Fluctuation absorption of light near the critical point of mercury

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Abstract. The peculiarities of absorption spectra of low-density fluid mercury are connected with fluctuation clusters. The form of the fundamental absorption edge depends on the cluster distribution. The exponential edge is spread out because of the large-scale density fluctuations near the critical point.

Below the critical density, fluid mercury has a characteristic absorption spectrum of a dielectric, namely a transparency window and an exponential absorption edge at low photon energies. At low densities the transparency window width can be extrapolated to the resonance excitation energy of a mercury atom [1, 2], indicating that the absorption edge forms because the atom levels shift and broaden. As the density increases, the absorption edge gradually closes the transparency window (figure 1, [2]).

The apparent closing of the transparency window could be connected with the transition of fluid mercury to a metallic state. However, in mercury a Mott transition is well above the critical density [3]; consequently its influence is indirect. It has been shown that small quanta are absorbed by the fluctuation clusters, i.e. the atom density fluctuations [4].

Some insight can be gained by considering a quasiatomic structure and a polarization energy shift [5]. First of all, a cluster can be generally considered as an atomic fluid. However, the valence electron shells overlap and screen each other from the ions; so a notion of quasiatoms has to be used [6]. Low states of a quasiatom valence electron have a small admixture of free motion above a screened potential. Quasiatoms have a continuous internal-energy spectrum just above the ground-state level of free atoms. The other energy zone arises above the resonance level (figure 2).

The second point is a shift of the bottom of the resonance energy band with respect to the ground-state zone. It is mainly caused by polarization of some atoms in the Coulomb field of the ionic core of an excited atom. In a quasiclassical state the Coulomb field is fully screened near the boundary of the classical accessible region. Therefore atoms are polarized only within this sphere. The radius of the polarization sphere is

$$r_{pol} = e^2/(I - \varepsilon) \tag{1}$$

where e is the electron charge, I is the ionization potential and ε is the resonance excitation energy. Substituting in (1) the energy values, one can see that the polarization
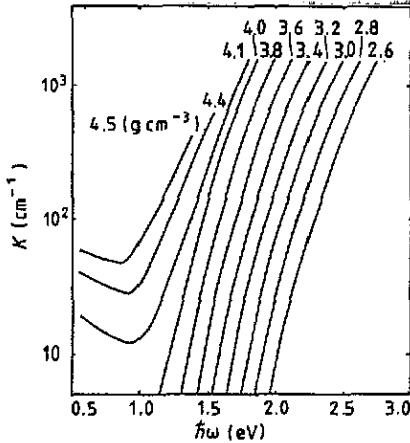
Figure 1. Experimental absorption spectra [2] of fluid mercury at $T = 1754$ K as a function of density $(\Delta T/T_c = 2.3 \times 10^{-3})$. The critical parameters are $T_c = 1751$ K and $\rho_c = 5.8\,\mathrm{g\,cm}^{-3}$.

radius is three times the ground-state radius of a mercury atom. So some atoms in the ground state are expected to be in the polarization sphere of an excited atom. The polarization shift increases directly as their number increases.

The gap between the bottom of the ground-state zone and the resonance energy zone is then

$$\Delta_s = \varepsilon - sq \tag{2}$$

where s is the number of atoms within the polarization sphere and q is the mean polarization energy of the atoms. Thus the gap depends mainly on the number s, whereas the dispersion around q is small. The random clusters obey the Poisson distribution

$$P_s = [(n_a\Omega_{pol})^s/s!]\,\exp(-n_a\Omega_{pol}) \tag{3}$$

where n_a is the atom density and Ω_{pol} is the volume of the polarization sphere. Of course, correlation can influence the probability distribution. Such an effect will be shown to be important near the critical point.

The small quanta $\hbar\omega < \varepsilon$ are mainly absorbed owing to transitions between the ground-state zone and the bottom of the resonance zone. Consider, at first, the transitions initiated from the bottom of the ground-state zone for $\hbar\omega = \Delta_s$. These transitions occur when the number of atoms in the polarization sphere is

$$s_0 = (\varepsilon - \hbar\omega)/q. \tag{4}$$

It follows that the smaller quanta can be absorbed by the larger clusters. According to the Poisson distribution, the number of large clusters falls exponentially. Therefore the absorption coefficient falls exponentially as the quantum value decreases.

In general, an initial state in the ground-state zone has the excitation energy ε_p, and so its population is proportional to $\exp(-\varepsilon_p/T)$, where T is the temperature, in accordance with the Boltzmann distribution. Because of the resonance condition $\varepsilon_p = \Delta_s - \hbar\omega$, the Boltzmann factor is proportional to $\exp(\hbar\omega/T)$; therefore at any $s < s_0$ the absorption falls exponentially when the quantum value decreases as well. This is the reason for the exponential edge.

Near the critical point a plateau in the absorption spectra has been observed in addition to the exponential edge (figure 1). It seems to be another process, e.g. the
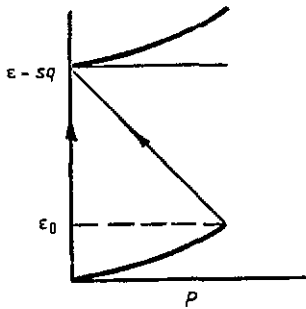
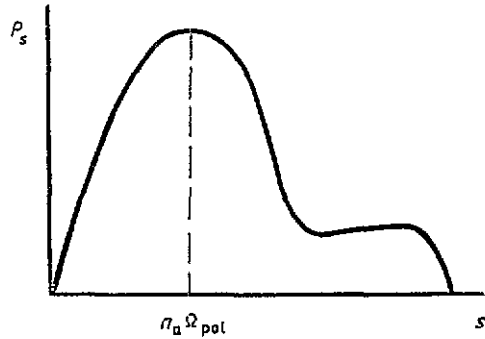**Figure 2.** Energy zones of quasiatoms.   **Figure 3.** Probability distribution of clusters.

absorption by the free electrons [7]. Because the electrical conductivity is small, this has met with difficulties. Another supposition, namely absorption by the excess electrons in the atomic clusters, is generally accepted [8]. However, it was not really verified by comparison between theory and experiments. This interpretation is not necessarily true. It will be shown that the plateau of the absorption spectra can be explained without assuming excess electrons in the clusters.

So far, the explanations have not taken account of the proximity of the critical point. As is well known, near the critical point, large-scale fluctuations increase anomalously. Critical fluctuations radically change the cluster distribution. This might be one reason for the absorption edge spread, i.e. plateau formation. Thus critical fluctuations can influence the broaden resonance absorption. It is worth noting that scattering of light (critical opalescence) plays a minor role.

In the vicinity of the critical point, long-range density fluctuations arise, i.e. a fluid is not homogeneous on a small scale. The maximum size of the fluctuations is the correlation radius r_c, which diverges at the critical point. When $r_{pol} < r_c$, the cluster distribution has two maxima as is expected for a two-phase system [9]. At the critical point, as the maxima are linked together, the cluster distribution has a plateau. Such distributions have been studied for a lattice gas model [10]. Not too close to the critical point, these are similar to the Poisson distribution with a shoulder on the decreasing branch (figure 3). The shoulder width is limited by the finite size of atoms.

The absorption spectrum is formed by overlapping bands of different clusters. The shoulder of the cluster distribution gives rise to the plateau in the absorption spectrum in the corresponding range (equation (4)):

$$K_\omega = 2\pi^2 (e^2/mc) f_{01} (\hbar/q) P_{sh} n_a \tag{5}$$

where m is the electron mass, c is the velocity of light and f_{01} is the oscillator strength of the resonance transition. The factor $\hbar/q$ is the density of the bands. For rough estimates of P_{sh} equation (3) can be used for $s = (\varepsilon - \hbar\omega_0)/q$, where $\hbar\omega_0$ is the limit of the edge.

A phenomenological description can be based on the fluctuation theory of the critical point. The critical fluctuations are described by the total order parameter [9]. Its modulus i.e. the root mean square value, is

$$\Phi_c = \left(\int_{\Omega_c} \langle [n(r) - n_c][n(r') - n_c] \rangle \, dr \, dr' \right)^{1/2} \propto r_c^{d/2+1-\eta/2} \tag{6}$$

where $n(r)$ is the local density, n_c is the critical density and the integration is over the

correlation volume Ω_c. The exponent on the right-hand side is the fractal dimensionality of the density fluctuations; there the space dimensionality $d = 3$ and the critical index η of the correlation radius is 0.05. By definition, Φ_c represents the variation in the number of atoms in the correlation volume. As the point of phase transition is approached along the critical isochor, the liquid phase occurs and the order parameter appears to be not zero simultaneously. So, Φ_c can be used as a measure of the quantity of liquid phase within the correlation volume.

One can suppose that the shoulder level of the cluster distribution is proportional to the modulus of the total order parameter:

$$P_{sh} \propto \Phi_c \tag{7}$$

for the following reasons. If r_{pol} and r_c are of the same order of magnitude ($r_{pol} \gtrsim r_c$), Φ_c can be used as a measure of the quantity of liquid phase within the polarization sphere as well. It follows that

$$\int P_{sh} \, ds \propto \Phi_c.$$

Because the shoulder width is limited, P_{sh} varies directly as Φ_c (equation (7)).

When r_c is much greater than r_{pol}, the dependence of the probability P_{sh} upon Φ_c saturates. At the critical point, r_c and Φ_c diverge, whereas P_{sh} approaches a finite limit. So, a finite variation in the function $P_{sh}(\Phi_c)$ is spread over an infinite interval of the argument. In this case the proportionality relation (7) take place even though r_c exceeds r_{pol}.

We are in a position now to express the probability P_{sh} through the thermodynamic variables. According to theory of phase transitions, in an external field h the correlation volume acquires the additional energy $-h\Phi_c$. A strong external field thus influences the fluctuations. The modulus of the total order parameter is then $\Phi_c \simeq T_c/h$, where T_c is the critical temperature. In the critical-point theory, the formal external field h is given by the expression $\Delta p - b \, \Delta T$, where Δp and ΔT are the pressure and the temperature minus their critical values. Far from the line, $h = \Delta p - b \, \Delta T = 0$, i.e. the critical isochor and the boundary of the two-phase region, we have

$$\Phi_c \propto n_c T_c/|\Delta p - b \, \Delta T|. \tag{8}$$

Substituting (8) in (7), we have on the critical isotherm and not too close to the critical point

$$P_{sh} \propto |\Delta p|^{-1} \propto |\Delta n|^{-\delta} \tag{9}$$

where Δn is the difference between the density and its critical value, and the critical index $\delta = 4.8$. The second proportionality follows from the definitions [11].

As stated above, the plateau of the absorption spectra varies as the shoulder of the cluster distributions. Therefore the absorption coefficient is described by the same power law (9).

Recently, the absorption spectra of fluid mercury near the critical isotherm have been measured at densities below the critical density [2]. These data are compared with the scaling law in figure 4 and are shown to agree. The estimate of the absorption coefficient from equation (5) also seems to be reasonable even though only indirect estimation of P_{sh} can be used (as $\rho = 4 \text{ g cm}^{-3}$ and $s_0 = 15$, $P_{sh} \simeq 10^{-6}$ and $K_\omega \simeq 5 \text{ cm}^{-1}$).
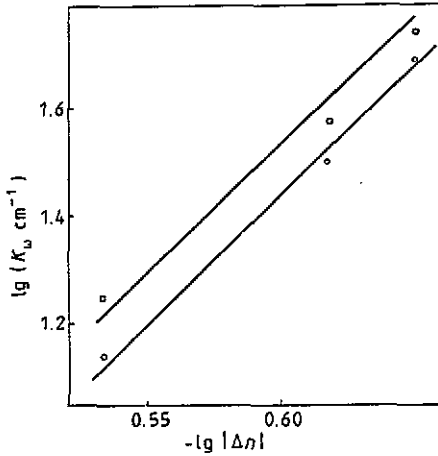
Figure 4. The absorption coefficient of the photons $\hbar\omega = 0.6$ eV ($\square$) and $\hbar\omega = 0.75$ eV ($\bigcirc$) by fluid mercury at $T = 1754$ K. The points have been taken from figure 1; the slopes of the lines correspond to the law $K_\omega \propto |\Delta n|^{-\delta}$, $\delta = 4.8$.

Using an expansion of the scaling equation of state, one can consider the temperature dependence of the absorption coefficient. Near the critical isotherm we have

$$P_{\text{sh}} \propto |\Delta n|^{-\delta}(1 - A\,\Delta T|\Delta n|^{-1/\beta} + \ldots) \tag{10}$$

where the critical index β of the order parameter is 0.34; A is a positive amplitude. It follows from (10) that

$$[\partial \ln P_{\text{sh}}/\partial T]_{T=T_c} \propto -|\Delta n|^{-1/\beta} \tag{11}$$

and the same law holds for the logarithm derivative of the absorption coefficient. So, the absorption coefficient increases as the temperature is lowered. It can be seen from (11) that the temperature dependence becomes greater as the critical point is approached. Additional experimental data are needed for a quantitative comparison with (11).

In conclusion, the resonance absorption due to transitions between the two energy zones was considered. The exponential absorption edge in fluid mercury is spread out by the critical fluctuations. Scaling laws are proposed for the absorption coefficient near the exponential edge.

References

[1] Uchtmann H and Hensel F 1975 *Phys. Lett.* 53A 239
[2] Uchtmann H, Brasious U, Yao M and Hensel F 1988 *Z. Phys. Chem.* 156 151
[3] Schonherr G, Schmutzler R W and Hensel F 1979 *Phil. Mag.* B 40 411
[4] Bhatt R N and Rice T M 1979 *Phys. Rev.* B 20 466
[5] Likalter A A 1988 *Thermophys. High Temp.* 26 707 (in Russian)
[6] Likalter A A 1988 *Sov. Phys.–JETP* 67 2478
[7] Hensel F 1976 *Liquid Metals, Proc. 3rd Int. Conf. (Bristol, 1976) (Inst. Phys. Conf. Ser. 30)* (Bristol: Institute of Physics) p 372
[8] Uchtmann H, Hensel F and Overhof H 1980 *Phil. Mag.* B 42 583
[9] Patashinsky A Z and Pokrovsky V L 1982 *Fluctuation Theory of Phase Transitions* (Moscow: Nauka)
[10] Guemez J, Velasco S and Hernandez A C 1988 *Physica* A 152 226
[11] Landau L D and Lifshitz E M 1976 *Statistical Physics* (Moscow: Nauka) p 1