H. K., J. Phys.: Condens. Matter **19**, 072102 (2007)

$$f(n,T;\sigma) \equiv \frac{F}{Nk_{\mathrm{B}}T}$$

density temperature

pair-distribution function

$$= f_{\mathrm{HS}}(\sigma) + \frac{n}{2k_{\mathrm{B}}T}\int_{\sigma}^{\infty} dr\, 4\pi r^2 V_{\mathrm{dimer}}(r)\, g_{\mathrm{HS}}(r) + f_6(\sigma)$$

$$+\sum_{z=1}^{12} p_{\mathrm{HS}}(z)\left[\int_{\sigma}^{r_{\max}} dr_{\mathrm{nn}} H_{\mathrm{HS}}(r_{\mathrm{nn}}) \frac{V_{\mathrm{mb}}(z, r_{\mathrm{nn}})}{Nk_{\mathrm{B}}T}\right]\left[\int_{\sigma}^{r_{\max}} dr_{\mathrm{nn}} H_{\mathrm{HS}}(r_{\mathrm{nn}})\right]^{-1}.$$

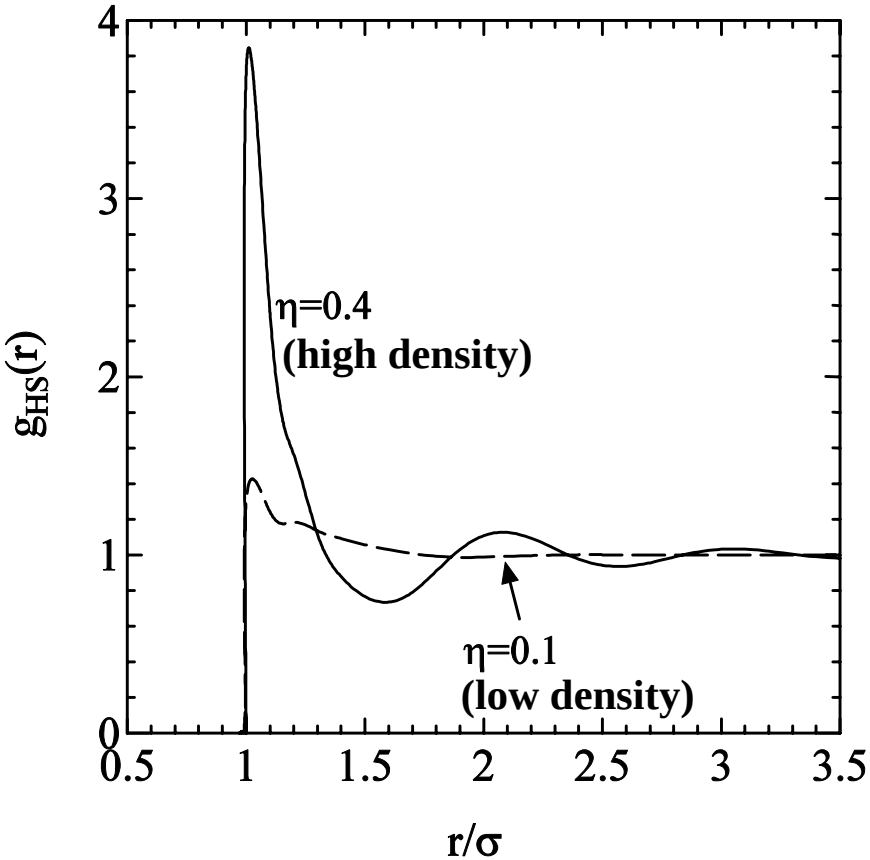
$$f_6 = -0.93271\eta - 0.49505\eta^2 - 2.12924\eta^3 + 0.50030\eta^4$$

soft-sphere correction (1/r^6 potential)

packing fraction $\eta \equiv \pi n \sigma^3 / 6$

$$\frac{\partial f(n,T;\sigma)}{\partial \sigma} = 0 \qquad \sigma \text{ optimized}$$

■pair-distribution function $g_{HS}(r)$



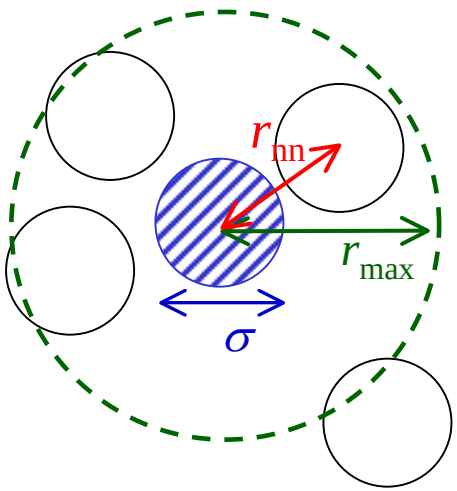
Enhanced short-range correlation at high densities

A. Trokhymchuk, I. Nezbeda, J. Jirsák, and D. Henderson, J. Chem. Phys. **123**, 024501 (2005)

■coordination-number distribution function $p_{\mathrm{HS}}(z)$

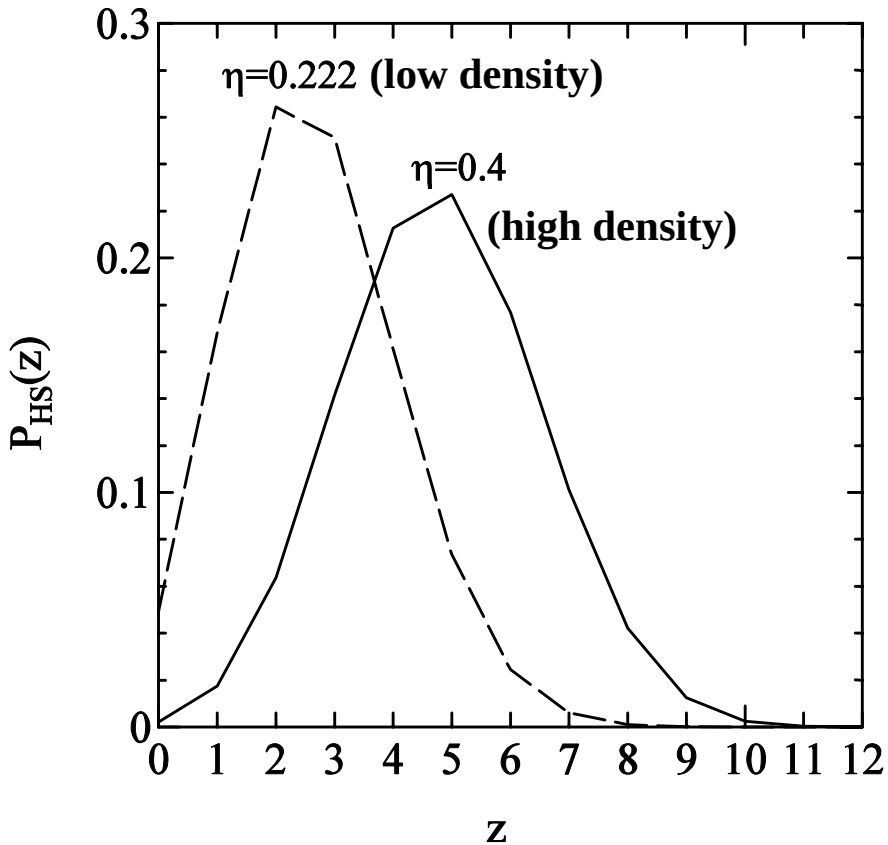
$$p_{\mathrm{HS}}(z) = \frac{12!}{z!(12-z)!}(1-\eta)^{12-z}\eta^{z} \qquad z = 0, 1, \ldots, 12$$

excluded-volume approximation



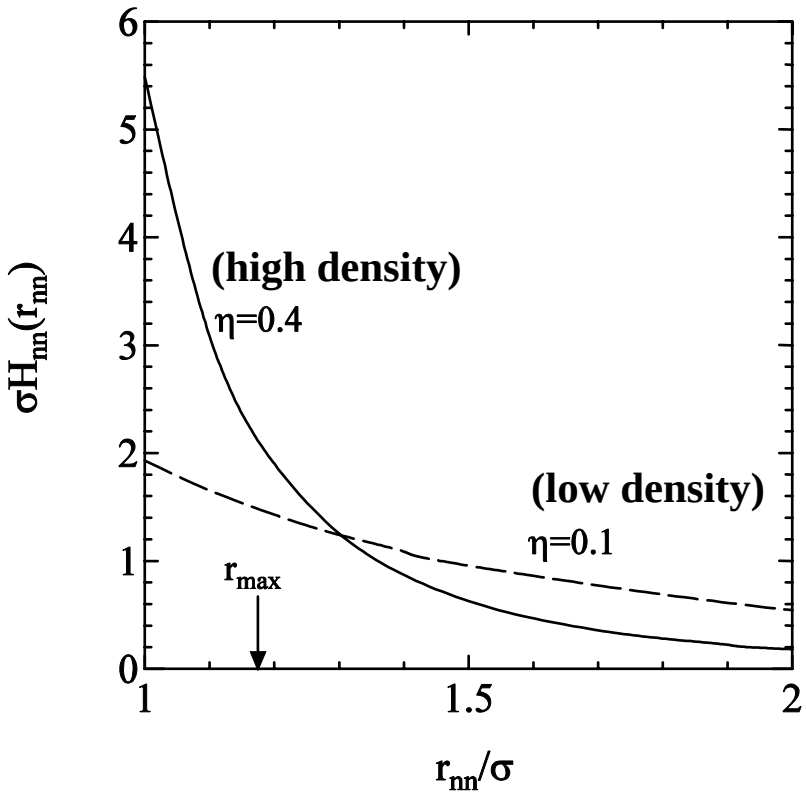
first coordination sphere

$r_{\mathrm{max}} = 1.176\sigma$



R.N. Bhatt, T.M. Rice, Phys. Rev. B **20**, 466 (1979)

■nearest-neighbor distribution function $H_{\mathrm{HS}}(r_{\mathrm{nn}})$

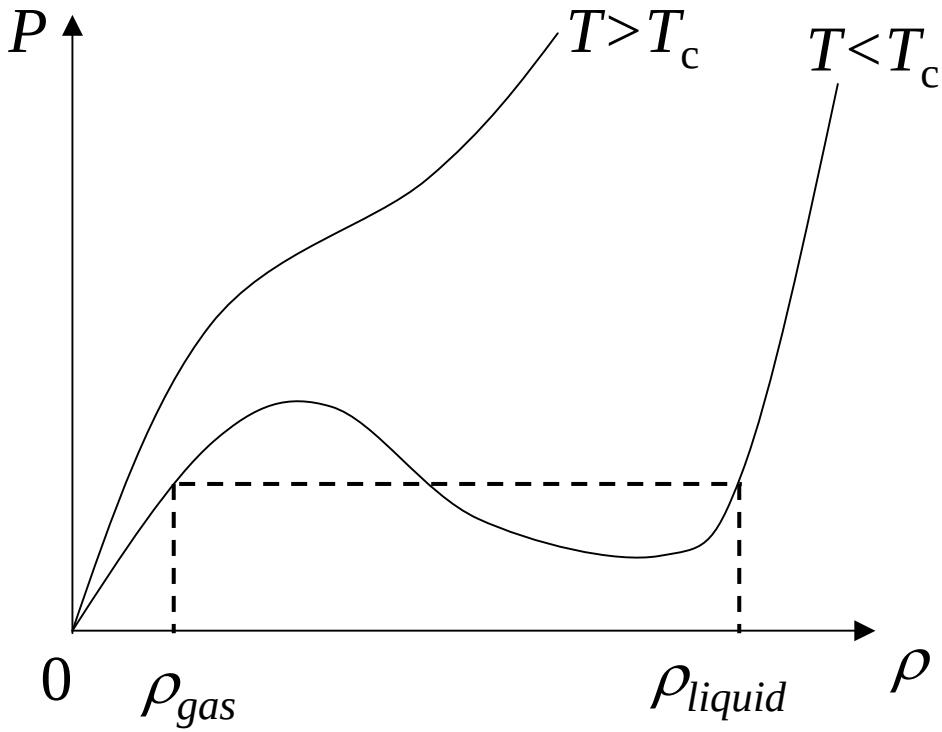


$$H(r_{\mathrm{nn}}) = 4\pi r_{\mathrm{nn}}{}^2 nG(r_{\mathrm{nn}})\exp\left[-\int_0^{r_{\mathrm{nn}}} dr\, 4\pi r^2 nG(r)\right]$$

$G(r)$: *conditional pair-distribution function*

[S. Torquato, Phys. Rev. E **51**, 3170 (1995)]

■ gas-liquid coexistence curve



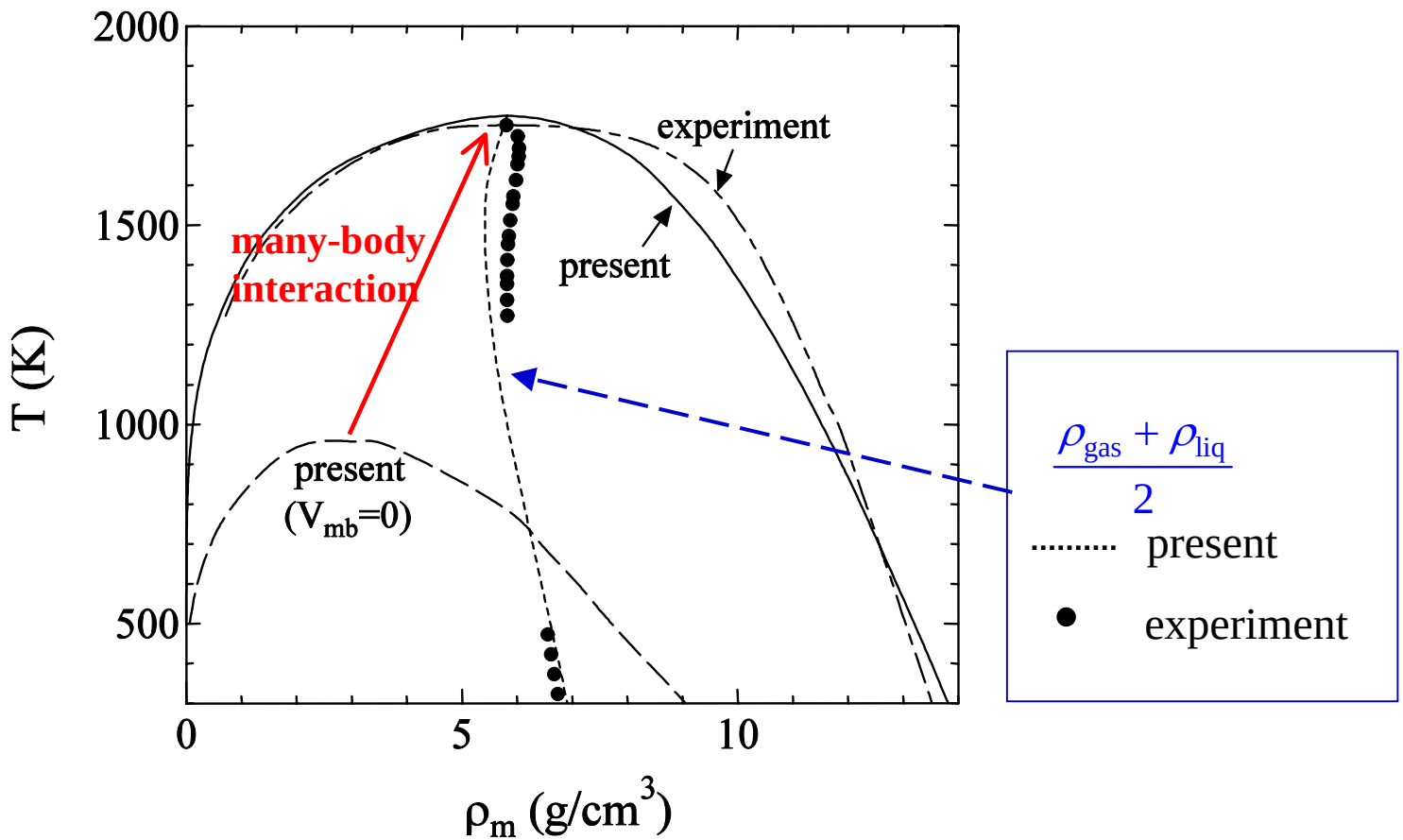
$$P = n^2 \left(\frac{\partial (F/N)}{\partial n} \right)_T$$

$P(\rho_{gas}, T) = P(\rho_{liquid}, T)$ pressure

$G(\rho_{gas}, T) = G(\rho_{liquid}, T)$ Gibbs free energy

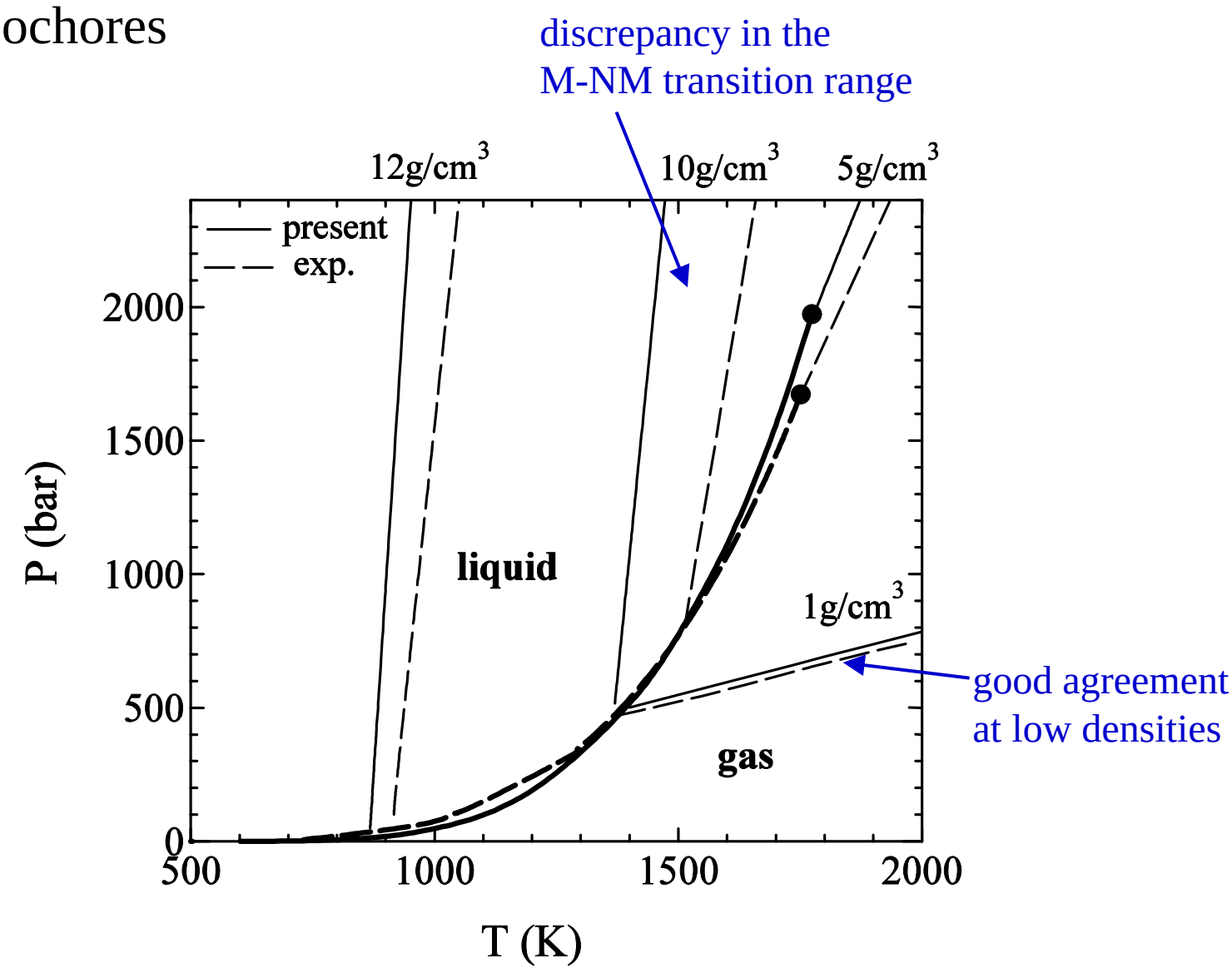
numerical results

- gas-liquid coexistence curves



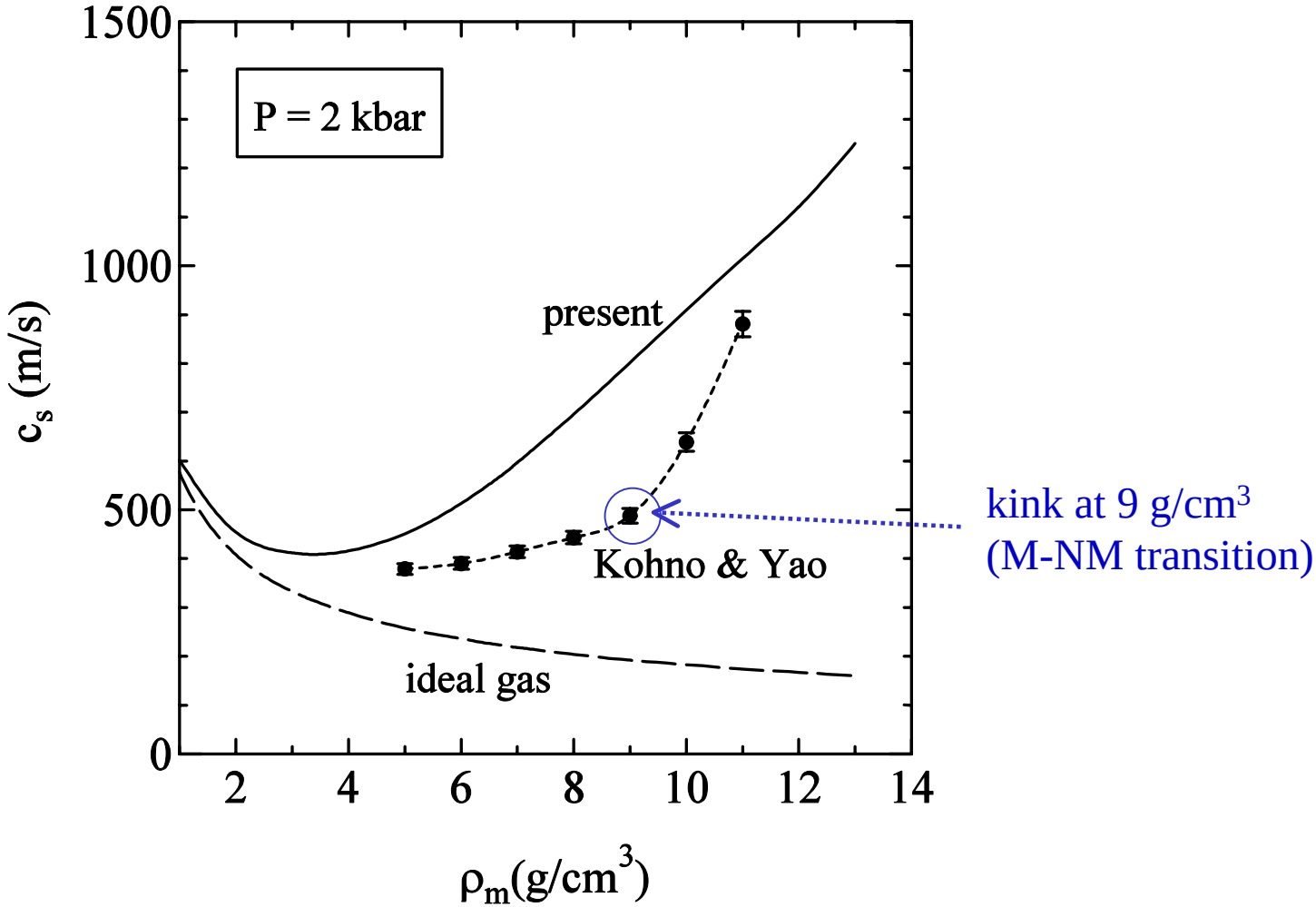
H. K., J. Phys.: Condens. Matter **19**, 072102 (2007)

- isochores



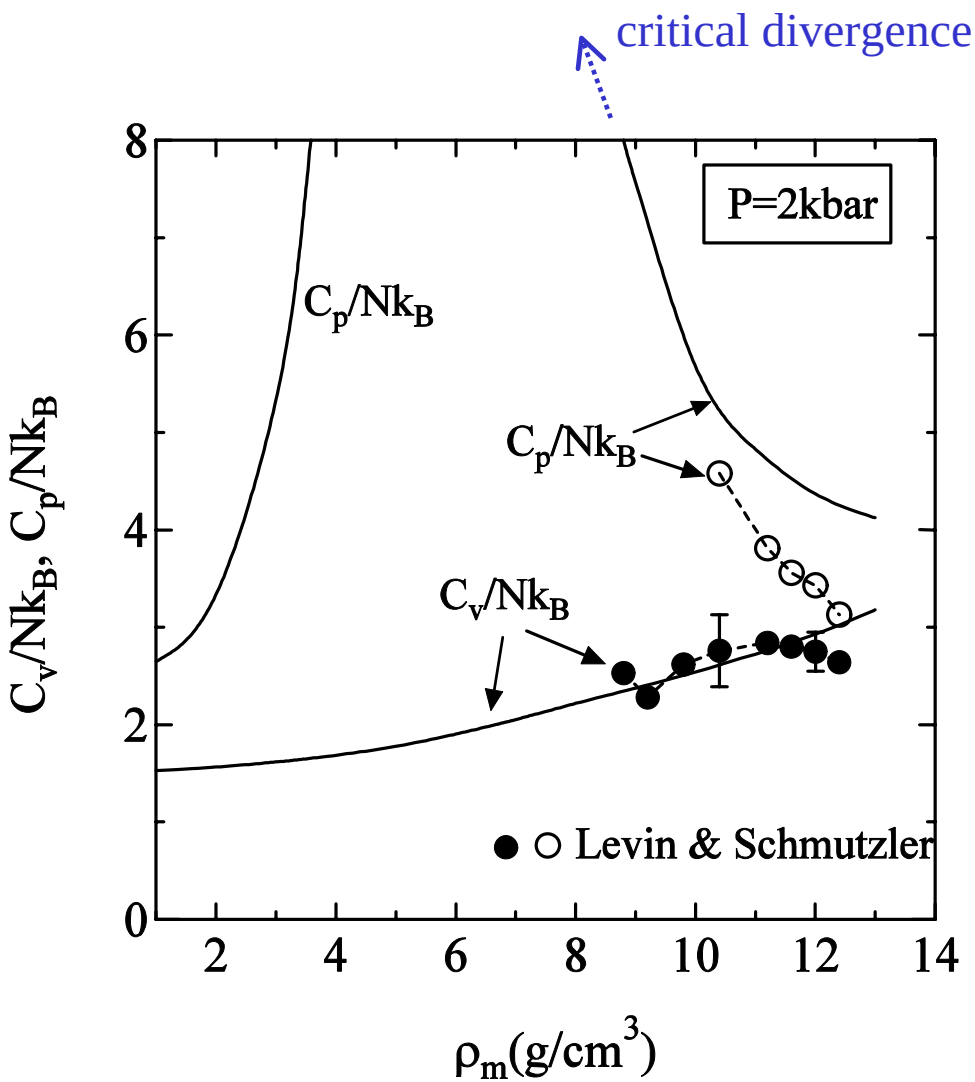
H. K., J. Chem. Phys. **126**, 134509 (2007)

- adiabatic sound velocity $c_s \equiv \sqrt{(\partial P / \partial \rho_{\mathrm{m}})_S}$



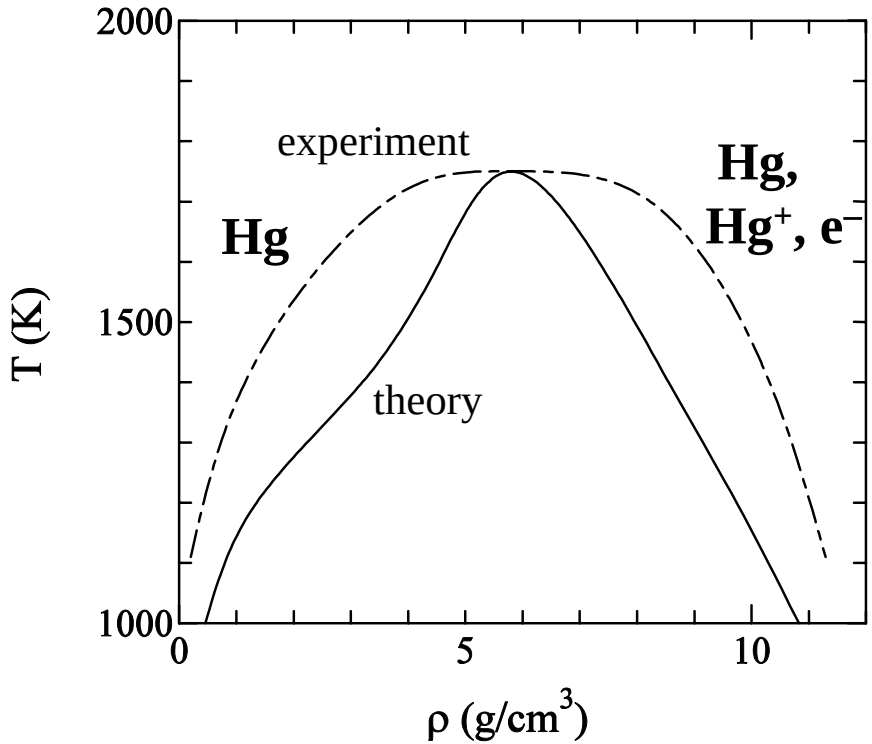
experiment --- H. Kohno & M. Yao, J. Phys.:Condens. Matter **11**, 5399 (1999)

- specific heat $C_V \equiv (\partial U / \partial T)_V$, $C_P \equiv (\partial U / \partial T)_P$



Calorimetric measurements
M. Levin & R.W. Schmutzler,
J. Non-Cryst. Solids **61&62**, 83 (1984)

■ Partially ionized plasma theory



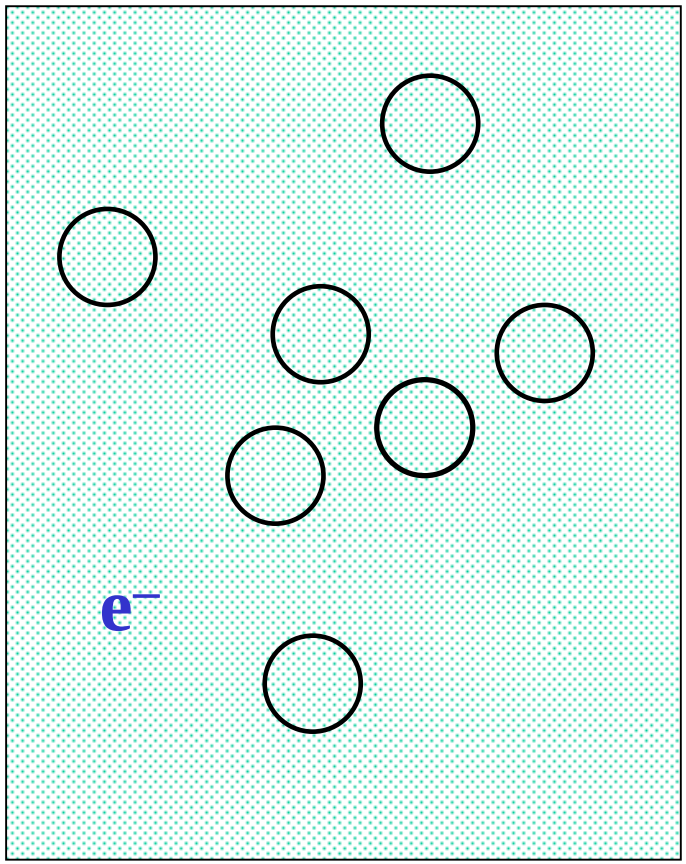
$$\mathrm{Hg} \leftrightarrow \mathrm{Hg}^{+} + e^{-}$$

The coexistence curve is ***too sharp.***

H.K., J. Phys.:Condens. Matter **15**, 6427 (2003)

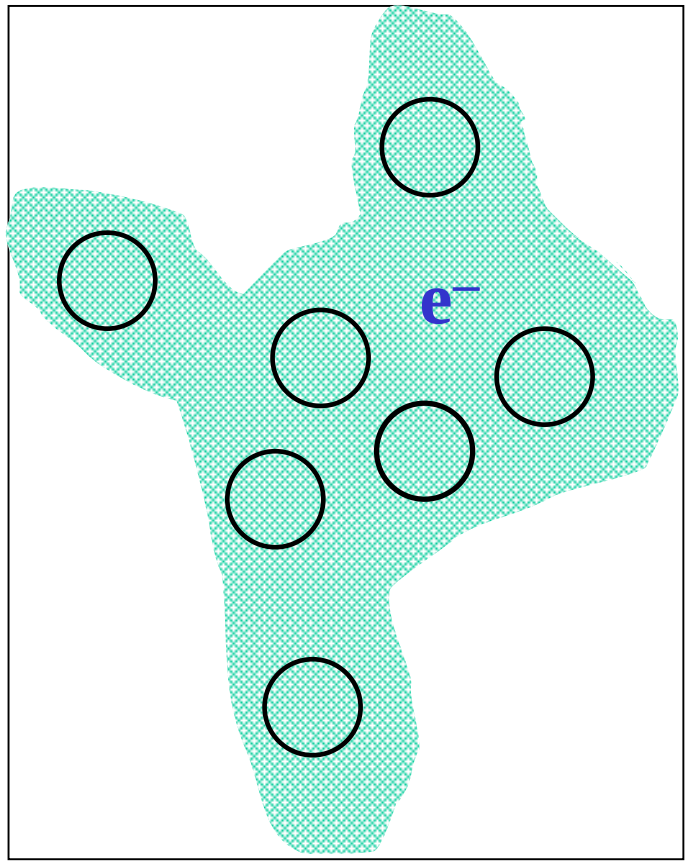
density distributions of conduction electrons

plasma theory



uniform

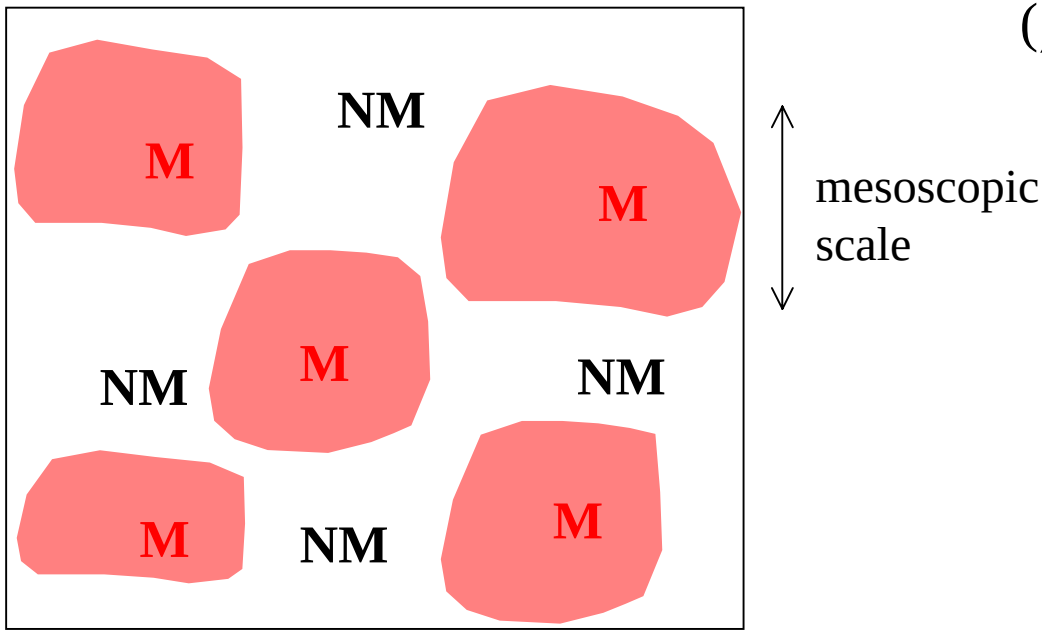
present theory



inhomogeneous

■ Possibility of **heterophase fluctuations** in the M-NM transition

($\rho \approx 9$ g/cm^3)

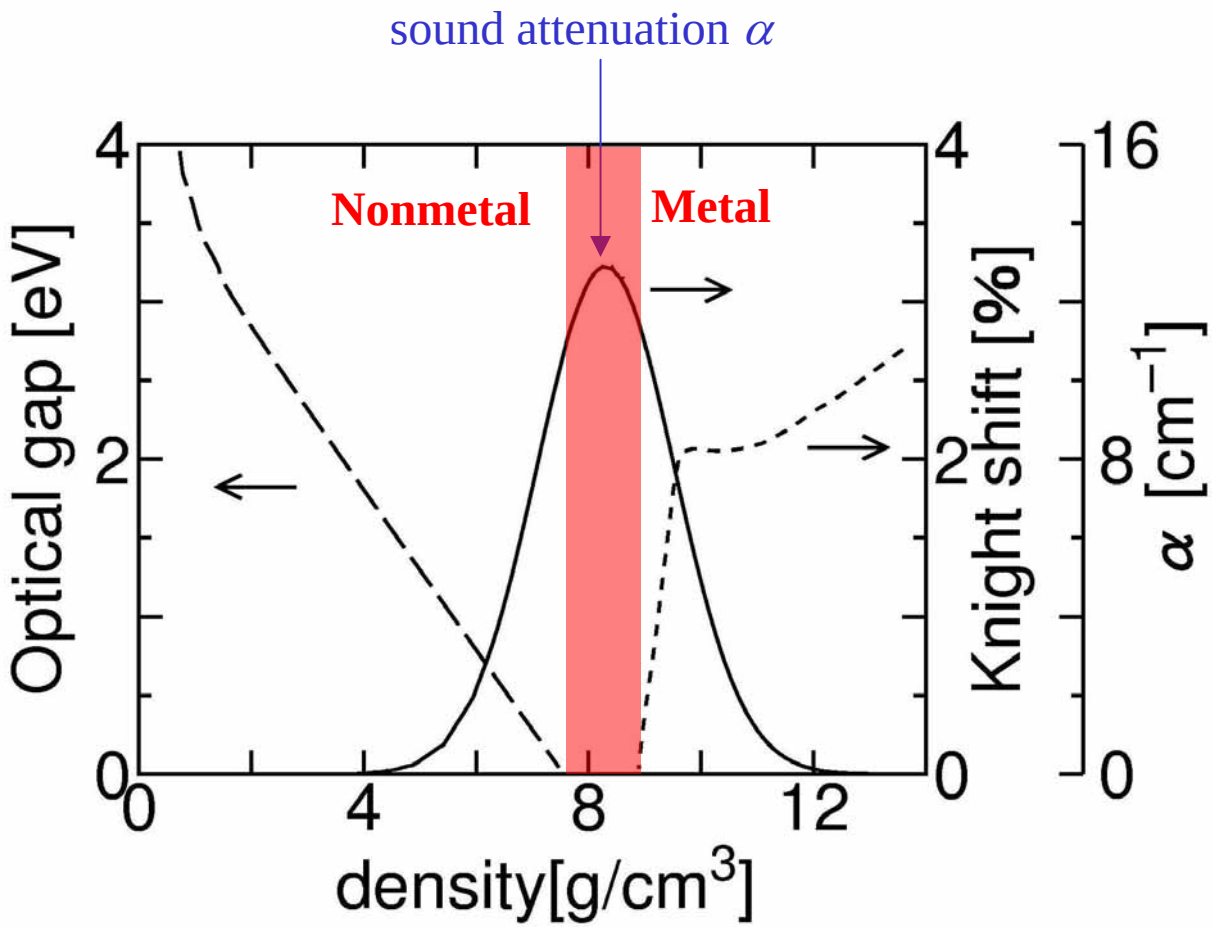


H.K., J. Phys.:Condens. Matter **15**, 6427 (2003)

<u>Metal-nonmetal transition: experimental evidence</u>

- thermodynamic quantities: **continuous**
- electrical conductivity: **continuous**
- **anomalous sound attenuation**
- **enhanced medium-range density fluctuations**

■ M-NM transition: ***anomalous sound attenuation***



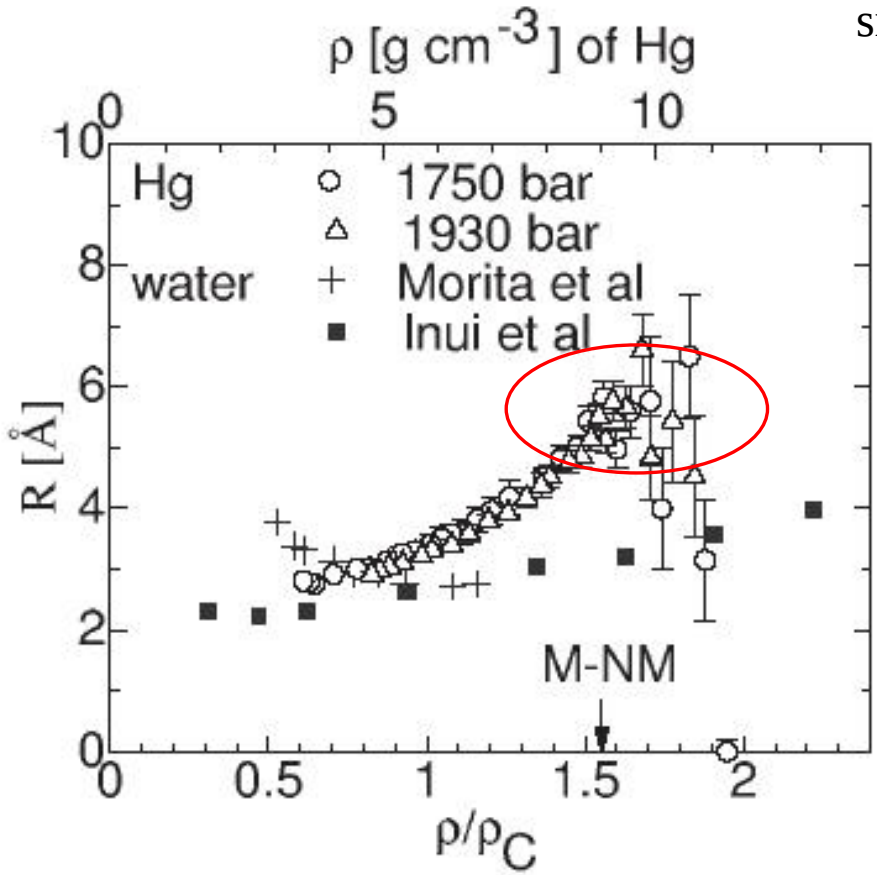
increase of bulk viscosity due to slow relaxation

Kohno & Yao, J. Phys.: Condens. Matter **13**, 10293 (2001)

M. Yao, Z. Phys. Chem. **185**, S73 (1994)

■ M-NM transition: ***medium-range fluctuations***

small-angle X-ray scattering experiment



enhancement of the correlation length

$$R \equiv \xi / \sqrt{S(0)}$$

$$S(k) = S(0)/(1+\xi^2 k^2)$$

static structure factor

Inui, Matsuda, Ishikawa, Tamura and Ohishi, Phys. Rev. Lett. **98**, 185504 (2007)

WDM as a basic science:

- Cross-hierarchical research

  microscopic, mesoscopic, macroscopic

- Theory of non-simple liquids

  cf. complex liquids (soft matter)

  simple material — monatomic system

  complex interaction — many-body potential