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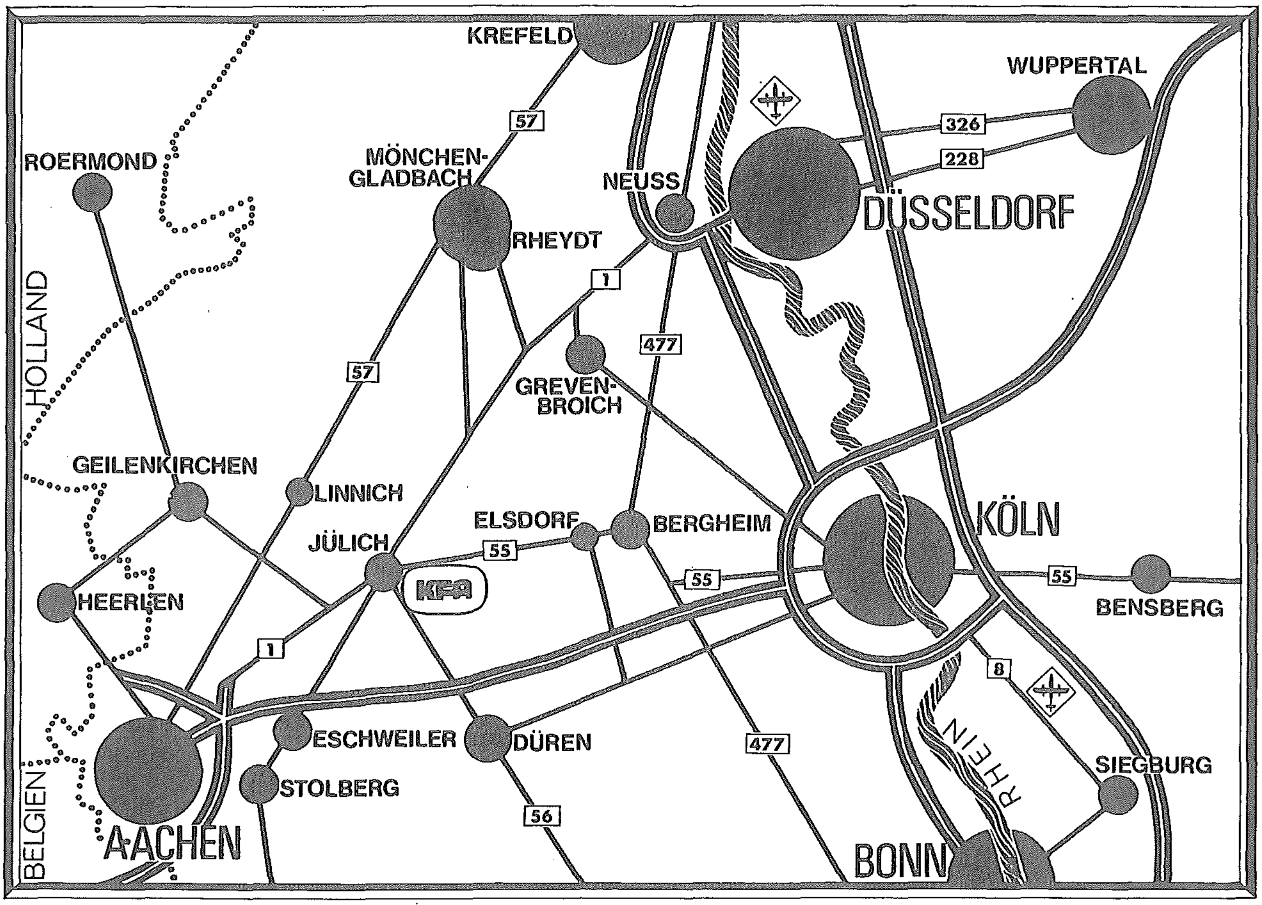
Jül - 1039 - FF
Januar 1974

Als Manuskript gedruckt



Berichte der Kernforschungsanlage Jülich - Nr. 1039
Institut für Festkörperforschung Jül - 1039 - FF

Dok.: Metal-Hydrogen Systems - Elastic Interaction
Metal-Hydrogen Systems - Phase Transition

Im Tausch zu beziehen durch: ZENTRALBIBLIOTHEK der Kernforschungsanlage Jülich GmbH,
Jülich, Bundesrepublik Deutschland

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Abstract

We study the statistical mechanics of hydrogen dissolved in metals. The underlying model is based on the assumption that the dominant attractive interaction between the protons in the metal is of elastic nature.

In the first part of the paper we review some general properties of the elastic interaction. We then discuss the importance of boundary conditions for the form of the elastic interaction, which turns out to be of the Curie-Weiss type with macroscopic range.

In the second part we investigate the α-α' ("gas-liquid") phase transition in the hydrogen lattice fluid. The long-range part of the elastic interaction is treated in mean field approximation. In the canonical ensemble as opposed to the grand canonical ensemble one finds no coexisting phases near the critical point. Instead there is a continuous transition which changes into a first-order transition at tricritical points. In the temperature-density region which normally corresponds to the two-phase coexistence region the hydrogen density is inhomogeneous and varies on a macroscopic scale.

The peculiar nature of the α-α' phase transition is due to the long-range character of the elastic interaction, which ultimately results from the requirement of coherency of the host crystal. We argue that coherent metal-hydrogen systems offer examples of real systems where the classical theory of phase transitions applies.

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§ 1 Introduction

Hydrogen dissolves exothermally in many metals. Important examples are the transition metals V, Nb, Ta and Pd, which show the highest solubility. In metallic solution the hydrogen molecule dissociates, donating its electrons to the conduction band, and the protons occupy interstitial sites.

Two important features distinguish metal-hydrogen systems from metallic solutions of heavier elements such as oxygen and nitrogen:

1. Solubility. The amount of hydrogen in the metals can be varied to a large extend. Concentrations up to 100 atomic per cent (i.e. one proton per metal ion) can be obtained.
2. Mobility. At lower concentrations the protons are rather mobile. Jump rates of the order of 10^{11} jumps/sec. at room temperature are observed. This is comparable to the mobility of water molecules in liquid water.

For heavier impurities the maximum concentration is limited to a few atomic per cents (typically less than 10 at.%) and the mobility at room temperature is about eight to ten orders of magnitude smaller.

Because of its high mobility the hydrogen fluid readily attains thermal equilibrium with the metal lattice and its thermodynamic properties can therefore be studied over a wide range of temperature and concentration.

For higher concentrations the interaction between the protons is no longer negligible and the hydrogen system is expected to behave like a nonideal liquid or gas. The phase diagram (Fig 1) of Nb-H, for example, as obtained from x-ray methods and solubility measurements is indeed identical in its general features to phase diagrams of normal one-component liquids. For concentrations $c < 0.8$ three phases of the hydrogen system are observed: a gaseous (α), a liquid (α') and a solid (β) phase. There is a triple point T_t and a critical point T_c. In the β-phase the subset of occupied interstitial sites forms a superlattice with long-range order, whereas in the α- and α'-phase all possible sites are occupied at random.

It is obvious that we are dealing with a physical system which resembles the lattice-gas model of fluids. The question then arises: what is the nature of the (attractive) interaction between protons which produces the gas-liquid phase transition?

The bare Coulomb potential of the protons is screened by the electrons of the metal. For the transition metals quantitative calculations of the screened potential are very difficult. Qualitatively we expect a predominantly repulsive interaction for small separation of the protons and a decaying oscillatory interaction at larger distances.

Even if we could solve the screening problem it would give us the electronic interaction between the protons only for dilute solutions. For higher concentrations, $c > 0.1$ H/Nb say, the proton liquid interpenetrating the metal lattice will give rise to a new electronic band-structure which is probably quite different from the band-structure of the pure host metal. As far as we know it is an open question at present whether the electronic interaction of protons in Nb for instance can account for the α- α' phase transition and the high value of $T_c \approx 450\ ^{\circ}K$.

There is one rather obvious but nevertheless important difference between the usual lattice-gas model and a real metal-hydrogen system which involves the role of host lattice: the real metal lattice is deformable, and the protons induce long-ranged strain fields in it. The elastic energy of the strained crystal is equivalent to an effective interaction between protons. This elastic interaction turns out to be attractive in crystals with a free surface, and it has been suggested (G. Alefeld 1969, 1972) that it is responsible for the gas-liquid phase transition of metallic hydrogen solutions.

The purpose of this paper is to study the elastic interaction between interstitial impurities in crystals in some detail. On the basis of the hypothesis that the elastic interaction is the dominant attractive interaction in metal-hydrogen systems, we investigate some of the unusual features of the gas-liquid phase transition which are a consequence of the long-range nature of this interaction.

The elastic interaction between lattice inhomogeneities has been studied extensively in the past. For the work based upon continuum elasticity theory we refer to Eshelby (1956) and to a more recent review by Siems (1968). Elastic degrees of freedom and the associated elastic interaction play an important role in Cahn's theory of spinodal decomposition

(Cahn 1961, 1962), and in the theory of structural and order-disorder phase transitions (Krivoglaz 1963, Khachaturyan 1966). The elastic interaction between point defects in harmonic crystals has been investigated by Hardy and Bullough (1967) on the basis of the microscopic theory of lattice statics. Cook and DeFontaine (1969, 1971) have studied the elastic free energy of solid solutions in the same framework.

This list of references is, of course, not complete. We only mentioned literature which bears some resemblance to our work here.

In most of the previous treatments of the elastic interaction either an infinite lattice or a lattice with periodic boundary conditions was assumed. For a system interacting via short-range forces the specific form of boundary conditions (i.e. the shape of the system) is of minor importance for the calculation of bulk properties. The free energy, for instance, is normally independent of the boundary condition in the thermodynamic limit. This is no longer true in the case of the elastic interaction, as we shall see.

The outline of the paper is as follows: In § 2 we introduce a lattice model for hydrogen in metals which is based on the assumption that the effect of protons on the metal ions can be described by forces which are linear in the density of protons. After elimination of the lattice degrees of freedom we obtain an effective interaction between protons which defines the elastic interaction. For later use we also give the continuum form of the model. One basic and experimentally accessible quantity entering into the theory is the force-dipole tensor. In § 3 it is shown that the familiar connection between the trace of the force-dipole tensor and the total volume change caused by the hydrogen load can also be derived from lattice statics. In § 4 we discuss the properties of the elastic interaction with special emphasis on its dependence on boundary conditions. The elastic degrees of freedom of a lattice with periodic boundary conditions are uniquely given by plane waves or phonons. For other boundary conditions (e.g. free surface) additional modes exist, which we call macroscopic modes because of their dependence on the shape of the crystal. These modes are discussed in subsection 4.3. Their spectrum and the resulting elastic interaction are then calculated in § 5 for a spherical crystal. In § 6 we study the free energy which is given as the sum of two parts: a "reference" free energy arising from the phonon modes and the electronic repulsion, and an elastic energy due to the macroscopic modes. The latter is of the Curie-Weis type. We argue that the molecular field treatment of this elastic energy with its macroscopic range should give the exact free energy. The α-α' phase transition is investigated in § 7. In § 8 we conclude with a brief discussion of the importance and implications of the requirement of coherency.

§ 2 Model for Metal-Hydrogen Systems

We consider a metal with N_L metal ions and N protons (or deuterons). Let us suppose that the electronic degrees of freedom have been taken into account within an adiabatic approximation. We are interested in the equilibrium properties of this system in a temperature range where classical statistics is assumed to be valid. Therefore we only need to consider the total potential energy of the protons and the metal ions which will consist of three parts: the potential energy $\Phi(Y)$ of the metal, the interaction $\Psi(X,Y)$ between protons and metal ions and the electronic interaction U(X) between protons. The configurations of protons and metal ions are symbolized by $X = \{\underline{X}^a\}$ and $Y = \{\underline{Y}^m\}$ respectively with $a = 1,...,N$ and $m = 1,..,N_L$.

2.1 Lattice Model

The metal lattice will be described in the harmonic approximation. The rest positions of the metal ions in the pure lattice (i.e. without protons) are denoted by $\underline{R}^m$ and the displacements by $\underline{v}^m$. The pure host lattice is taken as the reference system. The protons occupy interstitial sites which are defined by the rest positions $\underline{Q}^a$ and the displacements $\underline{u}^a$ with respect to the reference system. Thus

$$\underline{X}^a = \underline{Q}^a + \underline{u}^a \quad , \quad \underline{Y}^m = \underline{R}^m + \underline{v}^m \quad . \qquad (2\text{-}1)$$

We then have (with the summation convention)

$$\phi(Y) = \phi(R) + \phi^m_\mu(R)\, v^m_\mu + \frac{1}{2} v^m_\mu \phi^{mn}_{\mu\nu} v^n_\nu \quad . \tag{2-2}$$

The configuration of the protons is described by a set of occupation numbers $\tau = \{\tau_a = 0,1\}$ with $\tau_a = 1$ if the site $\underline{Q}^a$ is occupied. Lack of detailed information leads us to assume for $\Psi(X,Y)$ to be a sum of two-body central potentials

$$\Psi(X,Y,\tau) = \sum_{am} \psi(|\underline{X}^a - \underline{Y}^m|)\, \tau_a \,, \tag{2-3}$$

which is also expanded in powers of the displacements $\underline{u}^a$ and $\underline{v}^m$. We keep only linear terms and hence

$$\Psi(X,Y,\tau) = \Psi(R,Q,\tau) + \Psi^a_\alpha(R,Q,\tau)\, u^a_\alpha + \Psi^m_\mu(R,Q,\tau)\, v^m_\mu \,, \tag{2-4}$$

where, for example,

$$\Psi^m_\mu(R,Q,\tau) = \sum_a \partial^m_\mu \psi(|\underline{Q}^a - \underline{R}^m|)\, \tau_a \equiv \Psi^{ma}_\mu \tau_a \,, \tag{2-5}$$

with $\partial^m_\mu = \partial/\partial R^m_\mu$.

The rest positions $\underline{Q}^a$ and $\underline{R}^m$ are determined from the requirement that the forces on the metal ions and protons vanish in this configuration,

$$\underline{\phi}^m(R) = 0 \,, \quad \underline{\Psi}^a(R,Q,\tau) = 0 \quad . \tag{2-6}$$

Two comments should be made here:

1. We assume the protons to be well localized and in writing $\Psi(X,Y,\tau)$ in the form of eq. (2-3) we only take into account the ground state of a localized proton. The experimentally observed excited localized mode of protons in Nb, for instance, has an excitation energy of about 0.1 eV . In the temperature range around T_c this mode can be neglected.

2. We keep only leading terms in the expansion of Φ and Ψ in powers of the displacements. Since $\underline{\Psi}^m(\tau) \neq 0$ there is a linear term in eq. (2-4) whereas the linear term in the expansion of Φ, eq. (2-2), vanishes because of $\underline{\Phi}^m = 0$. The neglected quadratic terms in Ψ renormalize the force-constants $\Phi^{mn}_{\mu\nu}$. The second derivatives of $\psi(|\underline{Q}^a - \underline{R}^m|)$ which enter into these quadratic terms can be obtained by fitting the frequency of the localized mode. We have estimated the change of the elastic constants caused by the modification of $\Phi^{mn}_{\mu\nu}$ to be of the order of a few per cent.

The basic approximation of our model lies in the assumption that the effect of protons on the metal ions can be described by linear forces (Kanzaki (1957)) which allow superposition. This linear force model has also been employed by others (e.g. Hardy and Bullough (1967)).

Some general properties of the coefficients $\underline{\Phi}^{mn}$ and $\underline{\Psi}^m$ will be required later. They are

$$\sum_m \phi^{mn}_{\mu\nu} = 0 = \sum_n \phi^{mn}_{\mu\nu} \quad , \quad \sum_n \phi^{mn}_{\mu\nu} R^n_\alpha = \sum_n \phi^{mn}_{\mu\alpha} R^n_\nu \quad , \qquad (2\text{-}7)$$

and

$$\sum_m \Psi^m_\mu(\tau) = 0 \; , \quad \sum_m \Psi^m_\mu(\tau) R^m_\nu = \sum_m \Psi^m_\nu(\tau) R^m_\mu \; . \qquad (2\text{-}8)$$

These relations follow from the invariance of the total potential energy with respect to translations and rotations of the whole crystal together with eq. (2-6). In addition we have $\Phi^{mn}_{\mu\nu} = \Phi^{nm}_{\nu\mu}$.

The various possible interstitial sites $\underline{Q}^a$ are characterized by their point-group symmetry. Experiments indicate that the hydrogen occupies octahedral sites in fcc Pd (Worsham et al. (1957)) and tetrahedral sites in bcc Nb (Somenkov et al (1968)) and we shall only consider these two cases (see Fig 2a,b).
In the cubic elementary cell there are four sites in the fcc lattice and twelve sites (four of each type j = x,y,z) in the bcc lattice. We denote by N_H the total number of sites and by N_{Hj} the number of tetrahedral sites of type j. Then $N_H = N_L$ for fcc-octahedral sites and $N_H = 6N_L$, $N_{Hj} = 2N_L$ for bcc-tetrahedral sites.
We still have to consider the electronic interaction U(X) which is assumed to be short-ranged and predominantly repulsive. The electronic effect of the protons in Nb is believed to be screened out beyond a distance of about one metal-metal spacing. We make the rather crude assumption that U(X) can be replaced by a hard-core repulsion and set

$$U(X,\tau) = \frac{1}{2}\sum_{ab} U_{ab}\,\tau_a \tau_b \equiv U(\tau) \quad . \qquad (2\text{-}9)$$

The hard-core assumption for U(X) is not essential in the following discussion, but we point out that in writing U(X) in the form of eq. (2-9) we neglect any dependence of U on displacements $\underline{u}^a$.

Summing up the various contributions we obtain the following Hamiltonian for the metal-hydrogen system:

$$H_{tot} = \Phi + \frac{1}{2}\underline{v}^m \cdot \underline{\underline{\Phi}}^{mn} \cdot \underline{v}^n + U(\tau) + \Psi(\tau) + \underline{\Psi}^m(\tau) \cdot \underline{v}^m \quad . \tag{2-10}$$

We eliminate the last term on the right with a shift in the displacements. Formally, this corresponds to a canonical transformation of H_{tot} (see e.g. Wagner and Swift (1970)). The physical interpretation of this procedure is as follows: the displacements $\underline{v}^m$ consist of two parts

$$\underline{v}^m = \underline{v}^m_{el}(\tau) + \underline{v}^m_{vib} \quad . \tag{2-11}$$

The part $\underline{v}^m_{el}(\tau)$ describes the elastic deformation which is caused by the hydrogen in the configuration $\{\tau_a\}$. The sites $\underline{R}^m + \underline{v}^m_{el}(\tau)$ are the equilibrium or "relaxed" positions of the metal ions for given $\{\tau_a\}$. The metal ions vibrate around these relaxed positions with displacements $\underline{v}^m_{vib}$ having a time-average $\overline{\underline{v}^m_{vib}} = 0$. The displacements $\underline{v}^m_{el}(\tau)$ are determined from the condition that the time-averaged force $\overline{(\partial H_{tot}/\partial v^m_\mu)}$ on each metal ion vanishes. This leads to

$$\underline{\underline{\Phi}}^{mn} \cdot \underline{v}^n_{el} = -\underline{\Psi}^m(\tau) = -\underline{\Psi}^{ma}\tau_a \quad . \tag{2-12}$$

We define the inverse[†] $\underline{\underline{D}}^{mn}$ of the matrix $\underline{\underline{\Phi}}^{mn}$ by

$$\phi^{ml}_{\mu\lambda} D^{ln}_{\lambda\nu} = -\delta^{mn}_{\mu\nu} \equiv -\delta_{\mu\nu}\left(\delta_{mn} - \frac{1}{N_L}\right) , \quad D^{mn}_{\mu\nu} = D^{nm}_{\nu\mu} , \tag{2-13}$$

and obtain from eq. (2-12)

$$\underline{v}^{m}_{el}(\tau) = \underline{\underline{D}}^{mn} \cdot \underline{\Psi}^{n}(\tau) \quad . \tag{2-14}$$

With the help of eqs. (2-11) and (2-14) the Hamiltonian can be rewritten in the form

$$\begin{aligned} H_{tot} &= \Phi + \frac{1}{2}\, \underline{v}^{m}_{vib} \cdot \underline{\underline{\Phi}}^{mn} \cdot \underline{v}^{n}_{vib} \\ &\quad + U(\tau) + \Psi(\tau) + \frac{1}{2}\, \underline{\Psi}^{m}(\tau) \cdot \underline{\underline{D}}^{mn} \cdot \underline{\Psi}^{n}(\tau) \\ &\equiv H_L + H(\tau) \quad . \end{aligned} \tag{2-15}$$

The original hydrogen-lattice interaction has been transformed into a direct interaction between protons and the phonons have been decoupled from the hydrogen system.

2.2 Continuum Model

The Hamiltonian (2-15) is now in a suitable form for calculating the free energy of the hydrogen system. Apart from the statistical problem involved in the evaluation of the partition

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[†] Because of eq. (2-7) the inverse of $\underline{\underline{\Phi}}^{mn}$ exists only in the subspace of vectors $\underline{V}^m$ with $\sum_m \underline{V}^m = 0$. Therefore the projection operator $\delta^{mn}_{\mu\nu}$ on this subspace enters into eq. (2-13).

function for a given interaction we are faced here with an additional difficulty. The lattice Green's function (static phonon propagator) $\underline{\underline{D}}^{mn}$ turns out to be a quantity which is sensitive to boundary conditions and depends upon the shape of the crystal. It is rather difficult in general to calculate $\underline{\underline{D}}^{mn}$ for a finite discrete lattice. However, some progress can be made if one goes over to a continuum description. One essential restriction of this approach is then in the assumption that the density $\rho(\underline{r})$ of protons is a smoothly varying function.

Let us now write down the continuum version of the model, starting from the "elastic" part of the Hamiltonian, eq. (2-10),

$$H_{el} = \frac{1}{2} \underline{v}^m \cdot \underline{\underline{\phi}}^{mn} \cdot \underline{v}^n + \underline{\Psi}^m(\tau) \cdot \underline{v}^m \quad . \tag{2-16}$$

Here and in what follows we always understand $\underline{v}^m$ to mean $\underline{v}^m_{el}(\tau)$. If the hydrogen distribution is described by a macroscopically varying density we may also replace $\underline{v}^m$ by a slowly varying displacement field $\underline{v}(\underline{r})$. After some manipulations which are outlined in appendix A we obtain H_{el} in the continuum form

$$H_{el} = \frac{1}{2} \int \varepsilon_{\alpha\beta}(\underline{r})\, C_{\alpha\beta\mu\nu}\, \varepsilon_{\mu\nu}(\underline{r})\, d\underline{r} + \int \Pi_{\alpha\beta}(\underline{r})\, \varepsilon_{\alpha\beta}(\underline{r})\, d\underline{r} \ . \tag{2-17}$$

The various quantities in eq. (2-17) are: the strain field

$$2\,\varepsilon_{\alpha\beta}(\underline{r}) = \partial_\alpha v_\beta(\underline{r}) + \partial_\beta v_\alpha(\underline{r}) \quad , \tag{2-18}$$

the elastic constants of the pure host lattice

$$C_{\alpha\beta\mu\nu} = \frac{1}{V} \sum_{mn} R^m_\beta \, \phi^{mn}_{\alpha\mu} \, R^n_\nu = C_{\alpha\beta\nu\mu} = C_{\beta\alpha,\mu\nu} , \tag{2-19}$$

in harmonic approximation, and the density of the "force-dipole tensor"

$$\begin{aligned} \Pi_{\alpha\beta}(\underline{r}) &= \sum_j \rho_j(\underline{r}) \, P^j_{\alpha\beta} , \\ P^j_{\alpha\beta} &= \sum_m (R^m_\alpha - Q^a_\alpha) \, \psi^{ma}_\beta . \end{aligned} \tag{2-20}$$

The quantity $\rho_j(\underline{r})$ is the partial density of protons at sites of type j. The force-dipole tensor $P^j_{\alpha\beta}$ depends on the type of the site† $\underline{Q}^a$.

The expression (2-17) gives the difference in elastic energy between the crystal strained by the hydrogen load and the pure crystal, with the latter constituting the unstrained reference system with volume V and free surface S. The eq. (2-17) is valid provided the strain field obeys the differential equations

$$C_{\alpha\beta\mu\nu} \, \partial_\beta \, \varepsilon_{\mu\nu}(\underline{r}) = - \partial_\beta \, \Pi_{\alpha\beta}(\underline{r}) , \quad \underline{r} \text{ in } V , \tag{2-21}$$

with the boundary condition

$$C_{\alpha\beta\mu\nu} \, e_\beta(\underline{r}) \, \varepsilon_{\mu\nu}(\underline{r}) = - e_\beta(\underline{r}) \, \Pi_{\alpha\beta}(\underline{r}) , \quad \underline{r} \text{ on } S , \tag{2-22}$$

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† Sometimes we shall use the more detailed notation $a = (a_j, j)$.

where $\underline{e}(\underline{r})$ is a normal unit vector on S. Eqs. (2-21) and (2-22) are the continuum versions of the equation-of-state (2-12). Finally, one has for the force-dipole tensor

$$P^{j}_{\alpha\beta} = \begin{cases} P\,\delta_{\alpha\beta} & \text{, fcc-octahedral sites ,} \\ P'\,\delta_{\alpha\beta} + (P-P')\,\delta_{\alpha j}\,\delta_{\beta j}\,, & \text{bcc-tetrahedral sites .} \end{cases} \qquad (2\text{-}23)$$

(no summation on j)

These forms are easily obtained from eq. (2-20) using symmetry considerations.

In concluding this section we point out that the expression (2-17) for H_{el} is more general than the derivation (in the appendix A) indicates. It is not necessary to assume a harmonic crystal for eq. (2-17) to hold. One may simply define the elastic constants and the density $\Pi_{\alpha\beta}(\underline{r})$ by an expansion of H_{el} in terms of strains. $\Pi_{\alpha\beta}(\underline{r})$ is then interpreted to be the tensor describing the internal stresses caused by the hydrogen load. In this approach the basic approximation is the use of linear elasticity.

§ 3 Volume-Change, Elastic Constants

The expressions (2-12) and (2-13) will now be used to calculate the change in volume, ΔV, caused by the hydrogen. In carrying out the calculation, we introduce arguments, needed in the next section, which allow one to evaluate some expressions involving $\underline{\underline{D}}^{mn}$ without requiring an explicite form of the latter.

Consider a crystal with volume V and surface S. Let $\{\underline{e}^m\}$ be outward-directed normal unit vectors at lattice sites on S, i.e. $\underline{e}^m = 0$ for $\underline{R}^m$ on S, $\underline{e}^m = 0$ otherwise. For a given set $\{\tau_a\}$ we obtain the volume-change ΔV from

$$S_L^{(s)} \Delta V = \underline{e}^m \cdot \underline{v}^m(\tau) = \underline{\Psi}^m(\tau) \cdot \underline{\underline{D}}^{mn} \cdot \underline{e}^n \quad . \tag{3-1}$$

Here $\rho_L^{(s)}$ is the surface density of metal ions. The vectors $\{\underline{e}^m\}$ may be interpreted as fictitious surface forces, normal to S. Then $\underline{\underline{D}}^{mn} \cdot \underline{e}^n$ is the displacement of the metal ion at $\underline{R}^m$ due to these surfaces forces which correspond to a uniform pressure. The displacements will be homogeneous,

$$D^{mn}_{\mu\nu} e^n_\nu = \hat{\varepsilon}_{\mu\nu} R^m_\nu \quad , \tag{3-2}$$

where $\hat{\varepsilon}_{\mu\nu}$ is a homogeneous strain. We solve eq. (3-2) for e^m_μ, multiply by $- R^m_\kappa/V$ and sum over m. This yields

$$\begin{aligned} -\frac{1}{V} R^m_\kappa e^m_\mu &= \frac{1}{V} R^m_\kappa \phi^{mn}_{\mu\nu} R^n_\lambda \hat{\varepsilon}_{\nu\lambda} \\ &= C_{\kappa\mu\lambda\nu} \hat{\varepsilon}_{\lambda\nu} \end{aligned} \tag{3-3}$$

where we have used eq. (2-13).

The quantity

$$\frac{1}{V} R^m_\varkappa e^m_\mu = \sigma_L^{(s)} \delta_{\mu\nu} \tag{3-4}$$

is the stress tensor describing the fictitious surface forces. From eqs. (3-3),(3-4) we find

$$\hat{\varepsilon}_{\mu\nu} = -\sigma_L^{(s)} S_{\mu\nu\varkappa\varkappa} \quad , \tag{3-5}$$

with the elastic moduli $S_{\mu\nu\kappa\lambda}$ defined by $S_{\mu\nu\kappa\lambda}C_{\kappa\lambda\alpha\beta} = (1/2)(\delta_{\mu\alpha}\delta_{\nu\beta} + \delta_{\mu\beta}\delta_{\nu\alpha})$. Insertion of (3-5) for $\hat{\underline{\varepsilon}}$ into (3-2) together with (3-1) yields

$$\Delta V = -S_{\varkappa\varkappa\mu\nu} \Psi^m_\mu(\tau) R^m_\nu \quad . \tag{3-6}$$

The first moment of the force $\underline{\Psi}^m$ is given by the force-dipole tensor, eq. (2-20),

$$\Psi^m_\mu R^m_\nu = \sum_f P^f_{\mu\nu} N_f \quad . \tag{3-7}$$

In the case of cubic crystals we finally obtain (Eshelby 1956)

$$\Delta V = -S_{\varkappa\varkappa\mu\nu} \sum_f N_f P^f_{\mu\nu} = -\frac{1}{3}(P+2P')K_T N \, , \tag{3-8}$$

where

$$K_T \equiv S_{\varkappa\varkappa\mu\mu} = 3(S_{11}+2S_{12}) = \frac{3}{C_{11}+2C_{12}} \quad , \tag{3-9}$$

is the isothermal compressibility of the pure host-lattice.

The thermal average of eq. (2-12) is the (thermal) equation-of-state of the metal-hydrogen system. It can be used to obtain the change in the elastic moduli, $\Delta S_{\mu\nu\kappa\lambda}$, upon loading the crystal with hydrogen. The calculation closely parallels a similar calculation for the case of a deformable Ising lattice (Wagner and Swift 1970) and we only give the results (Benn 1972)

$$\Delta(S_{11}+2S_{12}) = (S_{11}+2S_{12})^2 (P+2P')^2 (\Gamma_{xx}+2\Gamma_{xy}) , \qquad (3\text{-}10)$$

$$\Delta(S_{11}-S_{12}) = (S_{11}-S_{12})^2 (P-P')^2 (\Gamma_{xx}-\Gamma_{xy}) , \qquad (3.11)$$

$$\Delta S_{44} = \sigma , \qquad (3\text{-}12)$$

with

$$\Gamma_{ij} = \frac{1}{k_B T V} \sum_{a_i b_j} \left[\langle \tau_{a_i} \tau_{b_j} \rangle - \langle \tau_{a_i} \rangle \langle \tau_{b_j} \rangle \right] , \qquad (3\text{-}13)$$

where we have set $a = (a_i, i)$ and the sum on a_i is over all interstitial sites of type i (= x,y,z). The brackets <..> denote the thermal average. The expressions (3-10),(3-11),(3-12) for the changes of the elastic moduli in cubic crystals are generalizations of known results (Alefeld et al. 1970).

The changes of the compressibility, $\Delta(S_{11} + S_{12})$, and of the shear modulus, $\Delta(S_{11} - S_{12})$, due to interstitial impurities are the Gorsky- and Snoek-relaxation strengths, respectively. In the high-temperature and low density limit the correlation functions Γ_{ij} for Nb-H, for example, reduce to

$$\Gamma_{ij} \rightarrow \frac{1}{k_B T} \delta_{ij} \frac{N_{H1}}{V} \langle \tau \rangle = \frac{1}{3 k_B T} \rho_L c \, \delta_{ij} \quad , \tag{3-14}$$

where $\rho_L = N_L/V$ is the metal density, $c = 6\langle\tau\rangle$ is the atomic concentration [H/Nb], and we assumed a grandcanonical ensemble.

Thus, measurements of ΔV, $\Delta(S_{11} + S_{12})$ and $\Delta(S_{11} - S_{12})$ for high temperatures and low densities therefore allow one to determine the components P and P' of the force-dipole tensor. Such measurements show that for hydrogen $P \approx P'$ (Buchholtz et al. 1973), i.e. the protons on tetrahedral sites act to a good approximation like pure dilation centers - a somewhat puzzling result.

§ 4 General Properties of the Elastic Interaction

According to eq. (2-15) the Hamiltonian for the hydrogen system is given by

$$H(\tau) = U(\tau) + \Psi(\tau) + \frac{1}{2}\, \underline{\Psi}^{m}(\tau) \cdot \underline{\underline{D}}^{mn} \cdot \underline{\Psi}^{n}(\tau) \quad . \tag{4-1}$$

The third term on the right side contains the elastic interaction. It can be written in the form

$$\underline{\Psi}^{m}(\tau) \cdot \underline{\underline{D}}^{mn} \cdot \underline{\Psi}^{n}(\tau) = \sum_{ab} W_{ab}\, \tau_a \tau_b \, , \tag{4-2}$$

where

$$W_{ab} = \underline{\Psi}^{ma} \cdot \underline{\underline{D}}^{mn} \cdot \underline{\Psi}^{nb} \quad . \tag{4-3}$$

We assume that the forces $\underline{\Psi}^{ma}$ have a microscopic range of the order of a few lattice spacings. We now discuss two cases: protons with arbitrary macroscopic density distribution in a lattice with periodic boundary conditions, and homogeneously distributed protons in a finite lattice of arbitrary shape.

4.1 Elastic Interaction in a Lattice with Periodic Boundary Conditions

We consider first a lattice with periodic boundary conditions and then go to the limit of an infinite crystal. For simplicity we discuss the case of octahedral sites in fcc lattices. Then we have $N_H = N_L$. It is straightforward to generalize the subsequent formulae for the case of tetrahedral sites in bcc lattices.

With periodic boundary conditions, $\underline{\underline{\Phi}}^{mn}$ and $\underline{\underline{D}}^{mn}$ depend only on $\underline{R}^m-\underline{R}^n$. We define

$$\phi^{mn}_{\mu\nu} = \frac{1}{N_L} \sum_{\underline{q}} \phi_{\mu\nu}(\underline{q})\, e^{i\underline{q}\cdot(\underline{R}^m-\underline{R}^n)} ,$$
$$D^{mn}_{\mu\nu} = \frac{1}{N_L} \sum_{\underline{q}} D_{\mu\nu}(\underline{q})\, e^{i\underline{q}\cdot(\underline{R}^m-\underline{R}^n)} . \tag{4-4}$$

The sum over the wave-vectors $\underline{q}$ is restricted to the first Brillouin zone. The matrix $\Phi_{\mu\nu}(\underline{q})$ can be expressed in terms of polarization vectors $e_\mu(\underline{q}\,s)$ and phonon frequencies $\omega(\underline{q}\,s)$ (s denotes the polarization)

$$\phi_{\mu\nu}(\underline{q}) = M_L \sum_{s} e_\mu(\underline{q}\,s)\,\omega^2(\underline{q}\,s)\,e_\nu(\underline{q}\,s) , \tag{4-5}$$

where M_L is the mass of the metal ion. From eq. (2-13), which now reads

$$\phi_{\mu\lambda}(\underline{q})\,D_{\lambda\nu}(\underline{q}) = -\delta_{\mu\nu}(1-\delta_{\underline{q},0}) , \tag{4-6}$$

we find for $\underline{q} \neq 0$

$$D_{\mu\nu}(\underline{q}) = -\sum_{s} \frac{e_\mu(\underline{q}\,s)\,e_\nu(\underline{q}\,s)}{M_L\,\omega^2(\underline{q}\,s)} \tag{4-7}$$

With[†]

$$W_{ab} = \frac{1}{N_L} \sum_{\underline{q}} W(\underline{q})\, e^{i\underline{q}\cdot(\underline{Q}^a - \underline{Q}^b)} , \qquad (4\text{-}8)$$

we obtain

$$W(\underline{q}) = \underline{\Psi}(-\underline{q}) \cdot \underline{\underline{D}}(\underline{q}) \cdot \underline{\Psi}(\underline{q}) , \qquad (4\text{-}9)$$

where

$$\Psi_\mu(\underline{q}) = \sum_m \Psi_\mu^{ma}\, e^{-i\underline{q}\cdot(\underline{Q}^a - \underline{R}^m)} . \qquad (4\text{-}10)$$

Let us introduce a coarse-grained distribution of protons, $\tau_a \rightarrow \bar{\tau}_a$. The averaging procedure involved in the coarse-graining should take into account that only one proton may occupy a site $\underline{Q}^a$ and hence $\tau_a^2 = \tau_a$. Therefore

$$\tau_a \tau_b \rightarrow \overline{\tau_a \tau_b} = \tau_a \delta_{ab} + (1 - \delta_{ab})\, \bar{\tau}_a \bar{\tau}_b . \qquad (4\text{-}11)$$

The elastic energy is then given by

$$H_{el} \equiv \frac{1}{2} \sum_{ab} W_{ab}\, \overline{\tau_a \tau_b} = \frac{1}{2} \sum_a W_{aa} \tau_a + H_{el}^{int} , \qquad (4\text{-}12)$$

[†] The reciprocal lattice of the interstitial sites $\{\underline{Q}^a\}$ is identical to the reciprocal lattice of the metal in the case of octahedral sites in fcc lattices.

with the elastic interaction energy , H_{el}^{int},

$$H_{el}^{int} = \frac{1}{2}\sum_{a\neq b} W_{ab}\,\bar{\tau}_a\bar{\tau}_b = \frac{1}{2}\sum_{ab} W_{ab}\,\bar{\tau}_a\bar{\tau}_b - \frac{1}{2}\sum_{a} W_{aa}\,\bar{\tau}_a^2 \,. \tag{4-13}$$

The meaning of eq. (4-13) is obvious: in order to find the interaction energy we have to subtract the elastic "self-energy" $(1/2)\sum_a W_{aa}\bar{\tau}_a^2$ from the average elastic energy $(1/2)\sum_{ab} W_{ab}\bar{\tau}_a\bar{\tau}_b$. Let us consider the latter, which can be written as

$$\sum_{ab} W_{ab}\,\bar{\tau}_a\bar{\tau}_b = \frac{1}{N_L}\sum_{\underline{q}} \tau(-\underline{q})\,W(\underline{q})\,\tau(\underline{q})\,, \tag{4-14}$$

where

$$\tau(\underline{q}) = \sum_a \bar{\tau}_a\, e^{-i\underline{q}\cdot\underline{Q}^a} \,. \tag{4-15}$$

We now assume that $\{\bar{\tau}_a\}$ describes a smoothly varying density distribution. Specifically we assume that only q-values with $q \ll 1/\ell_o$ contribute in eq. (4-14) where ℓ_o is a measure of the range of forces $\underline{\Psi}^{ma}$. Therefore we may expand $\underline{\Psi}(\underline{q})$, in powers of q:

$$\Psi_\mu(\underline{q}) = -i\,P_{\mu\alpha}\,q_\alpha + \frac{i}{3!}\,P_{\mu\alpha\beta\gamma}\,q_\alpha q_\beta q_\gamma + \dots, \tag{4-16}$$

with

$$P_{\alpha_1\cdots\alpha_n} = \sum_{\underline{l}} \frac{1}{l}\,\psi'(l)\,l_{\alpha_1}\cdots l_{\alpha_n}\,, \quad \psi(|\underline{Q}^a - \underline{R}^m|) \equiv \psi(l)\,. \tag{4-17}$$

The second term on the right side of eq. (4-16) contains the "force-octopole" tensor $P_{\alpha\mu\beta\gamma}$, which has the symmetry properties of the elastic constants of cubic crystals and is of the form

$$P_{\mu\alpha\beta\gamma} = P_{12}\,(\delta_{\mu\alpha}\,\delta_{\beta\gamma} + \delta_{\mu\beta}\,\delta_{\alpha\gamma} + \delta_{\mu\gamma}\,\delta_{\alpha\beta}) + (P_{11} - 3P_{12})\,\delta_{\mu\alpha\beta\gamma} \qquad (4\text{-}18)$$

where $P_{11} = P_{1111}$, $P_{12} = P_{1122} = P_{1212}$ and $\delta_{\mu\alpha\beta\gamma} = 1$ for $\alpha=\beta=\gamma=\mu$, = 0 otherwise. The multipole moments $P_{\alpha_1 \ldots \alpha_n}$ with odd n vanish in the case of fcc-octahedral sites.

With eqs. (4-16) and (4-9) we have

$$\begin{aligned} W(\underline{q}) = {} & q_\alpha\, P_{\alpha\mu}\, D_{\mu\nu}(\underline{q})\, P_{\nu\beta}\, q_\beta \\ & -\frac{1}{3}\, q_\alpha\, P_{\alpha\mu}\, D_{\mu\nu}(\underline{q})\, P_{\nu\gamma\kappa\lambda}\, q_\gamma\, q_\kappa\, q_\lambda + O(q^6 D)\,. \end{aligned} \qquad (4\text{-}19)$$

Let us consider the behaviour of $\underline{\underline{D}}(\underline{q})$ for $q \ll 1/\ell_0$. If q^{-1} is much larger than the range of the lattice forces $\Phi^{mn}_{\mu\nu}$ then we may use the elastic limit of $\Phi_{\mu\nu}(\underline{q})$ which is

$$\phi_{\mu\nu}(\underline{q}) \Rightarrow \frac{V}{N_L}\, C_{\mu\alpha\nu\beta}\, \hat{q}_\alpha\, \hat{q}_\beta\, q^2 \equiv \frac{V}{N_L}\, g^{-1}_{\mu\nu}(\hat{q})\, q^2 \,, \qquad (4\text{-}20)$$

with $\underline{\hat{q}} = \underline{q}/q$, and we obtain for $D_{\mu\nu}(\underline{q})$ from eq. (4-6),

$$D_{\mu\nu}(\underline{q}) = -\frac{N_L}{V}\,\frac{1}{q^2}\, g_{\mu\nu}(\underline{\hat{q}}) \quad . \qquad (4\text{-}21)$$

It is straightforward but somewhat tedious to compute $g_{\mu\nu}(\underline{\hat{q}})$ from eq. (4-20). The result is, with $d = C_{11} - C_{12} - 2C_{44}$

$$g_{\mu\nu}(\hat{\underline{q}}) = \frac{\delta_{\mu\nu}}{C_{44} + \hat{q}_\mu^2 d} - \frac{\hat{q}_\mu \hat{q}_\nu}{(C_{44} + \hat{q}_\mu^2 d)(C_{44} + \hat{q}_\nu^2 d)} \cdot \frac{C_{12} + C_{44}}{1 + \sum\limits_\alpha \frac{(C_{44} + C_{12})\hat{q}_\alpha^2}{(C_{44} + d\hat{q}_\alpha^2)}} . \tag{4-22}$$

In the case of isotropy, i.e. d = 0, this reduces to

$$g_{\mu\nu}(\hat{\underline{q}}) = \frac{1}{C_{11}} \hat{q}_\mu \hat{q}_\nu + \frac{1}{C_{44}} (\delta_{\mu\nu} - \hat{q}_\mu \hat{q}_\nu) . \tag{4-23}$$

For the leading dipole-dipole term in eq. (4-19) with $P_{\mu\nu} = P\delta_{\mu\nu}$ we obtain

$$P^2 q_\mu D_{\mu\nu}(\underline{q}) q_\nu \longrightarrow - \frac{N_L}{V} P^2 \hat{q}_\mu g_{\mu\nu}(\hat{\underline{q}}) \hat{q}_\nu . \tag{4-24}$$

If we now include the dipole-octopole contribution in eq. (4-19) we must also take into account the phonon dispersion in the dipole-dipole term. Instead of writing down the resulting expression for $W(\underline{q})$ which cannot be evaluted analytically anyway we shall assume an isotropic lattice for the rest of the discussion of $W(\underline{q})$. The features of the elastic interaction which are essential for the free energy can already be seen in this simple case. Isotropy is defined more generally (including dispersion) by

$$\sum_s \frac{e_\mu(\underline{q}s)\, e_\nu(\underline{q}s)}{\omega^2(\underline{q}s)} \longrightarrow \hat{q}_\mu \hat{q}_\nu \frac{1}{\omega_l^2(q)} + (\delta_{\mu\nu} - \hat{q}_\mu \hat{q}_\nu) \frac{1}{\omega_t^2(q)} . \tag{4-25}$$

In the dipole-dipole term of $W(\underline{q})$ only the longitudinal part enters and for the frequencies of longitudinal phonons we assume

$$\omega_\ell^2(q) = v_\ell^2 q^2 (1 - \delta_\ell q^2), \tag{4-26}$$

with the sound velocity $(N_L M_L/V) v_\ell^2 = c_{11}$.
The final expression for W($\underline{q}$) then is[†]

$$\frac{V}{N_L} W(\underline{q}) = -\frac{P^2}{C_{11}} + \frac{P}{C_{11}} (P_{12} - P\delta_\ell) q^2 + \frac{P}{3C_{11}} (P_{11} - 3P_{12}) q^2 \sum_\nu q_\nu^4 + \ldots \tag{4-27}$$

We insert eq. (4-2) for W ($\underline{q}$) into eq. (4-1) and change from sums on $\underline{q}$ to integrals. In this way we go to the limit of an infinite lattice. In addition we replace the $\underline{q}$-integration over the first Brillouin zone by an integration over the whole $\underline{q}$-space, which corresponds to the continuum limit. Transforming back into $\underline{r}$-space we obtain finally

$$\frac{1}{2}\sum_{ab} W_{ab}\bar{\tau}_a\bar{\tau}_b \rightarrow -\frac{P^2}{2C_{11}} \int \rho^2(\underline{r})\, d\underline{r} + \frac{P}{2C_{11}} (P_{12} - 3P_{12}) \int (\underline{\nabla}\rho(\underline{r}))^2 d\underline{r}$$

$$+ \frac{P}{24\pi C_{11}} (3P_{12} - P_{11}) \iint \rho(\underline{r}) \left[\frac{63}{|\underline{r}-\underline{r}'|^5} - \frac{105}{|\underline{r}-\underline{r}'|^9} \sum_\nu (r_\nu - r_\nu')^4\right] \rho(\underline{r}')\, d\underline{r}\, d\underline{r}' . \tag{4-28}$$

Here, we introduced the proton density by $(N_L/V)\tau_a \rightarrow \rho(\underline{r})$. The $(1/r^5)$-interaction in the third term was originally discovered by Hardy and Bullough (1967). When averaged over a sphere this interaction vanishes.

[†] This expression for W ($\underline{q}$) is also valid for an anisotropic lattice if $\underline{q}$ lies in the (100)-directions. Similar expressions for the (110)- and (111)-direction can also be found easily.

The expression (4-28) is also valid for bcc-tetrahedral sites if the densities of protons on the different typs of sites are equal, i.e. $\rho_j(\underline{r}) = \rho(r)/3$. In general there is a non-vanishing quadrupole moment $P^j_{\alpha\beta\gamma}$ of the forces $\underline{\Psi}^{ma}$ for tetrahedral sites, leading to a $(1/r^5)$-quadrupole-quadrupole interaction. If $\rho_j(r)$ is taken to be independent of j, then only $\sum_j P^j_{\alpha\beta\gamma}$ enters, which again vanishes.

We now consider the self-energy part in eq. (4-13). With $W_{aa} \equiv W$, we find

$$W = -\sum_{\underline{q}s}\sum_{mn} \Psi_\mu^{ma} \frac{e_\mu(\underline{q}s)\, e_\nu(\underline{q}s)}{N_L M_L\, \omega^2(\underline{q}s)} \Psi_\nu^{na}\, e^{i\underline{q}(\underline{R}^m - \underline{R}^n)} . \tag{4-29}$$

Here, all $\underline{q}$-values (except $\underline{q} = 0$) enter. An order-of-magnitude estimate can be obtained by noting that an important contribution arises from small q-values. Therefore we expand the exponential in eq. (4-29). This yields for the first non-vanishing contribution to W

$$W = -\frac{N_H}{V} P_{\alpha\beta} R_{\alpha\beta\mu\nu} P_{\mu\nu} , \tag{4-30}$$

$$R_{\alpha\beta\mu\nu} = \frac{V}{N_H N_L} \sum_{\underline{q}s} q_\beta q_\nu \frac{e_\alpha(\underline{q}s)\, e_\mu(\underline{q}s)}{M_L\, \omega^2(\underline{q}s)} .$$

If one furthermore assumes isotropy and the Debye-approximation $\omega_{\ell,t} = v_{\ell,t}q$, one obtains

$$R_{\alpha\beta\mu\nu} = \tag{4-31}$$

$$\frac{V}{15 N_H M_L}\left[\left(\frac{1}{v_\ell^2} - \frac{1}{v_t^2}\right)\left(\delta_{\alpha\beta}\delta_{\mu\nu} + \delta_{\alpha\nu}\delta_{\beta\mu}\right) + \left(\frac{1}{v_\ell^2} + \frac{4}{v_t^2}\right)\delta_{\alpha\mu}\delta_{\beta\nu}\right]$$

The eqs. (4-30) and (4-31) give for the self-energy

$$\frac{1}{2}\sum_{a} W_{aa}\,\bar{\tau}_a^{\,2} \rightarrow -\frac{P^2}{2C_{11}}\int \rho^2(\underline{r})\,d\underline{r} \quad . \qquad (4\text{-}32)$$

For bcc-tetrahedral sites we only have to replace N_H by N_{Hj} and $P_{\alpha\beta}$ by $P^j_{\alpha\beta}$ in (4-30) and (4-31). The right side of eq. (4-32) then reads

$$-\frac{1}{2}\sum_{j}\int \rho_j(\underline{r})\, P^j_{\alpha\beta}\, R_{\alpha\beta\mu\nu}\, P^j_{\mu\nu}\, \rho_j(\underline{r})\, d\underline{r} \,, \qquad (4\text{-}33)$$

which for $\rho_j = \rho/3$ and together with eq. (4-31) yields

$$\frac{1}{2}\sum_{a} W_{aa}\,\bar{\tau}_a^{\,2} \rightarrow -\left[(P'^2+2PP')\frac{1}{36C_{11}} + (P+P')^2\left(\frac{1}{60C_{11}}+\frac{1}{90C_{44}}\right)\right]\int \rho^2(\underline{r})\,d\underline{r} . \qquad (4\text{-}34)$$

With the use of the estimates (4-30) and (4-34) for the self-energy we finally obtain H^{int}_{el} for an infinite isotropic lattice in the continuum limit:

1. fcc-octahedral sites

$$\overset{\infty}{H}{}^{int}_{el} = \frac{\kappa^2}{2}\int (\underline{\nabla}\rho(\underline{r}))^2 d\underline{r} + \frac{1}{2}\iint \rho(\underline{r})\, V(\underline{r}-\underline{r}')\,\rho(\underline{r}')\, d\underline{r}\, d\underline{r}' \quad , \qquad (4\text{-}35)$$

2. bcc-tetrahedral sites, with $P^j_{\alpha\beta} = P\delta_{\alpha\beta}$

$$\overset{\infty}{H}{}^{int}_{el} = -\frac{5}{12}\frac{P^2}{C_{11}}\int \rho^2(\underline{r})\, d\underline{r} + \frac{\kappa^2}{2}\int (\underline{\nabla}\rho(\underline{r}))^2 d\underline{r} \qquad (4\text{-}36)$$

$$+ \frac{1}{2}\iint \rho(\underline{r})\, V(\underline{r}-\underline{r}')\,\rho(\underline{r}')\, d\underline{r}\, d\underline{r}' \quad ,$$

where[†]

$$\kappa^2 = \frac{P}{C_{11}} \left(P_{12} - P\delta_\ell \right) ,$$
$$V(\underline{r}) = \frac{P}{12\pi C_{11}} \left(3P_{12} - P_{11} \right) \left[\frac{63}{r^5} - \frac{105}{r^9} \left(x^4 + y^4 + z^4 \right) \right] . \qquad (4\text{-}37)$$

By using the expressions (4-32) and (4-34) for the elastic self-energy we are tacitly assuming that linear continuum elasticity theory is applicable for distancies of the order of the lattice spacing. However, one can calculate the quantity W = W_{aa} numerically for a realistic lattice. For Nb one finds[††] from eq. (4-29) $W/P^2 = -2.3 \cdot 10^{10}\ \mathrm{erg}^{-1}$ whereas the estimate yields $W/P^2 = -2.0 \cdot 10^{10}\ \mathrm{erg}^{-1}$. The latter value was obtained from $W/P^2 = -2/(C_{11}a^3)$ with $C_{11} = 2.46 \cdot 10^{12}$ dyn/cm^2 and with a lattice constant $a = 3.44 \cdot 10^{-8}$ cm.

[†] Note that κ^2 could also be negative. This would indicate an instability of a homogeneous hydrogen distribution with respect to spatial modulations of the density $\rho(\underline{r})$.

[††] The phonon frequencies are taken from experiments (Sharp, 1969). The force $\underline{\Psi}^{ma}$ is assumed to act only between a proton and its nearest and next-nearest Nb-neighbours. The two constants involved are determined from the force-dipole tensor.

4.2. Elastic Interaction in a Lattice with Free Surface

Suppose we have a constant density of hydrogen. In the case of bcc-tetrahedral sites the partial densities ρ_j are, however, allowed to be different. Then $\tau_a \rightarrow \bar{\tau}_i = N_i/N_{Hi}$ and the elastic interaction energy is given by

$$H_{el}^{int} = \frac{1}{2} \sum_{ij} \bar{\tau}_i \bar{\tau}_j \left[\sum_{a_i b_j} W_{a_i b_j} - \delta_{ij} N_{Hj} W \right] \quad . \tag{4-38}$$

In the expression for W,

$$W = \sum_{mn} \underline{\Psi}^{ma} \cdot \underline{\underline{D}}^{mn} \cdot \underline{\Psi}^{na} \quad , \tag{4-39}$$

the sums on m and n are restricted to $|\underline{R}^m - \underline{R}^n| = O(\ell_o)$ and we replace $\underline{\underline{D}}^{mn}$ by its form for a lattice with periodic boundary conditions, eq. (4-4) and eq. (4.7). Thus, W is again determined by eq. (4-29). Errors arise only if $\underline{R}^m$ and $\underline{R}^n$ are within a surface layer of depth ℓ_o. The contribution from this layer is of the order $V^{-1/3}$ relative to the bulk term in eq. (4-39). Therefore, we only have to compute

$$\sum_{a_i b_j} W_{a_i b_j} = \sum_{a_i b_j} \sum_{mn} \underline{\Psi}^{ma_i} \cdot \underline{\underline{D}}^{mn} \cdot \underline{\Psi}^{nb_j} \quad . \tag{4-40}$$

The forces

$$\underline{K}^{m,i} \equiv \sum_{a_i} \underline{\Psi}^{ma_i} \quad , \tag{4-41}$$

vanish in the bulk of the crystal since the $\underline{\Psi}^{ma_i}$ cancel each other in pairs in the sum over a_i. If however $\underline{R}^m$ is at the surface S, some of the interstitial sites neighbouring $\underline{R}_m$ are missing, and thus $\underline{K}^{m,i} \neq 0$ on S. These surface-forces lead to a homogeneous deformation of the crystal,

$$\underline{\underline{D}}^{mn} \cdot \underline{K}^{n,j} = \underline{\underline{\varepsilon}}^{j} \cdot \underline{R}^{m} , \tag{4-42}$$

and in the same way as in § 3 we find

$$\varepsilon^{j}_{\alpha\beta} = - \frac{N_{Hj}}{V} \sum_{\mu\nu} S_{\alpha\beta\mu\nu} P^{j}_{\mu\nu} . \tag{4-43}$$

From eqs. (4-40) to (4-43) we obtain

$$\sum_{a_i b_j} W_{a_i b_j} = - \frac{N_{Hi} N_{Hj}}{V} \sum_{\alpha\beta\mu\nu} P^{i}_{\alpha\beta} S_{\alpha\beta\mu\nu} P^{j}_{\mu\nu} . \tag{4-44}$$

With W from eq. (4-30) ($N_H \rightarrow N_{Hj}$, $P_{\alpha\beta} \rightarrow P^j_{\alpha\beta}$) and with eq. (4-44) we find

$$\begin{aligned} H^{int}_{el} &= - \frac{V}{2} \sum_{ij} s_i P^{i}_{\alpha\beta} \left(S_{\alpha\beta\mu\nu} - \delta_{ij} R_{\alpha\beta\mu\nu} \right) P^{j}_{\mu\nu} s_j \\ &= \frac{V}{2} \sum_{i} s_i P^{i}_{\alpha\beta} \varepsilon^{i,loc}_{\alpha\beta} . \end{aligned} \tag{4-45}$$

The "local" strain in eq. (4-45) is defined by[†]

[†] The local strain could have been defined already in connection with eq. (4-13). It has been introduced by Siems (1970) in the framework of continuum elasticity. However, in his expression corresponding to eq. (4-46) above, the factor δ_{ij} is missing.

$$\varepsilon^{i,loc}_{\alpha\beta} = -\sum_{j} \left(S_{\alpha\beta\mu\nu} - \delta_{ij} R_{\alpha\beta\mu\nu} \right) P^{j}_{\mu\nu}\, \rho_j \;, \tag{4-46}$$

and has an interpretation similar to the local electric field in dielectrics.

Whereas the expression (4-44) is rigorously valid, the form of W with $R_{\alpha\beta\mu\nu}$ as given by eq. (4-30) only holds approximately. However, we may calculate W numerically as indicated above and simply define $R_{\alpha\beta\mu\nu}$ by the first line of eq. (4-30). Following this procedure the result for H^{int}_{el}, eq. (4-45), is generally valid for finite anisotropic lattices of any shape in the case of homogeneously distributed protons. The H^{int}_{el} for fcc-octahedral sites is obtained if we drop the indices i and j and the corresponding sums in eqs. (4-45) and (4-46).

For comparison with the results for the infinite lattice we take $\rho_j = \rho/3$, insert eq. (4-31) for $R_{\alpha\beta\mu\nu}$ into eq. (4-45) and find in the case of bcc-tetrahedral sites

$$\begin{aligned} \frac{1}{V} H^{int}_{el} &= -\frac{1}{2} (\rho P)^2 \left(K_T - \frac{1}{6C_{11}} \right) \\ &= -\frac{1}{2} (\rho P)^2 K_T \left(1 - \frac{C_{11} + 2C_{12}}{18\, C_{11}} \right) \end{aligned} \tag{4-47}$$

Assuming $\rho(\underline{r}) = \rho$ in a sphere of volume V, $\rho(\underline{r}) = 0$ otherwise, we have from eq. (4-36)

$$\frac{1}{V} \overset{\infty}{H}{}^{int}_{el} = -\frac{5}{12} \frac{(\rho P)^2}{C_{11}} \;, \tag{4-48}$$

since the angular integral over $V(\underline{r})$ in eq. (4-36) vanishes. Normally one has $K_T - (1/C_{11}) > 0$, and the interaction is attractive in both cases. The H^{int}_{el} and $\overset{\infty}{H}{}^{int}_{el}$ differ by

$$\frac{1}{V}\left(H^{int}_{el} - \overset{\infty}{H}{}^{int}_{el}\right) = -\frac{1}{2}(\rho P)^2\left(K_T - \frac{1}{c_{11}}\right) \tag{4-49}$$

For fcc-octahedral sites the elastic interaction $\overset{\infty}{H}{}^{int}_{el}$ vanishes if $\rho(r) = \text{const.}$

These results indicate the importance of boundary conditions in the calculation of the elastic energy. Unfortunately it is impossible in practice to calculate $\underline{\underline{D}}^{mn}$ and W_{ab} analytically for a finite discrete lattice with the natural boundary conditions of a free surface; but some qualitative arguments can already be given which illustrate the role of the boundary conditions in the elastic energy.

4.3 Macroscopic Modes

For a finite crystal the hermitian matrix of force constants $\Phi^{mn}_{\mu\nu}$ can always be diagonalized in terms of eigenmodes and may be written as

$$\Phi^{mn}_{\mu\nu} = \sum_i \varphi^m_{i\mu}\,\Phi_i\,\varphi^{*m}_{i\nu} \quad , \quad \sum_m \varphi^m_{\underline{i}}\,\varphi^{*m}_{\underline{j}} = \delta_{ij} \; . \tag{4-50}$$

We label the eigenvalues in sequence such that† $0 = \Phi_0 < \Phi_1 \leqslant \leqslant \Phi_2 \leqslant \ldots \leqslant \Phi_{3N_L}$ and find from eq. (2-13)

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† Because $\sum_m \Phi^{mn}_{\mu\nu} = 0$, there is one threefold degenerate eigenvalue $\Phi_0 = 0$. Stability of the crystal requires that $\Phi_i > 0$ for $i > 0$.

$$D^{mn}_{\mu\nu} = -\sum_{i>0} \varphi^{m}_{i\mu} \frac{1}{\phi_i} \varphi^{n}_{i\nu} \quad . \tag{4-51}$$

With this expression we obtain for the elastic interaction

$$W_{ab} = -\sum_{i>0} f^{a}_{i} \frac{1}{\phi_i} f^{*b}_{i} \quad , \tag{4-52}$$

where †

$$f^{a}_{i} = \underline{\varphi}^{m}_{i} \cdot \underline{\psi}^{ma} \quad . \tag{4-53}$$

Consider a crystal of cubic shape with volume V = L^3. Let us first assume periodic boundary conditions. Then the label "i" abbreviates the set ($\underline{q}$,s), and we have

$$\begin{aligned} \phi_i &\rightarrow M_L\,\omega^2(\underline{q}\,s) \equiv \tilde{\phi}_i \\ \varphi^{m}_{i} &\rightarrow \frac{1}{\sqrt{N_L}}\, \underline{e}(\underline{q}\;s)\, e^{i\underline{q}\cdot\underline{R}^{m}} \equiv \tilde{\varphi}^{m}_{i} \\ f^{a}_{i} &\rightarrow \frac{1}{\sqrt{N_L}}\, \underline{e}(\underline{q}s)\cdot\underline{\psi}(\underline{q})\, e^{i\underline{q}\cdot\underline{Q}^{a}} \equiv \tilde{f}^{a}_{i} \quad . \end{aligned} \tag{4-54}$$

The resulting $W_{ab} \rightarrow \tilde{W}_{ab}$ has been discussed in § 4.1 . In order to see more specifically why W_{ab} is sensitive to boundary conditions we consider first the contribution to $\tilde{W}_{ab}$ of a single

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† Note that the f^a_i are not eigenvectors of the matrix W_{ab}.

mode i_o with a wave vector of the order[†] of L, $q \sim L$. Then $\tilde{\Phi}_{i_o} \sim L^{-2}$, $|\tilde{\varphi}^m_{i_o}| \sim L^{-3/2}$, $\underline{\Psi}(\underline{q}) \propto q \sim L^{-1}$ and thus $|\tilde{f}^a_i| \sim L^{-5/2}$. Therefore the contribution of this single mode to $\tilde{W}_{ab}$ is $\tilde{W}_{ab}(i_o) \approx L^{-3}$. Since the phase of $\tilde{f}^a_i$ varies on the scale L, the $\tilde{W}_{ab}(i_o)$ describes a long ranged interaction between all protons, and the elastic energy due to this single mode will be $\sum_{ab} \tilde{W}_{ab}(i_o)\tau_a\tau_b \sim L^3 = V$.

At first sight this argument seems to be contradict an earlier result in this section, where we only found a short-range interaction if we impose periodic boundary conditions. We have to keep in mind, however, that in the case of a finite crystal with periodic boundary conditions, W_{ab} is a periodic function of $(\underline{Q}^a - \underline{Q}^b)$ and constructive interference in the Fourier-sum (4-52) of terms with short wave-length largely cancels the above contribution of the long wave-length modes.

Let us now discuss what happens if we change the boundary conditions to those corresponding to a free surface. We have to modify the force constants $\Phi^{mn}_{\mu\nu}$ for $\underline{R}^m$ or $\underline{R}^n$ which are near or at the surface. More specifically, assume the lattice forces to be of strictly finite range ℓ_Φ. Then we have to modify a number Z_Φ of rows and columns in the matrix $\Phi^{mn}_{\mu\nu}$ with $Z_\Phi \approx L\ell_\Phi/a^3$, where "a" is the lattice spacing. According to the theorem of Ledermann (1944) the resulting shifts in the eigenvalues will be

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[†] The allowed q-values are $\underline{q} = \frac{2\pi}{L}(n_1, n_2, n_3)$, $n_\alpha = 0, \pm 1, \pm 2, \ldots$ In writing $q \sim L^{-1}$ we imply $n_\alpha = O(1)$.

such that the number of eigenvalues in any given finite interval changes at most by $2Z_\Phi \sim L^2$. In other words: the density of vibrational states in a large compact crystal is insensitive to boundary conditions - a wellknown result indeed.

We now indicate why this fact does not rule out the dependence of W_{ab} on boundary conditions. Consider again modes with $\Phi_i \sim L^{-2}$. The corresponding $|f_i^a|$ remain of the order $L^{-5/2}$ (this derives essentially from the normalization of φ_i^m and from $\sum_m \Psi^{ma} = 0$), and the f_i^a are slowly varying on the scale L. As compared to the $\tilde{\Phi}_i \sim L^{-2}$ the Φ_i are expected to be shifted by an amount which depends on the shape of the crystal and which is expected to be of the order of L^{-2} i.e. of the order of the level spacing in that part of the spectrum where $\tilde{\Phi}_i \sim L^2$. We have seen above that modes with $\Phi_i \sim L^{-2}$ contribute terms $\sim L^{-3}$ to W_{ab} and terms $\sim L^3$ to the elastic energy. Since the shifts in the Φ_i's are of the same size, namely $\sim L^{-2}$, as the Φ_i themselves, we expect the difference

$$\sum_{\substack{i \\ (\Phi_i < \Phi_L)}} f_i^a \frac{1}{\Phi_i} f_i^{*b} - \sum_{\substack{i \\ (\tilde{\Phi}_i < \Phi_L)}} \tilde{f}_i^a \frac{1}{\tilde{\Phi}_i} \tilde{f}_i^{*b} \sim L^{-3} , \tag{4-55}$$

(with $\Phi_L = \text{const.}\ L^{-2}$) to depend on the shape of the crystal. Furthermore since

$$\Delta W_{ab} \equiv W_{ab} - \tilde{W}_{ab} = \sum_i \left[f_i^a \frac{1}{\Phi_i} f_i^{*b} - \tilde{f}_i^a \frac{1}{\tilde{\Phi}_i} \tilde{f}_i^{*b} \right] , \tag{4-56}$$

we conclude that

$$H^{int}_{el} - \overset{\infty}{H}{}^{int}_{el} = H^{int}_{el} - \tilde{H}^{int}_{el} = \frac{1}{2}\sum_{ab} \Delta W_{ab}\, \tau_a \tau_b \sim L^3. \tag{4-57}$$

We call "macroscopic elastic modes" those eigenmodes (φ^m_i , Φ_i) which contribute to ΔW_{ab} and which normally depend upon the shape of the crystal. In general the phonon modes with $q \gg L^{-1}$ will not contribute to ΔW_{ab} since the shifts in the eigenvalues Φ_i induced by a change in the boundary conditions will be negliglible compared to $\tilde{\Phi}_i$. The corresponding φ^m_i will be slightly distorted plane waves. However, in the case of a free surface there exist short wave-length surface modes for which φ^m_i is localized at the surface and which enter into ΔW_{ab}.

The concept of macroscopic modes may also be introduced from a slightly different point of view. Since W_{ab} is a real symmetric matrix, it can be diagonalized

$$\sum_b W_{ab}\, \sigma_{kb} = w_k\, \sigma_{ak} \, , \tag{4-58}$$

$$W_{ab} = \sum_k \sigma_{ka}\, w_k\, \sigma^*_{kb} \, , \qquad \sum_a \sigma_{ka}\, \sigma^*_{\ell a} = \delta_{k\ell} \, .$$

We define displacements $v^m_{k\mu}$ by

$$\underline{\underline{\Phi}}^{mn} \cdot \underline{v}^n_k = - \underline{\Psi}^{ma}\, \sigma_{ka} \, . \tag{4-59}$$

With the help of the expression (4-3) for W_{ab} we then obtain from (4-58)

$$\sigma_{ka} = \frac{1}{w_\ell}\, \underline{\Psi}^{ma} \cdot \underline{v}^m_k \, , \tag{4-60}$$

and eq. (4-59) can be rewritten as

$$\sum_{n\nu} \left(\Phi^{mn}_{\mu\nu} + \frac{1}{w_k} \Theta^{mn}_{\mu\nu} \right) v^n_{k\nu} = \sigma , \qquad (4\text{-}61)$$

where $\Theta^{mn}_{\mu\nu} = \Psi^{ma}_{\mu}\Psi^{na}_{\nu}$. Eq. (4-61) is a generalized eigenvalue equation † for w_k. Among the eigenmodes $\{w_k, \sigma_{ka}\}$ there are modes which depend upon boundary conditions. As compared to the eigenvalues of $\underline{\underline{\Phi}}^{mn}$ the shifts in the w_k caused by a modification of the boundary conditions are expected to be of the order L^o.

The eigenmodes of W_{ab} and the eigenmodes of $\underline{\underline{\Phi}}^{mn}$ have a different physical meaning. The former correspond to special hydrogen distributions whereas the latter are special lattice displacements. The eigenmodes $\{\sigma_{ka}\}$ do cause lattice displacements $\{\underline{v}^n_k\}$ (cf eq. 4-59), but in general the $\underline{v}^n_k$ are not longer eigenmodes of $\underline{\underline{\Phi}}^{mn}$ as can be seen from eq. (4-61).

The modes $\{w_k, \sigma_{ka}\}$ which contribute to ΔW_{ab} and which depend upon boundary conditions will be called "macroscopic density modes".

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† In the case of an isotropic lattice with periodic boundary conditions and with $P_{\alpha\beta} = P\delta_{\alpha\beta}$ it is easily shown that $w_k \rightarrow w(q) = - Pq^2/(M_L\omega^2(q)) = - P^2N_L/(V c_{11})$ if $q^{-1} \gg \ell_o, \ell_\Phi$, i.e. w(q) is degenerate. This result for w_k leads back to eq. (4-27).

§ 5 Elastic Interaction of Protons in an Isotropic Sphere

The qualitative discussion in the last section about the role of macroscopic modes in the elastic interaction between interstitial impurities can be made quantitative in the continuum approximation. The essential features (long range, shape-dependence) of the elastic interaction are described correctly in this framework.

We start with the elastic energy H_{el} as given in eq. (2-17)

$$H_{el} = \frac{1}{2}\int \varepsilon_{\alpha\beta}(\underline{r})\, C_{\alpha\beta\mu\nu}\, \varepsilon_{\mu\nu}(\underline{r})\, d\underline{r} + \int \Pi_{\alpha\beta}(\underline{r})\, \varepsilon_{\alpha\beta}(\underline{r})\, d\underline{r} \; . \tag{5-1}$$

By a variation of H_{el} with respect to the strain tensor $\underline{\underline{\varepsilon}}$ we define the stress tensor

$$\sigma_{\alpha\beta}(\underline{r}) = \Pi_{\alpha\beta}(\underline{r}) + C_{\alpha\beta\mu\nu}\, \varepsilon_{\mu\nu}(\underline{r}) \quad . \tag{5-2}$$

In terms of the stress tensor $\underline{\underline{\sigma}}$ the eqs. (2-21) and (2-22) take the usual form of the mechanical equilibrium conditions

$$\partial_\beta \sigma_{\alpha\beta}(\underline{r}) = 0 \, , \quad \underline{r} \text{ in } V \, , \tag{5-3}$$

$$e_\beta(\underline{r})\, \sigma_{\alpha\beta}(\underline{r}) = 0 \, , \quad \underline{r} \text{ on } S \; . \tag{5-4}$$

If one inserts eq. (2-18) for $\varepsilon_{\alpha\beta}$ in the first term on the right side of eq. (5-1) and performs a partial integration then one finds with the help of eqs. (5-3) and (5-4) that H_{el} may simply be written as

$$H_{el} = \frac{1}{2} \int \Pi_{\alpha\beta}(\underline{r})\, \varepsilon_{\alpha\beta}(\underline{r})\, d\underline{r} \quad . \qquad (5\text{-}5)$$

In order to obtain the elastic interaction energy from H_{el} we have to replace $\underline{\underline{\varepsilon}}$ in eq. (5-5) by the local strain field (Siems 1969) which amounts to substract from H_{el} the elastic self-energy

$$-\frac{1}{2} \sum_{j} \int \rho_j(\underline{r})\, P^{j}_{\alpha\beta}\, R_{\alpha\beta\mu\nu}\, P^{j}_{\mu\nu}\, \rho_j(\underline{r})\, d\underline{r} \quad , \qquad (5\text{-}6)$$

with $R_{\alpha\beta\mu\nu}$ given by eq. (4-18), which is the appropriate form for the elastic, dispersion-free and isotropic continuum.

The strain field $\underline{\underline{\varepsilon}}(\underline{r})$ in eq. (5-5) depends upon the hydrogen distribution $\rho_j(r)$ and is determined by the differential equation (5-3) with the boundary condition (5-4). One solution for $\underline{\underline{\varepsilon}}$ is immediately obtained by setting $\underline{\underline{\sigma}} = 0$,

$$\varepsilon_{\alpha\beta}(\underline{r}) = - S_{\alpha\beta\mu\nu}\, \Pi_{\mu\nu}(\underline{r}) \quad . \qquad (5\text{-}7)$$

However, this solution is not acceptable in general. The reason is that the eqs. (5-2),(5-3) and (5-4) must be supplemented by the compatibility conditions, (e.g. Sneddon and Berry 1958) which read

$$\partial_\mu \partial_\nu \varepsilon_{\alpha\beta} + \partial_\alpha \partial_\beta \varepsilon_{\mu\nu} - \partial_\beta \partial_\nu \varepsilon_{\alpha\mu} - \partial_\alpha \partial_\mu \varepsilon_{\beta\nu} = 0 \qquad (5\text{-}8)$$

Formally, these relations express the requirement that the strain field has to be derivable from a unique displacement field $\underline{v}(\underline{r})$. They are identically fullfilled if one sets $2\varepsilon_{\alpha\beta} = \partial_\alpha v_\beta + \partial_\beta v_\alpha$, with displacements which have continuous second derivatives. In general the solution (5-7) with arbitrary $\underline{\underline{\Pi}}(\underline{r})$ does not obey the relations (5-8). Only if either the hydrogen density (and thus $\underline{\underline{\Pi}}(\underline{r})$) is a constant or a linear function of $\underline{r}$ (i.e. $\partial_\alpha \partial_\beta \Pi_{\mu\nu} = 0$) is the solution of the boundary-value problem given by eq. (5-7).

A strained crystal with $\varepsilon_{\alpha\beta}$ obeying eq. (5-8) is said to be a coherent crystal. The stresses $\sigma_{\alpha\beta}$ induced by these strains according to eq. (5-2) are called coherency stresses. The physical meaning of coherency is most clearly seen if we go back to the lattice-description. Let us imagine the metal ions of the pure lattice to be connected by bonds representing the lattice forces. After we have loaded the crystal with hydrogen this network of bonds will be deformed. If the topology of bond connections remains intact during any redistribution of protons we have a coherent crystal. In this case any strained configuration of the lattice is obtained from the unstrained reference state by a continuous elastic deformation with uniquely defined displacements.

There are wellknown mechanisms which destroy coherency. If, for instance, the stresses due to the protons are large enough to creat dislocations then plastic deformations will occur. Of course, in the idealized case of a strictly harmonic crystal there is no possibility to destroy coherency since the spring forces between metal ions increase indefinitely with increasing distance. We remind, however, that linear elasticity is more generally valid than the harmonic approximation. Thus, for real crystals the requirement of coherency is a nontrivial constraint which has important consequences on the form of the elastic interaction.

Not much progess has been made in solving eq. (5-3) for anisotropic crystals with arbitrary shape. In the special case of isotropic crystals of spherical shape and with a force-dipole tensor $P^{j}_{\alpha\beta} = P\,\delta_{\alpha\beta}$ the strain field $\underline{\underline{\varepsilon}}\{\rho\}$ can be calculated explicitly and is obtained as a series in terms of macroscopic density modes. We now consider this case in detail.
With the elastic constants in terms of the Lamé coefficients λ and μ

$$C_{44} = \mu \,, \quad C_{12} = \lambda \,, \quad C_{11} = \lambda + 2\mu \,, \tag{5-9}$$

and the stress tensor expressed by the displacements

$$\sigma_{\alpha\beta}(\underline{r}) = \Pi(\underline{r})\,\delta_{\alpha\beta} + \lambda\,\delta_{\alpha\beta}\,\partial_k v_k(\underline{r}) + \mu\left[\partial_\alpha v_\beta(\underline{r}) + \partial_\beta v_\alpha(\underline{r})\right], \tag{5-10}$$

with

$$\Pi_{\alpha\beta}(\underline{r}) = \Pi(\underline{r})\,\delta_{\alpha\beta} = P\rho(\underline{r})\,\delta_{\alpha\beta} \,, \tag{5-11}$$

we obtain from eq. (5-3)

$$\mu\,\nabla^2 v_\alpha + (\mu+\lambda)\,\partial_\alpha\partial_\beta v_\beta + \partial_\alpha \Pi = 0 \tag{5-12}$$

The ansatz

$$v_\alpha = \partial_\alpha \Lambda + u_\alpha \, , \tag{5-13}$$

with Λ satisfying the equation

$$\nabla^2 \Lambda = -\frac{1}{\lambda + 2\mu} \Pi \, , \tag{5-14}$$

reduces the boundary-value problem to the solution of the homogeneous equation for $\underline{u}$:

$$\mu \nabla^2 u_\alpha + (\mu + \lambda) \partial_\alpha \partial_\beta u_\beta = 0 \, . \tag{5-15}$$

In the elastic energy

$$\begin{aligned} H_{el} &= \frac{1}{2} \int \Pi(\underline{r}) \, \varepsilon_{\alpha\alpha}(\underline{r}) \, d\underline{r} = \frac{1}{2} \int \Pi(\underline{r}) \, \partial_\alpha v_\alpha(\underline{r}) \, d\underline{r} \\ &= -\frac{1}{2C_{11}} \int \Pi^2(\underline{r}) \, d\underline{r} + \frac{1}{2} \int \Pi(\underline{r}) \, \partial_\alpha u_\alpha(\underline{r}) \, d\underline{r} \, , \end{aligned} \tag{5-16}$$

only the local volume-change due to $\underline{u}$, $\partial_\alpha u_\alpha(\underline{r})$, contributes.

The intenal stress $\underline{\underline{\Pi}}(\underline{r})$ enters linearly into the boundary condition (5-4). Therefore $\partial_\alpha u_\alpha(\underline{r})$ is a linear functional of $\rho(\underline{r}) = \sum_j \rho_j(\underline{r})$

$$\partial_\alpha u_\alpha(\underline{r}) = -\frac{1}{P} \int M(\underline{r}, \underline{r}') \, \rho(\underline{r}') \, d\underline{r}' \, . \tag{5-17}$$

We may assume that $M(\underline{r},\underline{r}') = M(\underline{r}',\underline{r})$ since only the symmetric part of $M(\underline{r},\underline{r}')$ enters into H_{el}.

From eq. (5-15) it follows immediately that $\partial_\alpha u_\alpha$ is a harmonic function,

$$\nabla^2 \partial_\alpha u_\alpha = 0 \; , \tag{5-18}$$

and thus we also have

$$\nabla^2 M(\underline{r},\underline{r}') = 0 = \nabla'^2 M(\underline{r},\underline{r}') \, . \tag{5-19}$$

For spherical crystal it is convenient to expand M in a series of spherical harmonics

$$M(\underline{r},\underline{r}') = \sum_{\ell m} M_\ell(r,r') \, Y_{\ell m}(\Omega) \, Y^*_{\ell m}(\Omega') \; , \tag{5-20}$$

where $\Omega = (\vartheta,\phi)$ symbolizes the direction of $\underline{r}$, $Y^*_{\ell m}(\Omega) = (-1)^m *$ $Y_{\ell -m}(\Omega)$ and $M_\ell(r,r') = M_\ell(r',r)$. In writing (5-20) we have taken into account that $M(\underline{r},\underline{r}')$ depends on angles only through $\underline{r}\cdot\underline{r}'$, because of rotational symmetry.

Inserting the expression (5-20) into eq. (5-19) we obtain

$$M_\ell(r,r') = \hat{M}_\ell \, r^\ell r'^\ell \; , \tag{5-21}$$

with still arbitrary constants $\hat{M}_\ell$. We discard the other possible solution $M_\ell(r,r') \propto (r\,r')^{-\ell-1}$ because $\partial_\alpha u_\alpha(\underline{r})$ and $M(\underline{r},\underline{r}')$ must be finite at the origin.

Thus we find for $M(\underline{r},\underline{r}')$

$$\begin{aligned} M(\underline{r},\underline{r}') &= \sum_{\ell m} \hat{M}_\ell \, r^\ell \, Y_{\ell m}(\Omega) \, r'^\ell \, Y^*_{\ell m}(\Omega') \\ &\equiv \sum_{\ell m} M_\ell \, \chi_{\ell m}(\underline{r}) \, \chi^*_{\ell m}(\underline{r}') \; , \end{aligned} \tag{5-22}$$

with the orthonormalized eigenfunctions $\chi_{\ell m}(\underline{r})$ of the kernel $M\,(\underline{r},\underline{r}')$

$$\chi_{\ell m}(\underline{r}) = \left(\frac{2\ell+3}{R^3}\right)^{\frac{1}{2}} \left(\frac{r}{R}\right)^{\ell} Y_{\ell m}(\Omega) \,,$$

$$\int \chi_{\ell m}(\underline{r})\, \chi^{*}_{\ell' m'}(\underline{r})\, d\underline{r} = \delta_{\ell\ell'}\, \delta_{mm'} \,, \tag{5-23}$$

where R is the radius of the sphere. The eigenvalues M_ℓ cannot be found by general arguments, of course. They are obtained from an explicite solution of eq. (5-16) which is outlined in the appendix B. The result for a free surface is

$$M_\ell = P^2 \frac{2\mu}{\lambda+2\mu} \; \frac{(\ell+1)(\ell+2)}{2\mu(\ell^2+\ell+1)+\lambda(2\ell^2+4\ell+3)} \;. \tag{5-24}$$

From eqs. (5-22) and (5-23) we obtain

$$\int M(\underline{r},\underline{r}')\, d\underline{r}' = M_0 = P^2\left(K_T - \frac{1}{c_{11}}\right) = M_1 \;. \tag{5-25}$$

Stability of the lattice requires that $c_{11} = \lambda+2\mu>0$ $c_{44} = \mu>0$ and $c_{11}+2c_{12} = 3\lambda+2\mu>0$.

With the help of these inequalities it is easy to show that

$$M_0 = M_1 > M_2 > M_3 > \ldots > \frac{P^2\mu}{(\lambda+2\mu)(\lambda+\mu)} > 0 \;. \tag{5-26}$$

The largest eigenvalues M_0 and M_1 are the only degenerate ones. The spectrum is discrete and is bounded from below.

Using eqs. (5-17) and (5-22) we find for H_{el}, eq. (5-16)

$$H_{el} = -\frac{P^2}{2C_{11}} \int \rho^2(\underline{r})\, d\underline{r} - \frac{1}{2} \iint \rho(\underline{r})\, M(\underline{r}, \underline{r}')\, \rho(\underline{r}')\, d\underline{r}\, d\underline{r}'$$

$$= -\frac{P^2}{2C_{11}} \int \rho^2(\underline{r})\, d\underline{r} - \frac{V}{2} \sum_{\ell m} M_\ell \left|\rho_{\ell m}\right|^2 , \tag{5-27}$$

with

$$\rho_{\ell m} = \frac{1}{\sqrt{V}} \int \rho(\underline{r})\, \chi_{\ell m}(\underline{r})\, d\underline{r} . \tag{5-28}$$

The first term of eq. (5-27) arises from the solution Λ of the inhomogeneous equation (5-12) and is independent of the boundary condition. The second term arises from the macroscopic density modes. Only modes which change the volume enter into H_{el}. Modes which cause a pure shear do not contribute since we assumed the protons to be dilatation centers.

Suppose we have a proton density of the form

$$\rho(\underline{r}) = \rho_0 + \sqrt{V} \sum_{m=-1}^{1} \rho_{1m}\, \chi_{1m}(\underline{r}) , \qquad \rho_0 = \frac{N}{V} . \tag{5-29}$$

The elastic energy associated with this distribution of protons is obtained from eq. (5-27) to be

$$H_{el} = -\frac{1}{2} V P^2 k_T \left(|\rho_0|^2 + \sum_m |\rho_{1m}|^2 \right)$$

$$= -\frac{1}{2} V P^2 k_T \int \rho^2(\underline{r})\, d\underline{r} , \tag{5-30}$$

where we have used the fact that $M_0 = M_1$.
The degeneracy of the $\ell = 0$ and $\ell = 1$ modes is not an accidental feature of the isotropic sphere. The degeneracy in the elastic energy of the modes which describe homogeneous deformation

(excited by a constant density of protons) with modes excited by a density linear in $\underline{r}$ holds quite generally for any shape and even for anisotropic crystals. It is a consequence of the fact, discussed below eq. (5-8), that those densities do not creat coherency stresses. In this case eq. (5-7) is valid, which, after insertion into eq. (5-5) for H_{el}, again yields the result (5-30).

Now we write down the elastic interaction energy, using eq. (5-6) together with eq. (4-31):

$$\begin{aligned} H_{el}^{int} &= \frac{\zeta-1}{2C_{11}} P^2 \int \rho^2(\underline{r})\, d\underline{r} - \frac{1}{2} \iint \rho(\underline{r})\, M(\underline{r},\underline{r}')\, \rho(\underline{r}') \\ &\equiv \frac{1}{2} \iint \rho(\underline{r})\, W_{int}(\underline{r},\underline{r}')\, \rho(\underline{r}')\, d\underline{r}\, d\underline{r}' , \end{aligned} \qquad (5\text{-}31)$$

where $\zeta = 1$ for fcc-octahedral sites and $\zeta = \frac{1}{6}$ for bcc-tetrahedral sites.

Let us make a few comments in connection with this result:

1. The interaction potential $W_{int}(\underline{r},\underline{r}')$ is the sum of two terms

$$\begin{aligned} W_{int}(\underline{r},\underline{r}') &= \overset{\infty}{W}_{int}(\underline{r}-\underline{r}') - M(\underline{r},\underline{r}') , \\ \overset{\infty}{W}_{int}(\underline{r}-\underline{r}') &= \frac{\zeta-1}{C_{11}} P^2 \delta(\underline{r}-\underline{r}') . \end{aligned} \qquad (5\text{-}32)$$

The first term, $\overset{\infty}{W}_{int}$, describes the interaction in an infinite crystal (but see below) and is obtained from (5-12) simply by neclecting the boundary conditions (5-4). The second term, M, is the continuum analog of ΔW_{ab} and is the contribution of the macroscopic density modes.

The two parts of W_{int} behave differently in the thermodynamic limit N, V → ∞, $\varrho = N/V$ fixed. One has to be careful to define how the thermodynamic limit is taken. Consider for instance a spherical crystal (radius R) with a constant density $\rho \neq 0$ in a concentric sphere with radius $R' < R$, and $\rho = 0$ otherwise. We now let $R \to \infty$, keeping R' fixed, then the contribution of M to H_{el}^{int} vanishes like V_H/V, where $V_H = \frac{4\pi}{3} R'^3$. If we then let $R' \to \infty$ we find for fixed $\rho = N/V_H$ ("limit of the first kind")

$$\lim_{N, V_H \to \infty} \frac{1}{V_H} H_{el}^{int} = - \frac{1-\zeta}{2C_{11}} (P_S)^2 . \tag{5-33}$$

On the other hand, setting first $R' = R$, we have for $R \to \infty$ and fixed $\rho = N/V_H$ ("limit of the second kind")

$$\lim_{N, V_H \to \infty} \frac{1}{V_H} H_{el}^{int} = - \frac{1}{2} \left(\frac{1-\zeta}{C_{11}} + K_T \right) (P_S)^2 \tag{5-34}$$

The fact that both limits give different results is of course rather obvious and holds quite generally: if we confine the hydrogen to a region $\mathcal{D}$ inside of an anisotropic crystal of arbitrary shape then the effect of the free surface on the elastic interaction between protons in $\mathcal{D}$ vanishes as the crystal extends to infinity in all directions and $\mathcal{D}$ is kept fixed. The point we want to make here is that in working with periodic boundary conditions and changing from sums on $\underline{q}$ to integrals one is taking effectively the somewhat artifical first kind of thermodynamic limit.

2. In the literature (e.g. Cahn (1962), Khachaturyan (1966))

a slightly different definition of the elastic energy has been employed which we discuss briefly for comparison.

Turning back to eq. (5-2) we may write the stress tensor as

$$\begin{aligned} \sigma_{\alpha\beta}(\underline{r}) &= C_{\alpha\beta\mu\nu}\,\hat{\varepsilon}_{\mu\nu}(\underline{r}) \\ \hat{\varepsilon}_{\alpha\beta}(\underline{r}) &= \varepsilon_{\alpha\beta}(\underline{r}) + S_{\alpha\beta\mu\nu}\,\Pi_{\mu\nu}(\underline{r}) \quad , \end{aligned} \tag{5-35}$$

An elastic energy is now defined by

$$\hat{H}_{el} = \frac{1}{2}\int_V \sigma_{\alpha\beta}(\underline{r})\,\tilde{\varepsilon}_{\alpha\beta}(\underline{r})\,d\underline{r} \quad , \tag{5-36}$$

where V is the volume of the pure host lattice. The strain $\tilde{\underline{\underline{\varepsilon}}}(\underline{r})$ with arbitrary $\underline{\underline{\Pi}}$ is no longer derivable from a unique displacement field. From eqs. (5-35) and (5-36) we see that

$$\begin{aligned} \hat{H}_{el} &= H_{el} + \frac{1}{2}\int \Pi_{\alpha\beta}(\underline{r})\,S_{\alpha\beta\mu\nu}\,\Pi_{\mu\nu}(\underline{r})\,d\underline{r} \\ &\rightarrow H_{el} + \frac{1}{2}P^2K_T\int \rho^2(\underline{r})\,d\underline{r} \\ &= H_{el} - H_{el}^{incoh} \quad . \end{aligned} \tag{5-37}$$

Thus, $\hat{H}_{el}$ is the difference in elastic energy between the coherent and the incoherent state of the loaded crystal[†]. In

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[†] In the incoherent state can be visualized as follows: Cut the macroscopic crystal into small cubes. Take a proton density $\rho(\underline{r})$ which is constant within a cube. Now load the individual cubes with protons in accordance with $\rho(\underline{r})$. The loaded cubes will then be deformed differently since the density varies from cube to cube. They no longer fit together to form a coherent macroscopic crystal. The elastic energy stored in this collection of stress-free cubes is given by eqs. (5-5),(5-7) and reads $H_{el}^{incoh} = -(P^2K_T/2)V_\xi\Sigma_\xi\rho_\xi^2$, with the density ρ_ξ and volume V_ξ of the ξ-th cube.

order to compute the corresponding difference in elastic interaction energy we have to subtract the total self-energy (5-6) from H_{el} and H_{el}^{incoh}. The self-energy being a local functional of $\rho(\underline{r})$ is the same in both states and thus drops out from $\hat{H}_{el}$.

3. The part $M(\underline{r},\underline{r}')$ of the elastic interaction is obtained in eq. (5-22) from the continuum approximation in the form of an infinite sum over density modes. For large ℓ, the eigenfunctions $X_{\ell m}(\underline{r})$ are localized at the surface of the sphere and decay rapidly as $\underline{r}$ moves into the bulk. Clearly, any rapid variation of $X_{\ell m}(\underline{r})$ within one lattice distance is physically meaningless. In order to eliminate unphysical modes we introduce a Debye cut-off ℓ_{max}. Assumptions about the value for ℓ_{max} are necessarily somewhat ambignous. A reasonable choice is $\ell_{max} \approx R/d$, where d is a length of the order of the lattice constant. Then

$$\left(\frac{r}{R}\right)^{\ell_{max}} = \left(1 - \frac{R-r}{R}\right)^{\frac{R}{d}} \approx e^{-\frac{R-r}{d}} , \qquad (5\text{-}38)$$

and the number of modes is $\sim \ell_{max}^2 \sim V^{2/3}$.

There are some features of the spectrum of density modes of a sphere and the associated elastic interaction which are expected to occur also for other compact[†] shapes. These are:

<u>a.</u> The spectrum is discrete, with a level spacing independent of the volume.

<u>b.</u> The number of modes is of the order $V^{2/3}$.

<u>c.</u> The dilatation mode (uniform expansion or contraction) has the largest eigenvalue if the force dipole tensor is isotropic, $P_{\alpha\beta} = P\delta_{\alpha\beta}$.

[†] By "compact" we mean, roughly speaking, that all linear dimensions of the sample are of the same order of magnitude, or, the number of lattice sites at the surface is of the order $V^{2/3}$.

§ 6 Free Energy

We start with the Hamiltonian as given by eqs. (4-1) and (4-2),

$$H'(\tau) = \frac{1}{2}\sum_{ab} (U_{ab} + W_{ab}) \tau_a \tau_b \quad , \tag{6-1}$$

where we have dropped the term $\Psi(\tau)$ which is linear in the τ's and only renormalizes the chemical potential. We divide the volume V of the crystal into small cells $\{Z_A | A = 1,..,N_H/n_H\}$ of volume V_A containing n_H proton sites. The number of protons in the cell Z_A, $n_A = \sum_{a \subset Z_A} \tau_a$, is assumed to satisfy $1 \ll n_A \ll N = \sum_A n_A$.

We also introduce the elastic energy of the macroscopic density-modes averaged over the cells,

$$M_{AB} = - \frac{1}{n_H^2} \sum_{\substack{a \subset Z_A \\ b \subset Z_B}} \Delta W_{ab} \quad , \tag{6-2}$$

and write, if $a \subset Z_A$ and $b \subset Z_B$

$$W_{ab} = \Delta_{ab} - M_{AB} \quad . \tag{6-3}$$

Then the Hamiltonian reads

$$\begin{aligned} H' &= \frac{1}{2}\sum_{ab} (U_{ab} + \Delta_{ab}) \tau_a \tau_b - \frac{1}{2}\sum_{AB} M_{AB} n_A n_B \\ &\equiv H_o(\tau) + H_{el}^{m}(n) \quad . \end{aligned} \tag{6-4}$$

The Helmholtz free energy $\mathcal{F}(T,N,V)$ is obtained from the canonical partition function

$$\mathcal{Z} = e^{-\beta\mathcal{F}} = \sum_{\{n_A\}}{}' \, e^{-\beta\left[F_o(n_A) + H_{el}^{m}(n_A)\right]} \quad , \tag{6-5}$$

where

$$e^{-\beta F_o(n_A)} = \sum_{\{\tau_a\}}{}'' \, e^{-\beta H_o(\tau)} \quad . \tag{6-6}$$

In eqs. (6-5) and (6-6) the sums Σ' and Σ'' over configurations are restricted by $\sum_A n_A = N$ and $\sum_{a\in Z_A} \tau_a = n_A$, respectively.

Let $\rho(\underline{r})$ be the density of protons, so that $n_A = \rho(\underline{r}_A)V_A$ for some $\underline{r}_A \in V_A$. Then the partition function may be written formally as a functional integral

$$\mathcal{Z} = \int (\delta\varrho)\, e^{-\beta\left[F_o\{\varrho\} + H_{el}^{m}\{\varrho\}\right]} \quad , \tag{6-7}$$

where

$$H_{el}^{m}\{\varrho\} = -\frac{1}{2}\iint \varrho(\underline{r})\, M(\underline{r},\underline{r}')\,\varrho(\underline{r}')\, d\underline{r}\, d\underline{r}' \quad , \tag{6-8}$$

and the integration in (6-7) is over densities which satisfy

$$\int_V \varrho(\underline{r})\, d\underline{r} = N \quad . \tag{6-9}$$

In order to give a precise and explicite meaning to

the functional integral (6-7) we argue as follows:
The Hamiltonian H^{m}_{el} describes the contribution of the macroscopic density-modes to the free energy and $M(\underline{r},\underline{r}')$ is of macroscopic range. For dilatation centers in an elastically isotropic sphere we know the explicite form of $M(\underline{r},\underline{r}')$ (c.f. eqs. (5-22), (5-24),(5-28)). It is an interaction of the Curie-Weiss type involving the moments of the density $\rho(r)$. For example, the mode $\ell = 0$ leads to a term in H^{m}_{el} which is proportional to

$$-\frac{1}{V}\left[\int_V \rho(\underline{r})\,d\underline{r}\right]^2 = -\frac{N^2}{V} \quad . \tag{6-10}$$

Similar features of $M(\underline{r},\underline{r}')$ are certainly to be expected for other compact shapes of the crystal.

On the other hand, the interaction Δ_{ab}, which includes the microscopic part of W_{ab} and the elastic interaction corresponding to an infinite crystal, may still be of long range in the usual sense (lattice spacing $\ll$ range $\ll$ linear dimensions) but does not contain terms of macroscopic range. As far as the electronic interaction U_{ab} is concerned, lack of information leads us to replace it by a hard-core repulsion.
The specific form of F_o will not be essential for the following considerations. It will be assumed, however, that F_o may be written in the Landau-form

$$F_o = \int \left[\frac{\varkappa^2}{2}(\nabla \rho(\underline{r}))^2 + k_B T f(\rho(\underline{r}), T) \right] d\underline{r} , \tag{6-11}$$

with a gradient term deriving from those in eq. (4-35) and eq. (4-36).

Let us now expand $\rho(\underline{r})$ in a series of functions $\xi_K(\underline{r})$ forming an orthonormal and complete basis which is taken to include the orthonormal set of eigenfunctions[†] $\{\chi_{\ell m}\}$ of $M(\underline{r},\underline{r}')$. Then

$$\rho(\underline{r}) = \sqrt{V} \sum_K \rho_K \xi_K(\underline{r}) \quad . \tag{6-12}$$

Since $\rho(r)$ was defined to describe the mean density of protons in the cells, the sum on K in (6-12) has to be confined to those values of K for which $\xi_K(r)$ is (nearly) constant within a cell. The linear dimensions of the cells are taken to be much larger than the correlation length $\propto \kappa$.
After we insert the expansion (6-12) into F_o and H^m_{el}, we have $F_o\{\rho\} \rightarrow F_o(\rho_K)$ and $H^m_{el}\{\rho\} \rightarrow H^m_{el}(\rho_K)$. The functional integral in (6-7) is then understood as a short-notation for the finite product of conventional integrals over the variables ρ_K.

We now proceed in the discussion of the partition function. In view of the Curie-Weiss character of H^m_{el} it is rather plausible to regard the densities $\rho(r)$ as macroscopic thermodynamic variables in the integration in (6-7). Consequently,

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[†] The set $\{\chi_{\ell m}\}$ of eigenfunctions with non-zero eigenvalues does not provide in general a complete basis, as is obvious from the example of an isotropic sphere. A complete basis for a sphere may be contructed from direct products of spherical harmonics and Jacobi polynomials. The additional functions in the set $\{\xi_K\}$ which are orthogonal to the $\chi_{\ell m}$ can be regarded as eigenfunctions of $M(\underline{r},\underline{r}')$ with eigenvalue zero.

the partition function will be dominated by the maximum term in the integrand, i.e. by that density $\bar{\rho}(\underline{r})$, which minimizes

$$F\{\rho\} = F_o\{\rho\} + H^{m}_{el}\{\rho\} \, , \tag{6-13}$$

with the constraint (6-9). Hence

$$Z = \int(\delta\rho)e^{-\beta F\{\rho\}} \longrightarrow e^{-\beta F\{\bar{\rho}\}} \, , \tag{6-14}$$

with $\bar{\rho}(r)$ being the solution of

$$-\varkappa^2 \nabla^2 \rho(\underline{r}) + k_B T f_1(\rho(\underline{r})) - \int M(\underline{r},\underline{r}')\rho(\underline{r}')d\underline{r}' = \alpha \tag{6-15}$$

where α is a Lagrange-parameter for the constraint (6-9) and $f_n = \partial^n f/\partial\rho^n$.

In the (ρT)-region where $f_2(\rho,T) \geqslant f_2^{min}(T) > 0$ (see also § 7), the kernel

$$\frac{\delta^2 F\{\rho\}}{\delta\rho(\underline{r})\,\delta\rho(\underline{r}')} \equiv \Xi(\underline{r},\underline{r}') = \left[-\varkappa^2 \nabla^2 + k_B T f_2(\rho,T)\right]\delta(\underline{r}-\underline{r}') - M(\underline{r},\underline{r}') \, , \tag{6-16}$$

is positive definite if $T > T_c \equiv M_o/k_B f_2^{min}(T_c)$.

Here, M_o is the largest eigenvalue of the kernel $M(\underline{r},\underline{r}')$ which normally corresponds to the mode of homogeous dilatation.

Indeed we have with eq. (6-12)

$$\iint \rho(\underline{r})\, \Xi(\underline{r},\underline{r}')\, \rho(\underline{r}')\, d\underline{r}\, d\underline{r}'$$

$$= \int \left[\varkappa^2 (\underline{\nabla} \rho(\underline{r}))^2 + k_B T f_2(\rho(\underline{r}))\rho^2(\underline{r}) \right] - \iint \rho(\underline{r}) M(\underline{r},\underline{r}') \rho(\underline{r}')\, d\underline{r}\, d\underline{r}' \tag{6-17}$$

$$\geq \overline{\sum_{\ell m}} \left[k_B T f_2^{min}(T) - M_\ell \right] |\rho_{\ell m}|^2 \geq \left[k_B T f_2^{min}(T) - M_0 \right] \overline{\sum_{\ell m}} |\rho_{\ell m}|^2$$

$$> \sigma, \quad \text{for } k_B T f_2^{min}(T) > M_0 \quad .$$

From this it follows that F{ρ} is a convex functional of ρ and thus has at most one minimum provided $T>T_c$. Hence if we find one solution to (6-15) it will correspond to the absolute minimum of F{ρ} above T_c. Below T_c several solutions to eq. (6-15) will exist in general. If $\bar{\rho}(\underline{r})$ again denotes the one for which F{ρ} is an absolute minimum, then we have

$$\mathcal{F}(T, V, N) \rightarrow F(T, V, N, \{\bar{\rho}\}) = F_0(T, V, N, \{\bar{\rho}\}) + H_{el}^{m}\{\bar{\rho}\} . \tag{6-18}$$

We have distinguished between interactions which are long-ranged and those which are of macroscopic range. The elastic interaction in a finite crystal with free surface belongs to the latter class. Interactions of the first category have been studied by van Kampen (1964) in his analysis of the van der Waals theory. In this case eq. (6-15), with $M(\underline{r},\underline{r}')$ replaced by $v(|\underline{r}-\underline{r}'|)$, may be rewritten in the form

$$k_B T f_1(\rho) - v_0 \rho - \frac{1}{2} v_2 \nabla^2 \rho = \alpha , \tag{6-19}$$

where $v_o = \int v(r)\, d\underline{r}$ and $3v_2 = \int v(r) r^2 d\underline{r}$.
H^m_{el} is replaced by

$$\int [v_o \rho^2(\underline{r}) + \frac{1}{4} v_2 (\underline{\nabla} \rho(\underline{r}))^2] \, d\underline{r} \,, \tag{6-20}$$

and F_o is then the contribution from the hard-core repulsion ("reference free energy").

For T below the corresponding critical temperature T_c and in the two-phase region, the gradient term describes the interface between the two coexisting phases. In the thermodynamic limit, its contribution to the free energy vanishes but its existence guarantees the concavity of the free energy via the Maxwell-construction †.

In our case of the elastic interaction with its macroscopic range there is no gradient term in H^m_{el}, or rather, if one manipulates H^m_{el} to bring it into a form similar to (6-20), one finds that the correlation length replacing $\sqrt{v_2}$ is of the order of the linear dimension of the crystal. Consequently, its contribution to the free energy is (for compact shapes) proportional to the volume V, and there is no reason for the Maxwell-construction if F is non-concave.

We believe that the expression (6-18) becomes exact in the thermodynamic limit though we do not have a rigorous proof.

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† Van Kampen's arguments have been made rigorous by Lebowitz and Penrose (1966) for the case of a potential $v(\underline{r}) = \gamma \exp(-\gamma r)$ in the limit $\gamma \rightarrow 0$, which is taken after the thermodynamic limit $V,N \rightarrow \infty$.

If this conjecture is correct then the metal-hydrogen systems would provide an example where a van der Waals-type theory is strictly valid.

§ 7 Phase Transition

In this section we examine the qualitative aspects of the "gas-liquid" (α-α') phase transition in metal-hydrogen systems under the basic hypothesis that the elastic interaction causes this transition. A more quantitative discussion of the phase-diagram for Nb-H will be given in a subsequent paper.

7.1 Reference free energy

As we demonstrated in the last section, the Helmholtz free energy of the hydrogen system is obtained by minimizing the free energy functional

$$F = \int \left[\frac{\kappa^2}{2} (\underline{\nabla} \rho(\underline{r}))^2 + k_B T f(\rho(\underline{r})) \right] d\underline{r} - \frac{1}{2} \iint \rho(\underline{r}) M(\underline{r},\underline{r}') \rho(\underline{r}') \, d\underline{r} \, d\underline{r}' , \qquad (7\text{-}1)$$

with respect to $\rho(r)$ with the constraint (6-9).

The scale of spatial variations of the density is determined by the elastic interaction and is macroscopic. Therefore we may savely neclect the gradient term in (7-1) in the following discussion.

We discuss first some properties of the reference free energy $k_B T f(\rho,T)$ which is the thermodynamic limit of the first kind of the free energy F/V. We argued that no interactions of macroscopic range enter into $f(\rho,T)$. Accordingly we assume that $f(\rho,T)$ behaves like a "normal" free energy with the following well known properties:

1. $$\lim_{\rho\to 0} f(\rho,T) = 0\,, \quad \lim_{\rho\to 0} \frac{1}{\rho} f(\rho,T) = -\infty\,, \tag{7-2}$$

2. $$\lim_{\rho\to \rho_{max}} f(\rho,T) = \infty\,, \tag{7-3}$$

3. $$\text{If } \rho = \rho_1 + x(\rho_2-\rho_1)\,, \quad 0 \leq x \leq 1\,, \quad \text{then}$$
$$f(\rho,T) \leq f(\rho_1,T) + x\left[f(\rho_2,T) - f(\rho_1,T)\right]\,. \tag{7-4}$$

Eq. (7-3) is a consequence of the hard-core idealisation for the electronic interaction U_{ab}. Eq. (7-4) requires that $f(\rho,T)$ be a convex function of the density. Eq. (7-4) is equivalent to $f_2(\rho,T) \geqslant 0$ if this second derivative exists.

In principle $f(\rho,T)$ might also describe gas-liquid and liquid-solid phase transitions due to the hard-core and the residual attractive forces (see Fig. 3). An example for the latter is provided by H_{el}^{int} in eq. (5-33) for tetrahedral sites where $\zeta = 1/6$. Even without attractive forces there could be a gas-solid transition due to the hard-core, similar to the transition found for hard spheres.

Here, we are interested in a (ρ,T)-region around a critical point ρ_c, T_c induced by the elastic interaction via macroscopic density-modes (second term on the rhs of eq. (7-1)) and the critical temperature T_c^{∞} in $f(\rho,T)$ will be well below T_c , at least in Nb-H (Conrad et al. (1973)). For the sake of simplicity we furthermore neglect the temperature dependence of f which is equivalent to assuming either a pure hard-core interaction or, even simpler, taking f to be the density of the ideal mixing entropy,

$$f = \rho \ln\left(\frac{\rho}{\tilde{\rho}}\right) + (\tilde{\rho} - \rho) \ln\left(1 - \frac{\rho}{\tilde{\rho}}\right) . \qquad (7\text{-}5)$$

In this latter case we may fit $\tilde{\rho}$ by some ρ_{max} to include the effect of a hard-core in a crude way. The detailed form of f (ρ) will not be important for the present discussion. The only properties required are: $f_2(\rho) > 0$, analyticity of $f(\rho)$ in the neighborhood of ρ_c, and ρ_c sufficently less than any eventually existing ρ''_F (see Fig. 3), so that the hard-core transition does not interfere with the gas-liquid transition at T_c, ρ_c.

7.2 Minimization of the free energy

In order to procceed with the minimization of F we must know the kernel $M(\underline{r},\underline{r}')$, that is the spectrum and the eigenfunctions of the macroscopic density-modes. Therefore we discuss explicitly the special case of an isotropic sphere. It will be seen, however, that the important qualitative properties of F in the neighborhood of the critical point only depend upon some general features of $M(\underline{r},\underline{r}')$. These are:

1. The largest eigenvalue M_o is associated with a constant density ρ, i.e. with the dilatation mode.
2. The mode corresponding to a constant density-gradient is energetically degenerate with the M_o-mode.
3. The spectrum of the macroscopic density modes is discrete with a level spacing independent of the volume.

The statements 1. and 2. are quite generally valid, as we already observed in § 4 below eq. (5-30). We also expect statement 3. to be true for non-spherical compact shapes and anisotropic crystals.

Let us first rewrite eq. (7-1) for F in the following way

$$F = \bar{F}(T, V, N, \{\rho\}) + \tilde{F}(V, N, \{\rho\}) , \tag{7-6}$$

where

$$\bar{F} = k_B T \int f(\rho(\underline{r}))\, d\underline{r} - \frac{1}{2} M_0 \int \rho^2(\underline{r})\, d\underline{r} , \tag{7-7}$$

and

$$\tilde{F} = \frac{1}{4} \int [\rho(\underline{r}) - \rho(\underline{r}')]^2 M(\underline{r}, \underline{r}')\, d\underline{r}\, d\underline{r}' . \tag{7-8}$$

We used that $\int M(\underline{r},\underline{r}')d\underline{r}' = M_0$, which follows from eq. (5-22).

Now consider a constant density $\rho(\underline{r}) = \bar{\rho}$. Then $\tilde{F} = 0$ and

$$\frac{1}{V} F = \frac{1}{V} \bar{F}(T, V, \bar{\rho}) = k_B T f(\bar{\rho}) - \frac{1}{2} M_0 \bar{\rho}^2 . \tag{7-9}$$

A constant density $\bar{\rho}$ is a solution of eq. (6-15), i.e. $\bar{\rho}$ corresponds to an extremum of F, provided α is chosen to satisfy

$$\alpha = k_B T f_1(\bar{\rho}) - M_0 \bar{\rho} . \tag{7-10}$$

By virtue of the properties of $f(\rho)$ the rhs of (7-10) is a monotone nondecreasing function of $\bar{\rho}$ if $T > T_c$, where

$$k_B T_c = \frac{M_0}{f_2(\rho_c)} \tag{7-11}$$

and where ρ_c is the solution of

$$f_3(\rho) = 0 \tag{7-12}$$

Thus for each value of α there is a unique value of $\bar{\rho}$ if $T>T_c$. Since $f_2(\rho_c) = f_2^{\min}$, we see from eq. (6-17) that $\rho(\underline{r}) = \bar{\rho}$ corresponds to the absolute minimum of F as long as $T>T_c$. For $T<T_c$ the graph of the rhs of eq. (7-10) has the form of a van der Waals isotherm with a loop and $\bar{\bar{F}}(T,v,\bar{\rho})$ has the form shown in Fig. 4.

For densities $0<\bar{\rho}<\rho_F$ and $\rho_F<\bar{\rho}$ ($<\rho_F''$, cf. Fig. 3) the free energy $\bar{\bar{F}}$ has a unique minium. The free energy $\tilde{F}$ is also minimal for a constant density. Therefore, if $T<T_c$ the total free energy $F = \bar{\bar{F}}+\tilde{F}$ has an absolute minimum for $\rho(\underline{r}) = \bar{\rho}$ if $\bar{\rho}<\rho_G$ or if $\rho>\rho_F$, which correspond to the gaseous and the liquid phase, respectively.

In the density range $\rho_G<\rho<\rho_F$ the equilibrium free energy is minimal for a spatially varying density. In a normal system, the density profile is obtained from eq. (6-19) (van Kampen (1964)). The result is then the expected one: between ρ_G and ρ_F there are two phases in equilibrium, separated by an interface of thickness $\propto \left[v_2/(T_c-T)\right]^{1/2}$.

In our case the Maxwell-construction is not legitimate, as pointed out in § 6. There is no well-defined interface below T_c since a spatially varying density leads to a contribution in

F proportional to the volume V. We have in general

$$\tilde{F} = \frac{1}{2} M_0 \int \rho^2(\underline{r})\, d\underline{r} - \frac{1}{2} \sum_{\ell m} M_\ell |\rho_{\ell m}|^2 \geq 0 \,, \tag{7-13}$$

which follows from $M_0 \geq M_\ell$ and from the Bessel inequality $\int \rho^2(\underline{r}) d\underline{r} \geq \sum_{\ell m} |\rho_{\ell m}|^2$. The equality in (7-13) only holds if $\rho(\underline{r})$ is of the form of eq. (5-29), i.e. $\rho(\underline{r})$ is at most a linear function of $\underline{r}$. For other densities we have $\tilde{F} \sim V$ since $(M_0 - M_2)/M_0 = O(1)$. To illustrate this important fact we take spherically symmetric density of the form shown in Fig. 5.
The average density $\bar{\rho}$ is given by

$$\bar{\rho} = \rho_G + x(\rho_F - \rho_G) \,, \tag{7-14}$$

with $x = V_F/V$. Then

$$\frac{1}{V} \tilde{F} = \frac{1}{2V} M_0 \int \rho^2(r)\, d\underline{r} - \frac{1}{2} M_0 \bar{\rho}^2 \,, \tag{7-15}$$

and for the total free energy we find

$$\begin{aligned} \frac{1}{V} F\{\rho\} &= k_B T [f(\rho_G) + x (f(\rho_F) - f(\rho_G)) - \frac{1}{2} M_0 \bar{\rho}^2 \\ &> k_B T f(\bar{\rho}) - \frac{1}{2} M_0 \bar{\rho}^2 = \frac{1}{V} \bar{F}(\bar{\rho}) \,. \end{aligned} \tag{7-16}$$

This inequality holds irrespective of whether T is above or below T_c. The physical interpretation is, of course, that any rapid variation of the density of protons (rapid on the macroscopic scale) causes coherency stresses which drastically raise the free energy. This is in contrast to the case of a normal fluid where we would have $F\{\rho\}/V \lessgtr \bar{F}(\bar{\rho})/V$ for $T<T_c$ and[†] $V \to \infty$, if $\rho(r)$ is of the form as shown in Fig. 5.

Nevertheless one can lower the free energy F in the inhomogeneous region as compared to $\bar{F}(\bar{\rho})$ by minimizing F within the class of densities defined by eq. (6-12).

We examine the region in the neighborhood of the critical point which was defined by eqs. (7-11) and (7-12), and set

$$\rho(\underline{r}) = \bar{\rho} + \delta\rho(\underline{r}) = \rho_c + \delta\bar{\rho} + \delta\rho(\underline{r}) , \qquad (7\text{-}17)$$

with

$$\int \delta\rho(\underline{r})\, d\underline{r} = 0 . \qquad (7\text{-}18)$$

The free energy can be written as

$$F\{\rho(\underline{r})\} = F_{vdW}(\bar{\rho}) + \Delta F(\bar{\rho}, \{\rho(\underline{r})\}) , \qquad (7\text{-}19)$$

where $F_{vdW}(\bar{\rho})$ is the "van der Waals" free energy obtained from $F(\bar{\rho})$ via the double-tangent construction. The excess free energy,

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[†] For a normal fluid one has to take a density profile with a smooth transition at R_F between ρ_F and ρ_G. The contribution of this interface to F arising from the gradient term vanishes in the thermodynamic limit.

$$\Delta F = \bar{F}(\bar{\rho}) - F_{vdW}(\bar{\rho}) + \delta F(\bar{\rho}, \{\rho(\underline{r})\}) , \tag{7-20}$$

contains the contribution δF of the inhomogeneous density, and we have to minimize δF. As discussed above, the free energy density $k_B T f(\rho(\underline{r}))$ is an analytic function in a finite interval around ρ_c and we expand $f(\rho_c + \delta\bar{\rho} + \delta\rho(\underline{r}))$ in powers of $\delta\bar{\rho}$ and $\delta\rho(\underline{r})$ and neclect higher than fourth-order terms i.e. we set $f_i = f_i(\rho_c) = 0$ for $i>5$. For convenience we introduce the dimensionsless variables $\bar{n}$, $n(\underline{r})$, and t by

$$\delta\bar{\rho} = \rho_o \bar{n} , \quad \delta\rho(\underline{r}) = \rho_o n(\underline{r}) , \quad t = \frac{T_c}{T} - 1 , \tag{7-21}$$

where $\rho_o^2 = 2f_2/f_4$. We then find (Fig. 6)

$$\frac{T_c}{V M_o T \rho_o^2} \left(\bar{F} - F_{vdW} \right) = \frac{3}{4} t^2 - \frac{1}{2} t \bar{n}^2 + \frac{1}{12} \bar{n}^4 , \tag{7-22}$$

and

$$\frac{T_c}{V M_o T \rho_o^2} \delta F \equiv \delta\hat{F} = \frac{1}{2V} \sum_{\ell m} (\bar{n}^2 + \Delta_\ell - t) \left| \int \chi_{\ell m}(\underline{r}) n(\underline{r}) d\underline{r} \right|^2$$
$$+ \frac{1}{2V} (1+\bar{n}^2) \int m^2(\underline{r}) d\underline{r} + \frac{1}{3V} \bar{n} \int n^3(\underline{r}) d\underline{r} + \frac{1}{12V} \int n^4(\underline{r}) d\underline{r} . \tag{7-23}$$

with $\Delta_\ell = T_c(M_o - M_\ell)/TM_o$ and where $m(\underline{r})$ is that part of $n(\underline{r})$ which is orthogonal to all $\chi_{\ell m}(\underline{r})$.

If only a single eigenmode is taken into account by setting $n(\underline{r}) = n_{\ell m}\chi_{\ell m}(r)$ then it is easily seen from eq. (7-23) and the minimum condition that on the critical isochore $\bar{n} = 0$

one has $n_{\ell m} = 0$ for $T > T_{\ell c} = T_c(1-\Delta_\ell)$. Thus $T_{oc} = T_c = T_{1c} > T_{2c} > \ldots$, and the various critical temperatures are separated by finite gaps which are independent of the volume V. The excess free energy δF is, unfortunately, not diagonal in the $\chi_{\ell m}$. The cubic and quartic terms in eq. (7-23) induce a coupling between eigenmodes. Furthermore, because the set $\{\chi_{\ell m}\}$ is not complete there will be also a coupling to eigenmodes with eigenvalue zero which are orthogonal to the $\chi_{\ell m}$. In other words, the absolute minimum of δF will only be found for densities $\rho(\underline{r})$ of the general form of eq. (6-12). It may be expected, however, that near T_c the most important contribution to δF arise from eigenmodes with small values of ℓ. This is born out by a more detailed calculation as outlined in the appendix C. In order to simplify the discussion of δF in this section we therefore take

$$n(\underline{r}) = \sqrt{V}\left[n_1 \chi_{10}(\underline{r}) + n_2 \chi_{20}(\underline{r}) \right] , \tag{7-24}$$

where n_1 and n_2 are variational parameters. The ansatz (7-24) automatically satisfies the condition (7-18).

Using eq. (7-24) we obtain

$$\begin{aligned} \delta\hat{F} = {} & \frac{1}{2}(\bar{n}^2 - t)n_1^2 + \frac{1}{2}(\bar{n}^2 + \Delta_2 - t)n_2^2 + A\bar{n}n_1^2 n_2 \\ & + B\bar{n}n_2^3 + Cn_1^4 + Dn_1^2 n_2^2 + En_2^4 , \end{aligned} \tag{7-25}$$

with $A = \sqrt{20/21}$, $B = 2\sqrt{35}/27\sqrt{3}$, $C = 5/28$, $D = 55/54$ and $E = 35/132$. The extremum conditions $\partial\delta\hat{F}/\partial n_\ell = 0$ yields

$$0 = n_1 \quad , \quad \text{or} \tag{7-26}$$

$$0 = \bar{n}^2 - t + 2A\bar{n}n_2 + 4Cn_1^2 + 2Dn_2^2 \quad , \tag{7-27}$$

and

$$0 = (\bar{n}^2 + \Delta_2 - t)n_2 + A\bar{n}n_1^2 + 3B\bar{n}n_2^2 + 2Dn_1^2n_2 + 4En_2^3 \ . \tag{7-28}$$

Along the critical isochore $\bar{n} = 0$ the only solution for $t>0$ with real n_1 and n_2 is

$$n_1 = \frac{1}{2}\sqrt{\frac{t}{C}} \quad , \quad n_2 = 0 \quad . \tag{7-29}$$

This gives $\delta\hat{F} = -t^2/4C = -7t^2/20$, which leads to $\Delta F = (8/15)\left[\bar{F} - F_{vdW}\right]$ at $\bar{n} = 0$.

Now we consider $\bar{n} \neq 0$ and set $n_2 = \bar{n}x$. Inserting eq. (7-27) for n_1^2 into eq. (7-25) we find

$$\begin{aligned}\delta\hat{F} = &-a(\bar{n}^2 - t)^2 - b(\bar{n}^2 - t)\bar{n}^2x - \frac{1}{2}\left[d(\bar{n}^2 - t) + g(\bar{n}^2 - \Delta(t))\right]\bar{n}^2x^2 \\ &- h\bar{n}^4x^3 - k\bar{n}^4x^4 \quad ,\end{aligned} \tag{7-30}$$

with coefficients $a = 1/16C$, $b = A/2C$, $d = (D/2C) - 1$, $g = A^2/2C$, $h = (AD/2C) - B$, $k = (D^2/4C) - E$, which are all positive, and $\Delta(t) = \Delta_2/g = 3(1+t)(M_0 - M_2)/8M_0$.

Since n_1 and n_2 must be real we see from eq. (7-28) that x has to be confined to the interval $x_- \leqslant x \leqslant x_+$ with

$$x_\pm = \frac{A}{2D}\left\{-1 \pm \left[1-\frac{2D}{A^2}\left(1-\frac{t}{\bar{n}^2}\right)\right]^{\frac{1}{2}}\right\} \quad . \tag{7-31}$$

A necessary condition for $\delta F \neq 0$ is that $x_\pm$ is real. Hence we have $\delta\hat{F} = 0$ for

$$t < \bar{n}^2\left(1-\frac{A^2}{2D}\right) = \frac{41}{77}\,\bar{n}^2 \quad , \tag{7-32}$$

and $F = \bar{F}(\bar{\rho}) > F_{vdW}$ in the temperature-density region $\bar{n}^2/3 < t < 41\,\bar{n}^2/77$.

Let us now examine $\delta\hat{F}$ in the neigborhood of the spinodal $t = \bar{n}^2$ of the $\ell = 1$ eigenmode for $\bar{n} \ll 1$. The minimum of $\delta\hat{F}$ then occurs for small negative values of x. Therefore we may neglect the x^4-term in $\delta\hat{F}$ and obtain

$$x_{min} = -\frac{1}{6h\bar{n}^2}\Big\{d(\bar{n}^2-t) + g(\bar{n}^2-\Delta(t)) + \left[\left(d(\bar{n}^2-t)+g(\bar{n}^2-\Delta(t))\right)^2 - 12bh\bar{n}^2(\bar{n}^2-t)\right]^{\frac{1}{2}}\Big\} . \tag{7-33}$$

On the spinodal we have

$$\begin{aligned} x_{min} &= -\frac{g}{3h}\left(1-\frac{\Delta(\bar{n}^2)}{\bar{n}^2}\right) \quad , \quad \bar{n}^2 > \Delta(\bar{n}^2) \; , \\ &= 0 \quad , \quad \bar{n}^2 < \Delta(\bar{n}^2) \; . \end{aligned} \tag{7-34}$$

Two special points exist on the spinodal: $t = t_{tr} = n_{tr}^2$, $\bar{n} = \pm\, n_{tr}$, where $n_{tr}^2 \equiv \Delta(n_{tr}^2)$ or

$$n_{tr}^2 = \frac{3}{8}\,\frac{M_0-M_2}{M_0}\left[1-\frac{3}{8}\,\frac{M_0-M_2}{M_0}\right]^{-1} . \tag{7-35}$$

Using the elastic constants of Nb we estimate $(M_o-M_2)/M_o \gtrsim 0.07$ and $n_{tr}^2 \approx 0.03$. Hence $3(M_o-M_2)/8M_o$ can be neglected in the denominator in eq. (7-35). Equivalently we may set $\Delta \approx n_{tr}^2$.

These points, at which the coefficients of the x- and the x^2-term in $\delta\hat{F}$ vanish, are the analogues of tricritical points. x_{min} is discontinous along the line $t_\tau(\bar{n})$ where the square root in eq. (7-33) equals zero,

$$d(\bar{n}^2-t) + g(\bar{n}^2-n_{tr}^2) = \left[12\,b\,h\,\bar{n}^2(\bar{n}^2-t)\right]^{\frac{1}{2}} , \tag{7-36}$$

which[†] corresponds to a line of inflection points of $\delta\hat{F}$. x_{min} jumps from zero for $t<t_\tau$ to the value

$$x_\tau = -\frac{1}{6h\bar{n}^2}\left[d(\bar{n}^2-t) + g(\bar{n}^2-n_{tr}^2)\right] \leqslant 0 , \tag{7-37}$$

at $t = t_\tau+0$. For $\bar{n}^2 \rightarrow n_{tr}^2+0$ the eq. (7-36) yields

$$t_\tau = \bar{n}^2 - \frac{g^2}{3bh}(\bar{n}-n_{tr})^2 , \tag{7-38}$$

and the jump-size vanishes according to

[†] In eq. (7-36) the positive square root has to be taken, since the conditions $\partial^2\partial\hat{F}/\partial x^2 \geqslant 0$ at X_{min} and $X_{min} \leqslant X_+$ require $d(\bar{n}^2-t) + g\,(\bar{n}^2-n_{tr}^2) \geqslant 0$.

$$x_\tau = -\frac{g}{3h}\left(1-\frac{n_{tr}}{\bar{n}}\right) \quad . \tag{7-39}$$

The discontinuity of x_{min} leads to a discontinuity of n_1^{min} via eq. (7-28):

$$\begin{aligned} (n_1^{min})^2 &= 0 \, , & t < t_\tau \\ &= \frac{Ag}{6Ch}\, n_{tr}^2 \left(1-\frac{n_{tr}}{\bar{n}}\right) \, , & t = t_\tau + 0 \, , \; \bar{n}^2 \to n_{tr}^2 + 0 \, . \end{aligned} \tag{7-40}$$

In the region $t<t_{tr}$ both n_1^{min} and n_2^{min} are continuous. One finds

$$\begin{aligned} (n_1^{min})^2 &= 0 \, , & t < \bar{n}^2 \, , \\ &= \frac{t-\bar{n}^2}{4C}\left[1 + \frac{2Ab}{g} \cdot \frac{\bar{n}^2}{n_{tr}^2 - \bar{n}^2}\right] \, , & t \to \bar{n}^2 + 0 \, , \end{aligned} \tag{7-41}$$

and

$$\begin{aligned} n_2^{min} &= 0 \, , & t < \bar{n}^2 \\ &= -\frac{b}{g}\, \bar{n}\, \frac{t-\bar{n}^2}{n_{tr}^2 - \bar{n}^2} \, , & t \to \bar{n}^2 + 0 \end{aligned} \tag{7-42}$$

The preceding discussion illustrates the behaviour of the free energy in the neighbourhood of the spinodal $t \equiv t_s = \bar{n}^2$. In order to obtain a more complete picture, also for other temperatures and densities, we have calculated ΔF numerically with the approximation $f_i = 0$ for $i>6$. The values of f_i for $i \leq 6$ were taken from eq. (7-5). In the computation we included the eigenmodes $\chi_{\ell m}$ with[†] $\ell \leq 5$, m = 0, and the leading contribution from the modes with zero eigenvalue. The contribution of the latter is also

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[†] There is no problem in principle to include also modes with $m \neq 0$. However, the resulting expression for $\delta\hat{F}$ is lengthy and difficult to analyze. We believe that the assumption of an axially symmetric density is not too restrictive.

discussed in appendix C. The dominant terms in the excess free energy are due to the $\ell = 1$ and $\ell = 2$ eigenmodes. The effect of modes with zero eigenvalue and of the eigenmodes with $\ell > 4$ on ΔF is of the order of 1 %, which indicates that all significant contributions have been taken into account. The results are summarized in the Figs. 7a,b, 8, 9 .

The phase diagram is shown in Fig. 7a. The curve t_I would be the coexistence line if the system would be normal or incoherent. In the present case of a coherent system there is no two-phase region in the usual sense. In region I the density of protons remains homogeneous and the Helmholtz free energy F equals $\bar{F}(\bar{n}) > F_{vdW}$. In region II, i.e. for $t > t_s$ $(t < t_{tr})$ or $t > t_\tau$ $(t > t_{tr})$, the density is inhomogeneous and varies on a macroscopic scale. The free energy is reduced as compared to $\bar{F}(\bar{n})$ but is still larger than F_{vdW} .

In Fig. 7b the temperature dependence of n_ℓ^{min} along the lines (1), (2) and (3) in Fig. 7a is shown. Obviously, the n_ℓ^{min} may be interpreted as order parameters and $\bar{n}$ acts like an external field shifting the critical temperature.

The excess free energy $(T_c/TVM_o\rho_o^2)\left[\Delta F(t,\bar{n}) - \Delta F(t,0)\right]$ is plotted in Fig. 8 as a function of density for various temperatures. At the lines t_τ in Fig. 7a, ΔF has a kink due to the discontinuities in n_ℓ^{min}.

In Fig. 9, density profiles along the symmetry axis are drawn for the points denoted by A and B in Fig. 7a.

Up to now we have discussed the Helmholtz free energy for a canonical ensemble of spherical crystals. In view of the shape-dependence of the spectrum of density modes one may ask whether the free energy also depends on the shape of the host crystal, and furthermore, whether the canonical and the grand canonical ensemble are equivalent. We shall make some brief remarks on these questions.

Shape-Dependence

The spectrum of macroscopic density modes in non-spherical crystals is not known, and the first question cannot be answered in detail. But we can give arguments which indicate that the excess free energy ΔF is indeed sensitive to the shape of the crystal.

The spectrum of density modes of any crystal contains the mode of uniform dilatation ($\ell = 0$ for a sphere). This mode is shape-independent and does not create coherency stresses. We assume that it corresponds to the largest eigenvalue M_o, say. Above T_c (given by eqs. (7-11) and (7-12)) the free energy then has an absolute minimum for a constant density $\bar{\rho}$, and we have $F = \bar{F}$. This also holds below T_c (where $\bar{F}$ is of the form shown in Fig. 4, also for non-spherical crystals), provided $\bar{\rho}$ is outside of the interval between ρ_G and ρ_F. Consequently, in the $(T\rho)$-region where $F = \bar{F} = F_{vdW}$, $\Delta F = 0$, the Helmholtz free energy is shape-independent. On the other hand, for $\rho_G < \bar{\rho} < \rho_F$, F will be minimized by an inhomogeneous density.

Consider now a cylindrical crystal of length L and diameter $d \ll L$. For a variational ansatz we take an axially symmetric $\rho(\underline{r})$ as shown in Fig. 10, where the constant densities ρ_F and ρ_G are matched by a transition region of width δ. The effect of the part of the cylinder containing the homogeneous liquid phase on the remaining part can be replaced by shear forces acting in a cross section at L_F. According to St. Venant's principle the strains produced by these stresses will have a range of the order of the linear dimension of the area in which the stresses are acting.

From this we conclude that the variational parameter δ is of the order of the diameter d, irrespective of the location of the transition region within L. The excess free energy $\Delta F/Ld^2 \propto d/L$ caused by the coherency stresses which are confined to the volume $\delta^3 \approx d^3$ vanishes in the thermodynamic limit L, $d \rightarrow \infty$, $d/L \rightarrow 0$. In other words, for a long thin wire we have, as in a normal liquid, two coexisting phases separated by an "interface" which contributes negligibly to the bulk free energy. Hence we find that $F = F_{vdW}$ throughout the whole $(T\rho)$-plane[†].

[†] In going from a spherical shape to a long cylinder we expect the gaps in the spectrum of macroscopic density-modes to decrease steadily. Consequently the tricritical points P_τ in Fig. 7 will move towards the critical point $\bar{n} = 0$, $t = 0$ and the lines t_τ of first-order transition will approach the "coexistence curve" $t = \bar{n}^2/3$.

Grand Canonical Ensemble, Gibbs Free Energy.

Consider an ensemble of crystals which can freely exchange hydrogen with a surrounding hydrogen atmosphere. This constitutes a grand canonical ensemble for the protons in the metal. We denote by $G(T,\mu)$ the associated Gibbs free energy, where μ is the chemical potential[†] of the protons in the metal. According to the rules of statistical mechanics the Gibbs free energy G is related to the Helmholtz free energy by a Legendre transformation $G(T,\mu) = F(T,\bar{\rho}) - V\mu\bar{\rho}$, where $\bar{\rho}(T,\mu)$ is determined from $(1/V)\partial F/\partial\bar{\rho} = \mu$, provided this equation has a unique solution. Thus, the Gibbs free energy is well defined in the $(T\rho)$-region where $F = F_{vdW}$. However, by prescribing a constant μ instead of $\bar{\rho}$ we cannot enter the region $t>\bar{n}^2/3$ (see Fig. 6) within the "coexistence" curve, except in those cases like the wire, where we have the two phases simultaneously within one specimen. Let us consider only compact shapes and suppose the chemical potential to be fixed at its critical value $\mu_c = k_B T_c f_1(\bar{\rho}_c) - M_o\bar{\rho}_c$. For temperatures $T \geq T_c$ the average density of protons in the crystals is ρ_c. As we cool to $T<T_c$, the

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[†] Since the hydrogen molecule dissociates in the metal we have in equilibrium $\mu_{H_2} = 2\mu + 2\mu_B$, where μ_{H_2} is the chemical potential of the hydrogen gas and μ_B is the binding energy for a single proton. Varying the pressure and the temperature of the gas, we can adjust μ.

average density in a given crystal will be either $\rho_G = \rho_c - \rho_0 \times \sqrt{3t}$ or $\rho_F = \rho_c + \rho_0\sqrt{3t}$, with equal probability. Those crystals with ρ_F, for example, have absorbed hydrogen from the surrounding gas and have uniformly expanded. No coherency stresses are created in this way[†]. In the neighbourhood of T_c critical fluctuations in the number of dissolved protons occur, and the isothermal compressibility of the hydrogen lattice gas diverges as $(T-T_c)^{-1}$. The only mode which contributes to these critical fluctuations is the mode of uniform dilatation. The divergence of the isothermal compressibility leads to a divergence in the Gorsky relaxation strength according to eqs. (3-10) and (3-13) where $\Gamma_{xx} + 2\Gamma_{xy} \propto \langle (N-\langle N\rangle)^2 \rangle$.

In the case of the elastic interaction there is a conceptual difference between the grand canonical and the canonical ensemble where the number of protons in each crystal is fixed. If the forces between protons were short-ranged than a collection of subvolumes within each crystal, which is a member of the canonical ensemble, would already constitute a grand canonical ensemble[††]. Below T_c, for instance, we would have subvolumes

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[†] In practice, coherency stresses do arise, of course, since during a change in density the protons require a certain amount of time to penetrate through the surface into the bulk or vice versa. During this transient period the density in the crystals is inhomogeneous.

[††] This statement is a crude version of the equivalence of the ensembles, which holds strictly only in the thermodynamic limit.

containing the liquid phase in contact with subvolumes containing the gaseous phase.

This is no longer true if we consider the elastic interaction. The above configuration describing liquid droplets immersed in the gaseous phase is energetically unfavourable because of large coherency stresses which are caused by the sharp interfaces. Instead of the equilibrium condition μ = constant within a crystal, we have the requirement of coherency which is a global property of the whole crystal. The thermal density fluctuations in the subvolumes of a large coherent crystal are not representative for a grand canonical ensemble, especially, if the system is near T_c or in the region of inhomogeneous density.

§ 8 Conclusion

We have based our study of the statistical mechanics and thermodynamics of metal-hydrogen solutions on the assumption of a predominant elastic interaction between the protons in the metal. There exists some experimental evidence in favour of this hypothesis (Alefeld 1972). In a subsequent paper we will also show that our model, despite its simplifications, accounts reasonably well for the gas-liquid part of the phase-diagram of Nb-H.

Here, our aim was to explore the theoretical consequences which result from the long range of the elastic interaction. The features of the phase transition governed by the elastic interaction are indeed unusual: shape dependent and non-concave free energy, absence of coexisting gaseous and liquid phases, suppression of critical density fluctuations by coherency stresses.

One knows that similar features are found in Curie-Weiss type models where in the case of a ferromagnet for instance, every spin interacts with every other spin with an exchange coupling proportional to V^{-1}. The exciting prospect here is, of course, that an interaction of this type exists in a real material, and there is a basis for expecting the classical theory of phase transitions to hold rigorously for metal-hydrogen systems.

At first sight this conjecture seems to contradict a fundamental theorem of statistical mechanics, proved recently by Lieb and Lebowitz (1972) in its most general form. Any piece of matter can ultimately be described as an electrically neutral collection of nuclei and electrons interacting via Coulomb forces. The theorem asserts that the Helmholtz free energy of such a system in thermal equilibrium must be concave.

One has to realize, however, that a crystal subject to coherency stresses is generally not in total thermodynamic equilibrium. The requirement of coherency keeps the crystal in a metastable state. For a strictly harmonic crystal the coherent state is the total equilibrium state. In this case the forces between lattice atoms increase indefinitely with distance and the theorem does not apply. On the other hand, any real crystal is anharmonic and the forces tend to zero with increasing separation of the atoms. Therefore, in a real crystal under coherency stresses there exists a finite probability for the formation of dislocations which reduce the stresses until the crystal finally relaxes into a stress-free but incoherent state.

The important question now is whether and to what extend coherency can be achieved in experiments for temperatures below T_c. It will be difficult to provide a reliable answer but we try to give a very crude estimate which leads us to believe that coherency can be realized in experiments.

Consider a spherical crystal with a hydrogen density $\rho \approx \rho_c$, and let it contain a number of dislocations. As we cool slowly to temperatures below T_c the hydrogen density becomes inhomogeneous and coherency stresses build up[†].

If the maximum shear stress exceeds some critical value the dislocations will start to move in such a way as to reduce the stresses and additional dislocations will be created (by a Frank-Read mechanism, for example). For a spherical sample one finds (Burkhardt 1973) that the maximum shear stress is of the order of $10^{-3}C_{44}$ at about 10 degrees below T_c ($\approx 450\ ^{\circ}K$ in Nb). The empirical values for critical stresses determining the onset of plastic deformations are of magnitude $10^{-4}C_{44}$. A much larger temperature interval for coherency results if we optimistically start with a dislocation-free crystal. The critical stresses for the creation of a dislocation are then expected to come close the "theoretical" limit $10^{-1}C_{44}$, as found in whiskers.

[†] With the variational ansatz (7-24) the coherency stresses vanish along the critical isochore $\bar{n} = 0$ since $n_2 = 0$. Eq. (7-24) is only valid for very small t. As t increases, we have to take into account modes with $\ell > 2$. The contribution of the $\ell = 3$ mode is finite at $\bar{n} = 0$. It is still true, however, that the coherency stresses in a sphere are smallest at $\bar{n} = 0$.

Acknowledgement

We wish to thank Professor G. Alefeld for many invaluable conversations about the physics of metal-hydrogen systems.

We are indebted to Professor R. Bausch, Professor R. B. Griffiths, Dr. K. Kehr, and Dr. F. Wegner for stimulating and clarifying discussions.

We also thank Dr. T. Burkhardt and Professor R. B. Griffiths for a critical reading of the manuscript.

Appendix A

Continuum approximation for H_{el}.

In the textbooks and monographs on lattice dynamics the transition from a discrete lattice with free surface to the continuum is usually discussed only for the special case of spatially constant strains. Therefore it might be helpful to sketch the arguments for the more general case of inhomogeneous strains.

We start with the Hamiltonian

$$H_{el} = \underline{v}^{m} \cdot \underline{\Psi}^{ma} \tau_a + \frac{1}{2} \underline{v}^{m} \cdot \underline{\underline{\Phi}}^{mn} \cdot \underline{v}^{n} \quad , \tag{A-1}$$

and the condition of mechanical equilibrium

$$\underline{\underline{\Phi}}^{mn} \cdot \underline{v}^{n} = - \underline{\Psi}^{ma} \tau_a \quad . \tag{A-2}$$

We now replace $\underline{v}^m$ and τ_a by smooth functions $\underline{v}(\underline{r})$ and $\tau_j(\underline{r})$ which are assumed to be slowly varying within the range of the forces $\underline{\Psi}^{ma}$ and $\underline{\underline{\Phi}}^{mn}$. Hence we may expand $\tau_a \rightarrow \tau(\underline{Q}_a)$ and $\underline{v}^n \rightarrow \underline{v}(\underline{R}^n)$ in (A-1) and (A-2) around $\underline{R}^m$. Then eq. (A-2) becomes

$$\begin{aligned} &\sum_n \Phi^{mn}_{\mu\nu} v_\nu (\underline{R}^m) + \sum_n \Phi^{mn}_{\mu\nu} (R^n_\alpha - R^m_\alpha) \partial_\alpha v_\nu (\underline{R}^m) \\ &+ \frac{1}{2} \sum_n \Phi^{mn}_{\mu\nu} (R^n_\alpha - R^m_\alpha)(R^n_\beta - R^m_\beta) \partial_\alpha \partial_\beta v_\nu (\underline{R}^m) \\ &= - \sum_a \Psi^{ma}_{\mu} \tau_j (\underline{R}^m) - \sum_a \Psi^{ma}_{\mu} (Q^a_\alpha - R^m_\alpha) \partial_\alpha \tau_j (\underline{R}^m) \quad . \end{aligned} \tag{A-3}$$

We have only kept leading contributions (c.f. 2nd. comment after eq. (2-6)). The first term on the ℓhs vanishes because of eq. (2-7) (translational invariance). The second term on the ℓhs and the first term on the rhs are non-zero only if $\underline{R}^m$ is on the surface S ($\underline{R}^m \in S$) of the crystal, where some lattice - or hydrogen-sites in the neighbourhood of $\underline{R}^m$ are missing. Let us consider first the case where $\underline{R}^m$ is in the bulk of the crystal.

$\underline{R}^m \in V$:

The configuration $\{\underline{R}^m\}$ is determined from $\underline{\Phi}^m(R) = 0$, i.e. there are no external surface forces. Then

$$\sum_n \phi^{mn}_{\mu\nu}(R^n_\alpha - R^m_\alpha)(R^n_\beta - R^m_\beta) = -\frac{V}{N_L}\left(C_{\mu\alpha\nu\beta} + C_{\mu\beta\nu\alpha}\right), \qquad \text{(A-4)}$$

where the $C_{\mu\alpha\nu\beta} = C_{\mu\alpha\beta\nu} = C_{\nu\beta\mu\alpha}$ are the elastic constants (see e.g. Ludwig 1969).

Similarly, with $a = (a_j, j)$

$$\sum_{a_j} \psi^{ma_j}_\mu (Q^{a_j}_\alpha - R^m_\alpha) = -\frac{N_{Hj}}{N_L}\sum_m \psi^{ma_j}_\mu (R^m_\alpha - Q^{a_j}_\alpha) \equiv -\frac{N_{Hj}}{N_L} P^j_{\mu\alpha}. \qquad \text{(A-5)}$$

With (A-4) and (A-5) we find from (A-3)

$$\frac{V}{N_L} C_{\mu\alpha\nu\beta}\, \partial_\alpha \partial_\beta v_\nu(\underline{R}^m) = -\frac{N_{Hj}}{N_L}\sum_j P^j_{\mu\alpha}\, \partial_\alpha \tau_j(\underline{R}^m). \qquad \text{(A-6)}$$

Introducing the strain tensor (eq.(2-18)) and the proton densities $\rho_j(r) = N_{Hj}\tau_j(\underline{r})/V$ we obtain eq. (2-21).

Now consider eq. (A-3) for $\underline{R}^m$ on the surface S .

$\underline{\underline{R^m \subset S}}$:

$$-\sum_a \Psi^{ma}_\mu \tau_j(\underline{R}^m) = \sum_n \phi^{mn}_{\mu\nu} (R^n_\alpha - R^m_\alpha)\, \partial_\alpha v_\nu(\underline{R}^m) \quad . \tag{A-7}$$

Here, $\partial_\alpha v_\nu$ can be replaced by $\varepsilon_{\alpha\nu}$ because of eq. (2-7) (rotational invariance). From eq. (2-7) (translational invariance) and eq. (A3) we find

$$\sum_m \sum_a \Psi^{ma}_\mu \tau_a = 0 = \sum_{m\subset S} \sum_a \Psi^{ma}_\mu \tau_j(\underline{R}^m) - \frac{N_{Hj}}{N_L} \sum_m \sum_j P^j_{\mu\alpha}\, \partial_\alpha \tau_j(\underline{R}^m) . \tag{A-8}$$

We define the density of surface forces, $k_\mu(\underline{r})$, by

$$\sum_{m\subset S} \sum_a \Psi^{ma}_\mu \tau_j(\underline{R}^m) \equiv \oint_S k_\mu(\underline{r})\, df = \int P^j_{\mu\alpha}\, \partial_\alpha \rho_j(\underline{r})\, d\underline{r} \quad . \tag{A-9}$$

Since $\rho_j(\underline{r})$ is arbitrary we have

$$k_\mu(\underline{r}) = e_\alpha(\underline{r})\, \Pi_{\mu\alpha}(\underline{r}) \quad , \qquad \underline{r} \subset S \quad , \tag{A-10}$$

where $\underline{e}(\underline{r})$ is an outward-directed normal unit vector on S .

Finally, we transform H_{el}, (A-1), into its continuum form:

$$\underline{v}^m \cdot \underline{\Psi}^{ma} \bar{\tau}_a = \sum_m \sum_a v_\mu(R^m) \Psi^{ma}_\mu \left[\tau_j(\underline{R}^m) + (Q^a_\alpha - R^m_\alpha)\, \partial_\alpha \tau_j(R^m)\right]$$

$$\rightarrow \oint_S v_\mu(\underline{r})\, k_\mu(\underline{r})\, df - \sum_j \int_V v_\mu(\underline{r})\, P_{\mu\alpha}\, \partial_\alpha \rho_j(\underline{r})\, d\underline{r} \tag{A-11}$$

$$= \int_V \varepsilon_{\mu\alpha}(\underline{r})\, \Pi_{\mu\alpha}(\underline{r})\, d\underline{r} \quad ,$$

$$\frac{1}{2}\underline{v}^m\cdot\underline{\underline{\phi}}^{mn}\underline{v}^n = \frac{1}{2}\sum_{mn} v_\mu(\underline{R}^m)\phi^{mn}_{\mu\nu}(R^n_\alpha - R^m_\alpha)\partial_\alpha v_\nu(\underline{R}^m)$$

$$+\frac{1}{4}\sum_{mn} v_\mu(\underline{R}^m)\phi^{mn}_{\mu\nu}(R^n_\alpha - R^m_\alpha)(R^n_\beta - R^m_\beta)\partial_\alpha\partial_\beta v_\nu(\underline{R}^m)$$

$$= -\frac{1}{2}\sum_{m\subset S}\sum_a v_\mu(R^m)\psi^{ma}_\mu\,\tau_f(\underline{R}^m) \tag{A-12}$$

$$-\frac{V}{2N_L}\sum_m v_\mu(\underline{R}^m)C_{\mu\alpha\nu\beta}\partial_\alpha\partial_\beta v_\nu(\underline{R}^m)$$

$$\longrightarrow -\frac{1}{2}\oint_S v_\mu(\underline{r})k_\mu(\underline{r})df - \frac{1}{2}\int_V v_\mu(\underline{r})C_{\mu\alpha\nu\beta}\partial_\alpha\partial_\beta v_\nu(\underline{r})\,.$$

We impose the boundary condition

$$k_\mu(\underline{r}) = e_\alpha(\underline{r})C_{\mu\alpha\nu\beta}\,\varepsilon_{\nu\beta}(\underline{r})\,,\qquad \underline{r}\subset S\,, \tag{A-13}$$

Then eqs. (A-10) and (A-13) lead to eq. (2-22). Furthermore

$$\frac{1}{2}\underline{v}^m\cdot\underline{\underline{\phi}}^{mn}\cdot\underline{v}^n \longrightarrow \frac{1}{2}\int_V \varepsilon_{\alpha\beta}(\underline{r})\,C_{\alpha\beta\mu\nu}\,\varepsilon_{\mu\nu}(\underline{r})\,d\underline{r}\,. \tag{A-14}$$

Appendix B

Spectrum of macroscopic density-modes in an isotropic sphere

The solution of the "problem of a sphere" in elasticity theory goes back to Lord Kelvin. A detailed discussion can be found in Love's book (1959), chapter XI, where the displacements in a sphere subject to body forces which have a potential are calculated. The corresponding equilibrium condition is formally identical to our eq. (5-12). For the convenience of the interested reader we sketch here the computation of the eigenvalues M_ℓ, employing the so called Papkovitch-Neuber ansatz (Sneddon and Berry 1958), whereby the displacements are determined in terms of four harmonic functions.

The stress tensor which enters into the boundary condition (5-4) reads, after the insertion of eq. (5-13) into eq. (5-10)

$$\sigma_{\alpha\beta} = -\frac{2\mu}{\lambda+2\mu}\,\Pi\,\delta_{\alpha\beta} + 2\mu\,\partial_\alpha\partial_\beta\Lambda + \lambda\,\delta_{\alpha\beta}\,\underline{\nabla}\cdot\underline{u} + \mu(\partial_\alpha u_\beta + \partial_\beta u_\alpha)\,. \tag{B-1}$$

Λ obeys the Poisson equation (5-14). Writing

$$\Lambda(\underline{r}) = \sum_{\ell m} \Lambda_{\ell m}(r)\,Y_{\ell m}(\Omega)\,, \qquad \Pi(\underline{r}) = \sum_{\ell m} \Pi_{\ell m}(r)\,Y_{\ell m}(\Omega)\,, \tag{B-2}$$

one obtains from eq. (5-14) the ordinary differential equation

$$\Lambda''_{\ell m} + \frac{2}{r}\Lambda' - \frac{\ell(\ell+1)}{r^2}\Lambda_{\ell m} = -\frac{1}{\lambda+2\mu}\,\Pi_{\ell m}\,, \tag{B-3}$$

which is solved by "variation of the constants". The solution regular at r = 0 is

$$\Lambda_{\ell m}(r) = \frac{1}{(\lambda+2\mu)(2\ell+1)} \left[r^{-\ell-1} \int_0^r \Pi_{\ell m}(x)\, x^{\ell+2}\, dx \right. \tag{B-4}$$

$$\left. + \; r^{\ell} \int_r^R \Pi_{\ell m}(x)\, x^{1-\ell}\, dx \right] \quad .$$

For the displacements u we make the Papkovitch-Neuber ansatz

$$\underline{u}(\underline{r}) = \underline{\nabla}\left(\phi(\underline{r}) + \underline{r} \cdot \underline{\Psi}(\underline{r}) \right) - \frac{2\lambda + 4\mu}{\lambda + \mu}\, \underline{\Psi}(\underline{r}) \; . \tag{B-5}$$

Then eq. (5-15) is identically fulfilled if

$$\nabla^2 \phi = \sigma = \nabla^2 \underline{\Psi} \quad . \tag{B-6}$$

We set

$$\phi(\underline{r}) = \sum_{\ell m} \phi_{\ell m}(r)\, Y_{\ell m}(\Omega) \quad . \tag{B-7}$$

A solution of eq. (B-6) for ϕ, regular at r = 0, is

$$\phi_{\ell m}(r) = A_\ell\, r^{\ell} \quad . \tag{B-8}$$

For $\underline{\Psi}$ we may write

$$\underline{\Psi}(\underline{r}) = \sum_{\ell m} \left[\frac{1}{r} \Psi^{(1)}_{\ell m}(r)\, \underline{r} + \Psi^{(2)}_{\ell m}(r)\, \underline{L} - \frac{i}{r^2} \Psi^{(3)}_{\ell m}(r)\, \underline{r} \times \underline{L} \right] Y_{\ell m}(\Omega) \; , \tag{B-9}$$

in terms of three mutually orthogonal vectors with $\underline{L} = -i(\underline{r} \times \underline{\nabla})$.

Without loss of generality we may set $\Psi_{\ell m}^{(2)} = 0$ (see below). Using the identities $\underline{\nabla} = (\underline{r}/r)\partial_r - (i/r^2)\,(\underline{r}\mathrm{x}\,\underline{L})$, $\nabla^2 = \partial_r^2 + (2/r)\partial_r - L^2/r^2$ and $L^2 Y_{\ell m} = \ell(\ell+1)Y_{\ell m}$, we find

$$\Delta\underline{\Psi} = \underline{\nabla}\sum_{\ell m}\left[2\left(\frac{1}{r}\Psi_{\ell m}^{(1)} - \frac{1}{r}\partial_r\Psi_{\ell m}^{(3)}\right)Y_{\ell m} + \nabla^2\left(\Psi_{\ell m}^{(3)}\,Y_{\ell m}\right)\right]$$
$$+\underline{r}\sum_{\ell m}\nabla^2\left[\left(\frac{1}{r}\Psi_{\ell m}^{(1)} - \frac{1}{r}\partial_r\Psi_{\ell m}^{(3)}\right)Y_{\ell m}\right], \tag{B-10}$$

and eq. (B-6) for $\underline{\Psi}$ is obeyed if

$$\Psi_{\ell m}^{(1)} = B_\ell\, r^{\ell+1}, \quad \Psi_{\ell m}^{(3)} = -\frac{1}{\ell+1}B_\ell\, r^{\ell+2}. \tag{B-11}$$

After insertion of (B-5) into (B-1), the boundary condition (5-4) finally becomes

$$\frac{\lambda\mu}{\lambda+\mu}\,\underline{r}\,(\underline{\nabla}\cdot\underline{\Psi}) - \mu(\underline{r}\cdot\underline{\nabla})\,\underline{\nabla}\,(\phi + \underline{r}\cdot\underline{\Psi})$$
$$+\frac{\mu(\lambda+2\mu)}{\lambda+\mu}\left[\underline{\nabla}(\underline{r}\cdot\underline{\Psi}) + (\underline{r}\cdot\underline{\nabla})\underline{\Psi} - \underline{\Psi}\right] \tag{B-12}$$
$$= \frac{\mu}{\lambda+2\mu}\,\underline{r}\,\Pi + \mu(\underline{r}\cdot\underline{\nabla})\,\underline{\nabla}\Lambda,$$

with r = R = radius of the sphere. The rhs of eq. (B-12) is orthogonal to $\underline{L}$. This fact justifies setting $\Psi_{\ell m}^{(2)} = 0$ in (B-8). The remaining manipulations are straightforward. We have to insert the expressions (B-4), (B-7) with (B-8), (B-9) with $\Psi_{\ell m}^{(2)} = 0$ and (B-11) into (B-12) and compare the coefficients of $\underline{r}$ and $\underline{\nabla}Y_{\ell m} = -(i/r^2)\,(\underline{r}\mathrm{x}\underline{L})\,Y_{\ell m}$, respectively.

One obtains

$$A_\ell \frac{\ell(\ell-1)}{R^2} + B_\ell \left[\ell(\ell-1) - \frac{3\lambda+2\mu}{\lambda+\mu}\right] = -\frac{(\ell+1)(\ell+2)}{(2\ell+1)(\lambda+2\mu)R^{2\ell+3}}\hat{\Pi}_{\ell m}$$

$$A_\ell \frac{\ell-1}{R^2} + B_\ell \left[\ell+1 - \frac{\lambda+2\mu}{(\ell+1)(\lambda+\mu)}\right] = \frac{\ell+2}{(2\ell+1)(\lambda+2\mu)R^{2\ell+3}}\hat{\Pi}_{\ell m} , \tag{B-13}$$

where

$$\hat{\Pi}_{\ell m} = \int_0^R \Pi_{\ell m}(r)\, r^{\ell+2}\, dr . \tag{B-14}$$

We are ultimately interested in

$$\underline{\nabla}\cdot\underline{u} = -\frac{2\mu}{\lambda+\mu}\,\underline{\nabla}\cdot\underline{\Psi} = -\frac{2\mu}{\lambda+2\mu}\sum_{\ell m}(2\ell+3)B_\ell r^\ell Y_{\ell m}(\Omega) . \tag{B-15}$$

Solving (B-13) for B_ℓ, we arrive at

$$\underline{\nabla}\cdot\underline{u} = -\frac{2\mu}{\lambda+2\mu}\sum_{\ell m}\frac{(\ell+1)(\ell+2)(2\ell+3)}{\lambda[2\ell^2+4\ell+3]+2\mu[\ell^2+\ell+1]}\,\frac{r^\ell}{R^{2\ell+3}}\,Y_{\ell m}(\Omega)\,\hat{\Pi}_{\ell m} \tag{B-16}$$

$$= -\frac{1}{P}\int M(\underline{r},\underline{r}')\,\rho(\underline{r}')\,d\underline{r}' ,$$

with $M(\underline{r},\underline{r}')$ given by the eqs. (5-22) with (5-23) and (5-24).

It is of interest to compare the above spectrum of macroscopic density-modes of a sphere with a free surface (i.e. $e_\beta\sigma_{\alpha\beta} = 0$) with the spectrum obtained from the boundary condition $\underline{v} = \underline{\nabla}\Lambda + \underline{u} = 0$, at the surface r = R. For the latter case one finds

$$M_\ell = -\frac{\mu}{\lambda+2\mu}\,\frac{P^2}{(\ell+1)[\ell(\lambda+3\mu)+\mu]} < 0 . \tag{B-17}$$

Thus the elastic interaction H_{int} (cf. eq. 5-31) is repulsive if the surface of the sphere is held fixed.

Appendix C

Correction to $\delta\hat{F}$

The dominant coupling term between density-modes in $\delta\hat{F}$ is the cubic term in eq. (7-23). Consider a density variation $n(\underline{r})$ of the form

$$n(\underline{r}) = n_1 \chi_1(\underline{r}) + n'(\underline{r}) , \tag{C-1}$$

with n' orthogonal to $\chi_0 = 1/\sqrt{V}$ and $\chi_1 (\chi_\ell \equiv \chi_{\ell 0})$. The cubic term $\propto n^3$ in eq. (7-23) leads to a coupling between the $\ell = 1$ eigenmode and n',

$$n_1^2 \int \chi_1^2(\underline{r})\, n'(\underline{r})\, d\underline{r} \equiv n_1^2\,(\chi_1 , n') . \tag{C-2}$$

From the expansion of n' in a series of spherical harmonics, only the $\ell = 0$ and $\ell = 2$ components contribute in (C-2). Therefore n' may be written as

$$n'(\underline{r}) = n_2 \chi_2(\underline{r}) + m(\underline{r}) \tag{C-3}$$

with

$$(m, \chi_0) = (m, \chi_1) = (m, \chi_2) = 0 . \tag{C-4}$$

Furthermore, from the stationary property of $\delta\hat{F}$ with respect to variation of $m(\underline{r})$ one concludes that $m \propto n_1^2$, as is the case for n_2 in the neighbourhood of the $\ell = 1$ spinodal. This can be seen after inserting eqs. (C-1) and (C-3) into eq. (7-23) :

$$\delta\hat{F}(n_1\, n_2\, \{m\}) = \delta\hat{F}(n_1\, n_2\, 0) + \tfrac{1}{2}(1+\bar{n}^2)(m, m) + \bar{n}\, n_1^2\,(m, \chi_1^2) + \ldots , \tag{C-5}$$

where the terms dropped are of order $n_1 n_2 m \propto n_1^2 m$, etc. Varying $\delta\hat{F}$ with respect to m and using Lagrange parameters for the constraints (C-4) we obtain

$$0 = (1+\bar{n}^2)\, m(\underline{r}) + \bar{n}\, n_1^2 \chi_1^2(\underline{r}) - \sum_\ell \mu_\ell \chi_\ell(\underline{r}) + \ldots , \tag{C-6}$$

with the solution

$$m(\underline{r}) = -\frac{\bar{n}\, n_1^2}{1+\bar{n}^2}\left[\chi_1^2(\underline{r}) - \chi_0(\underline{r})(\chi_0, \chi_1^2) - \chi_2(\underline{r})(\chi_2, \chi_1^2)\right] + O(n_1^3) . \tag{C-7}$$

With this expression for $m(\underline{r})$ we find

$$\delta\hat{F}(n_1\, n_2\, \{m\}) \rightarrow \delta\hat{F}(n_1\, n_2\, 0) - \frac{2}{21}\,\frac{\bar{n}^2}{1+\bar{n}^2}\, n_1^4 + O(n_1^6) . \tag{C-8}$$

Thus the effect of $m(\underline{r})$ is only to renormalize the coefficient of the n_1^4- term in eq. (7-25),

$$C \rightarrow C' = C\left(1 - \frac{8}{15}\,\frac{\bar{n}^2}{1+\bar{n}^2}\right) > 0 . \tag{C-9}$$

References

1 Alefeld, G., 1969, Phys. Stat. Sol., 32, 67; 1972, Ber. Bunsenges. physik. Chem. 76, 746.

2 Alefeld, G., J. Völkl, and Schaumann, G., 1970, Phys. Stat. Sol. 37, 337.

3 Benn, R., 1972, Diplomarbeit, Univ. Köln, unpublished.

4 Buchholtz, J., Völkl, J., and Alefeld G., 1973, Phys. Rev. Lett. 30, 318.

5 Buchholtz, J., 1973, Thesis, Technische Hochschule Aachen.

6 Burkhardt, T., 1973, private communication.

7 Cahn, J.W., 1961, Acta Met. 9, 795; 1962, Acta Met. 10, 179.

8 Conrad, H., Bauer, G., Alefeld, G., Springer, T., and Schmatz, W., 1973, to be published in Z. Physik.

9 Cook, H.E., and DeFontaine, D., 1969, Acta Met. 17, 915; 1971, Acta Met. 19, 607.

10 Eshelby, J.D., 1956, Solid State Phys. 3, 79, edited by F. Seitz and D. Turnbull, Academic Press, New York and London.

11 Hardy, J.R., and Bullough, R., 1967, Phil. Mag. 15, 237.

12 Kanzaki, H., 1957, Physics Chem. Solids 2, 24.

13 Khachaturyan, A.G., 1966, Fiz. Tverd. Tela 8, 2709, translated in Sov. Phys. Solid State 8, 2163 (1967).

14 Krivoglaz, M.A., 1963, Fiz. Tverd. Tela 5, 3439, translated in Sov. Phys. Solid State 5, 2526 (1964).

15 Lebowitz, J.L., and Penrose, O., 1966, J. Math. Phys. 7, 98.

15a Ledermann, W., 1944, Proc. Roy. Soc. Ser. A182, 362.

16 Lieb, E., and Lebowitz, J.L., 1972, Advances in Math. 9, 316.

17 Love, A.E.H., A Treatise on the Theory of Elasticity, Fourth Edition, Cambridge 1959, chapter XI.

18 Ludwig, W., 1967, Recent Developments in Lattice Theory, in Springer Tracts in Modern Physics, Bd. 43., Berlin.

19 Sharp, R.I., 1969, J. Phys. C 2, 421.

20 Siems, R., 1969, Phys. Stat. Sol. 42, 105.

21 Sneddon, I.N., and Berry, D.S., 1958, The Classical Theory of Elasticity, in Encyclopedia of Physics, vol. VI, edited by S. Flügge, Springerverlag, Berlin.

22 Somenkov, V.A., Gurskaya, A.V., Zemlyanov, M.G., Kost, M.E., Chernoplekov, N.A., and Chertkov, A.A., 1968, Fiz. Tverd. Tela 10, 1355, translated in Sov. Phys. Solid State 10, 1076 (1968).

23 Van Kampen, N.G., 1964, Phys. Rev. 135, A362.

24 Wagner, H., and Swift, J., 1970, Z. Physik 239, 182.

25 Worsham Jr., J.E., Wilkinson, M.K., and Shull, C.G., 1957, Physics Chem. Solids 3, 303.

Figure Captions

Fig. 1 Phase diagram of Nb-H according to Walter and Chandler (1965).

Fig. 2a Tetrahedral sites (o) in a bcc lattice. The proton sites are labelled by the axis which they distinguish. For clarity the sites on the front face are not shown.

Fig. 2b Octahedral sites (o) in a fcc lattice.

Fig. 3 Schematic plot of the reference free energy density as a function of ρ ; $f_2(\rho,T) = 0$ for $\rho_G' < \rho < \rho_F'$ (gas-liquid transition) and for $\rho_F'' < \rho < \rho_S$ (liquid-solid transition).

Fig. 4 Schematic plot of the free energy $\bar{F}(T,\bar{\rho})$, eq. (7-9), for $T<T_c$.

Fig. 5 Density profile for two coexisting phases in a sphere.

Fig. 6 Excess free energy $\Delta\hat{F} = T_c(\bar{F}-F_{vdW})/TVM_o\rho_o{}^2$.

Fig. 7 a. Phase diagram in the neighbourhood of T_c. The heavy dots (t_{tr}) denote tricritical points. For $t<t_{tr}$ the spinodal (light solid) of the $\ell = 1$ mode is a line of critical points. Along the lines t_τ the phase transition is of first order. The spinodal for $t>t_{tr}$ is dashed. For the points A and B see Fig. 9.

b. Order parameters n_ℓ^{min} as functions of temperature for average densities indicated by (1), (2) and (3) in Fig. 7a.

Fig. 8 Excess free energy as obtained from the numerical calculation. The dash-dotted line shows the result if only the $\ell = 0$ and $\ell = 1$ modes are taken into account.

Fig. 9 Density profiles along the z-axis of a sphere for the points A (lower figure) and B (upper figure) indicated in Fig. 7a. The density profile for an incoherent crystal is dashed.

Fig. 10 Variational density profile for a cylindrical crystal.

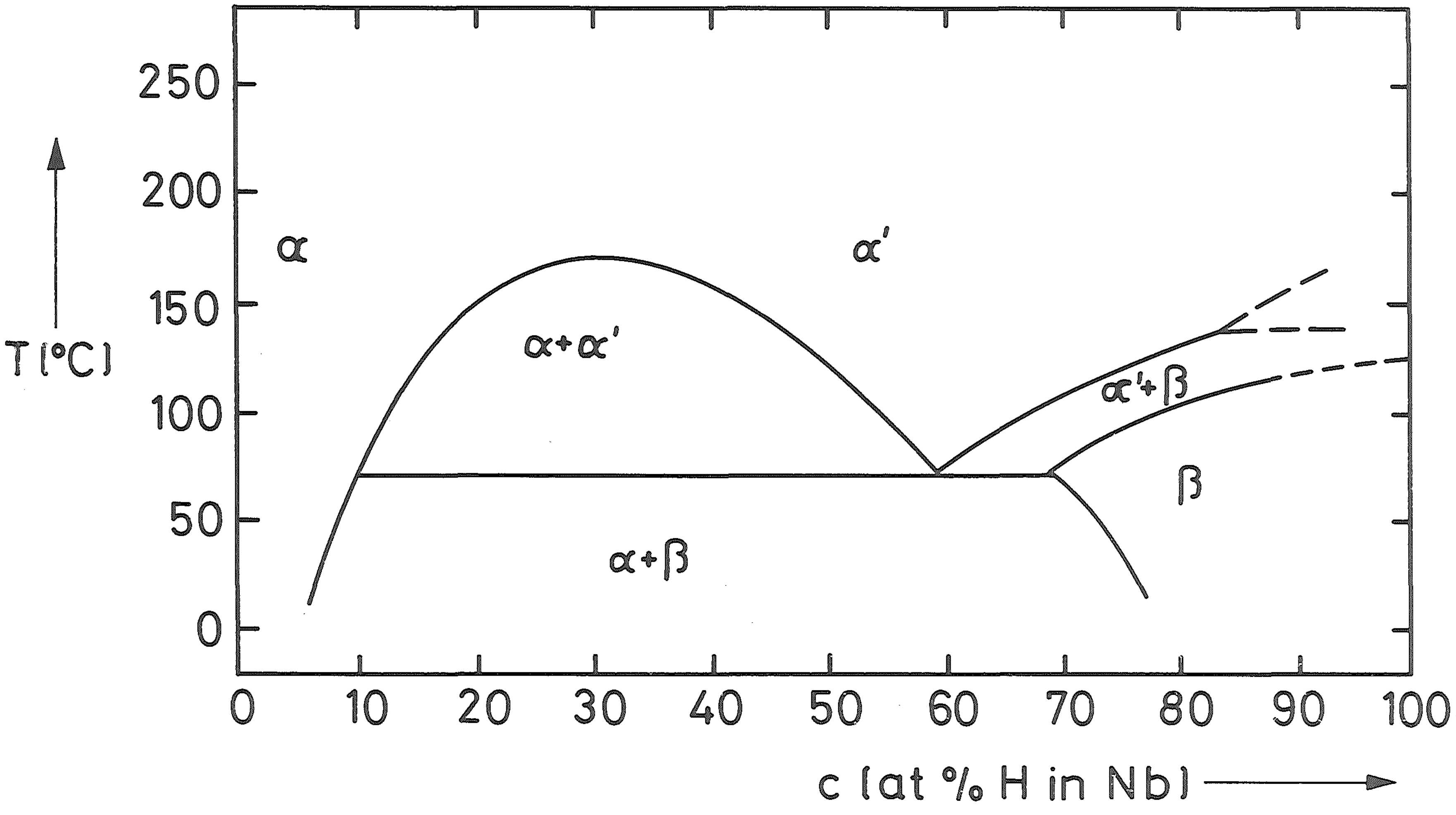

T [°C]
250
200
150
100
50
0
α
α'
α+α'
α'+β
β
α+β
0
10
20
30
40
50
60
70
80
90
100
c [at % H in Nb]

Fig. 1

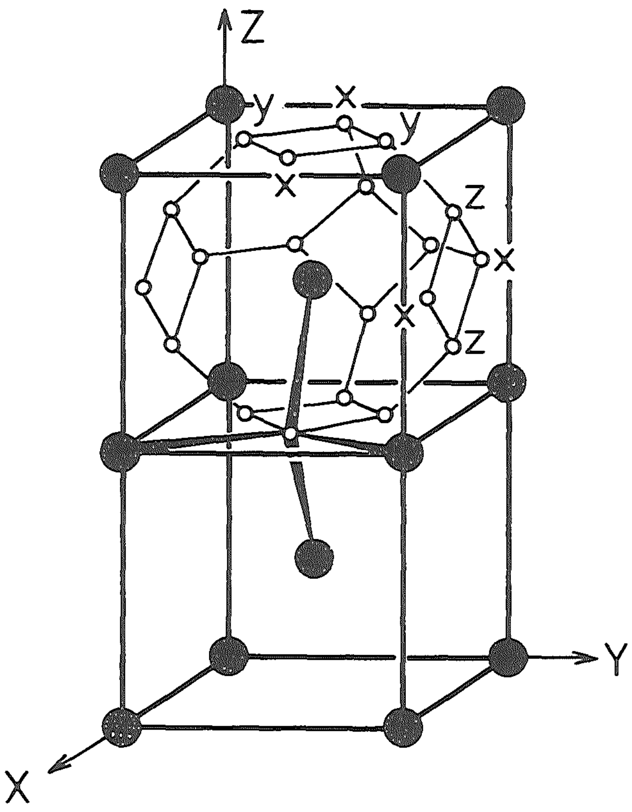


Fig. 2a

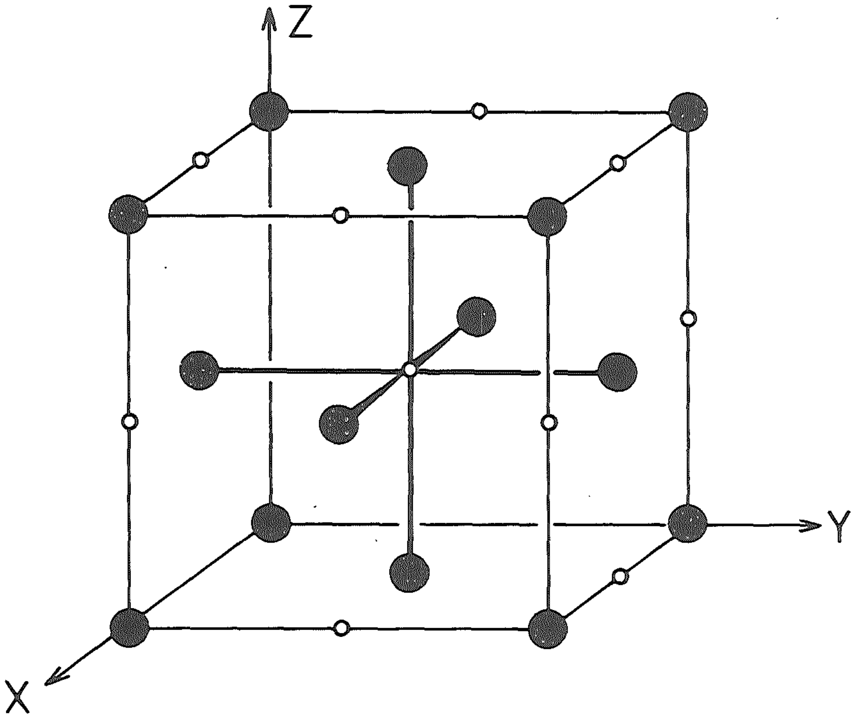


Fig. 2b

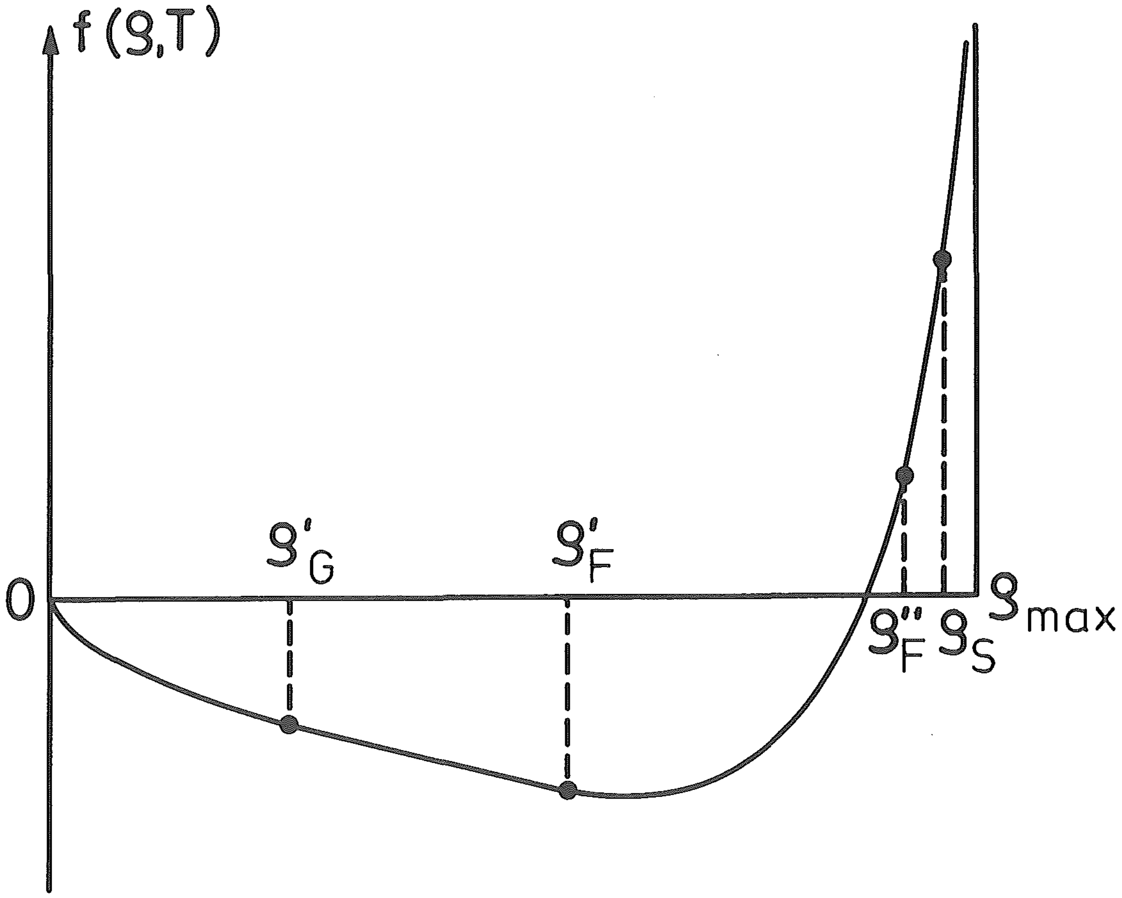


Fig. 3

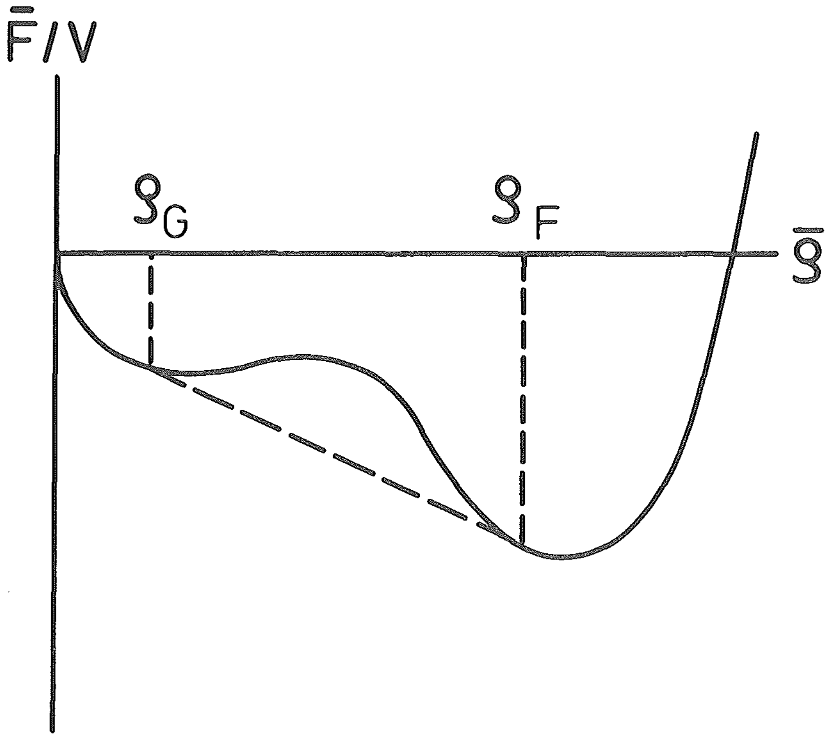


Fig. 4

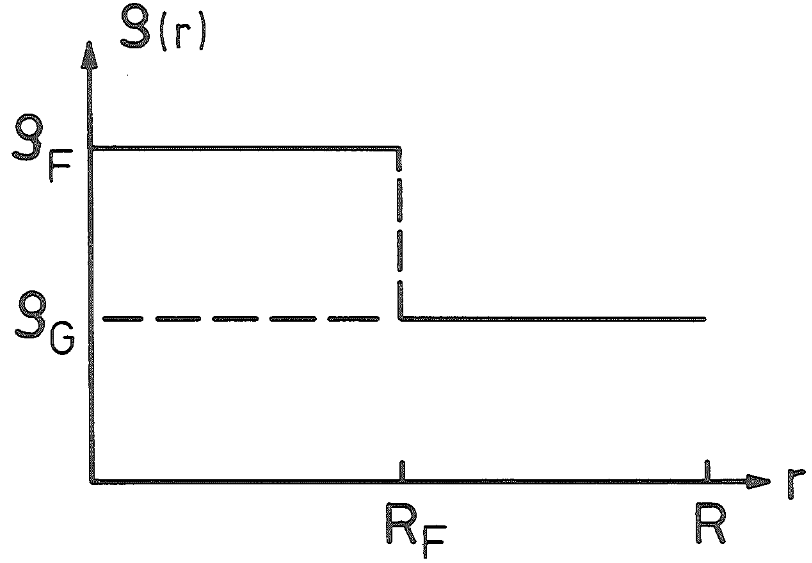
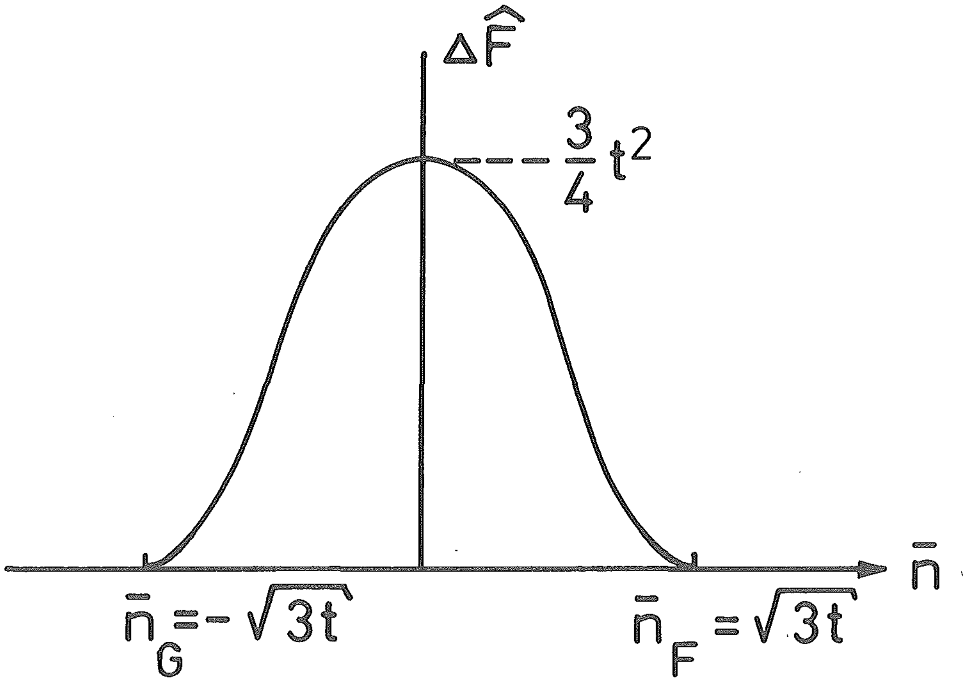


Fig. 5



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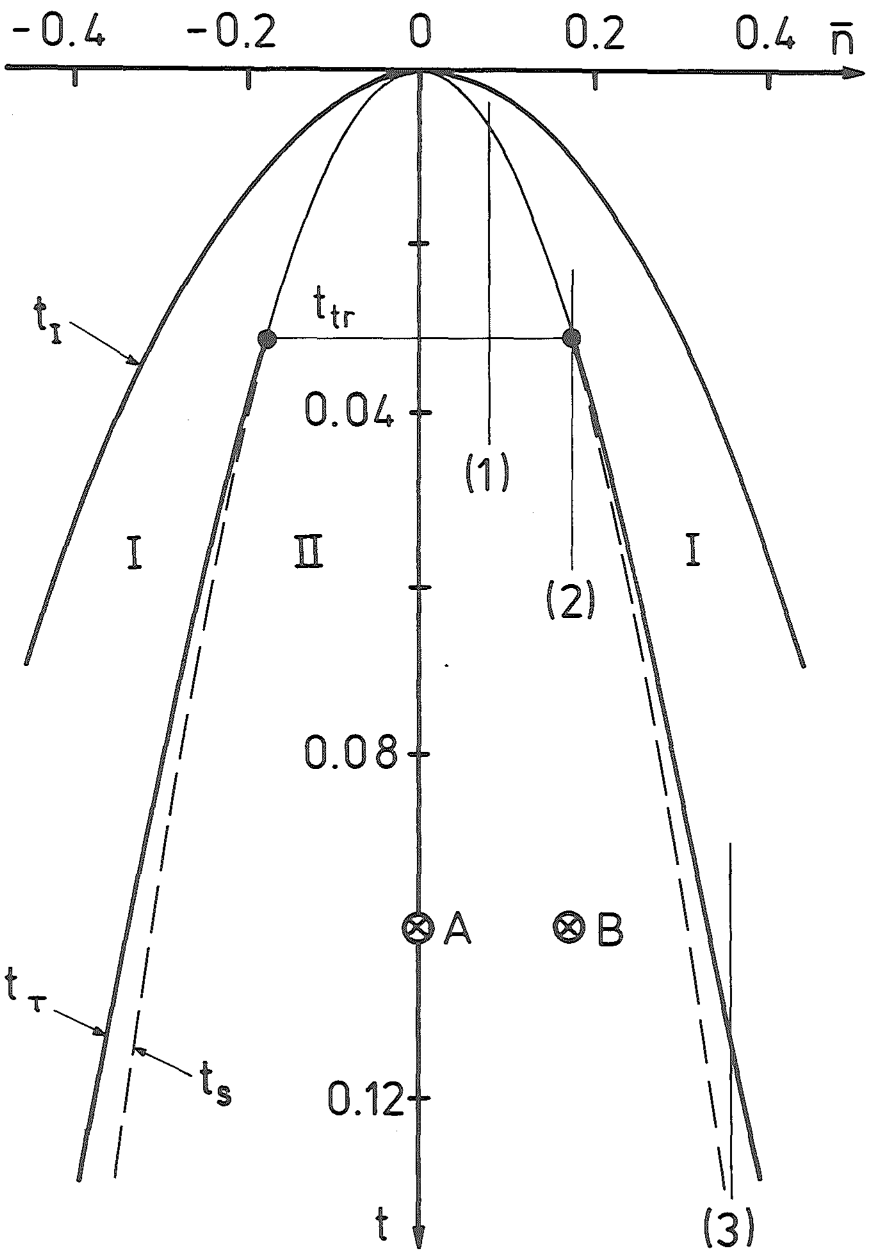
-0.4
-0.2
0
0.2
0.4
$\bar{n}$
t_I
t_{tr}
0.04
0.08
0.12
(1)
(2)
(3)
I
II
I
A
B
t_τ
t_s
t

Fig. 7a

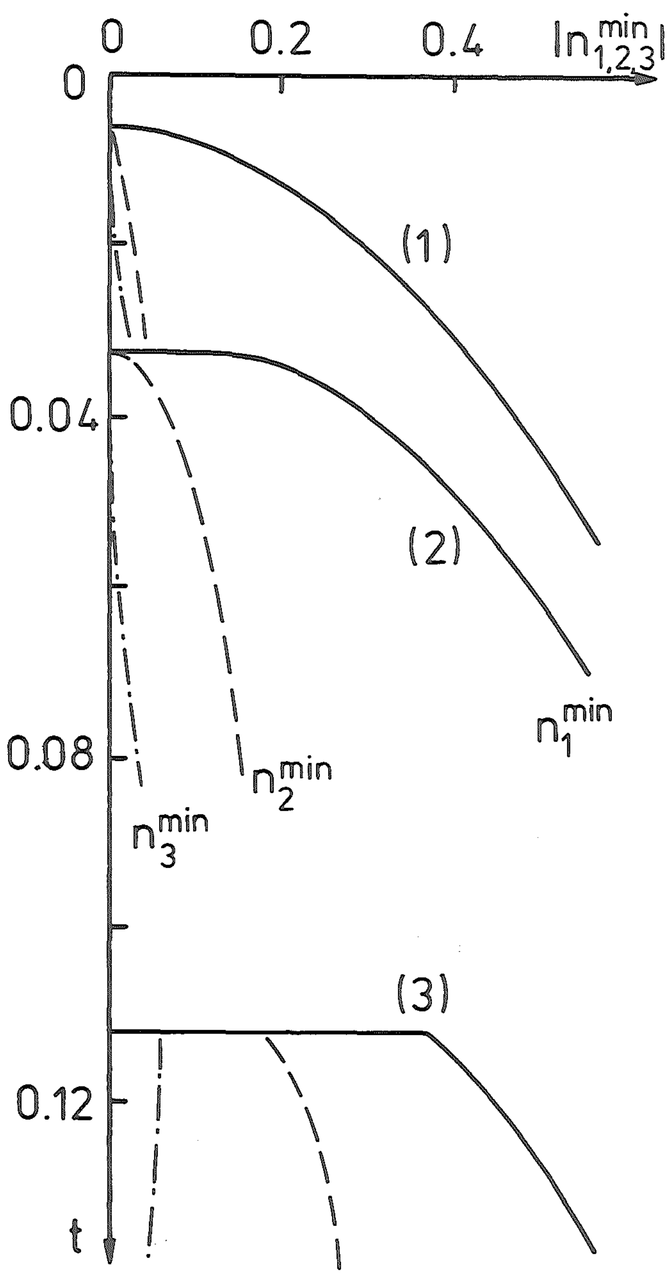
0
0.2
0.4
$|n^{min}_{1,2,3}|$
0
0.04
0.08
0.12
(1)
(2)
(3)
n_1^{min}
n_2^{min}
n_3^{min}
t

Fig. 7b

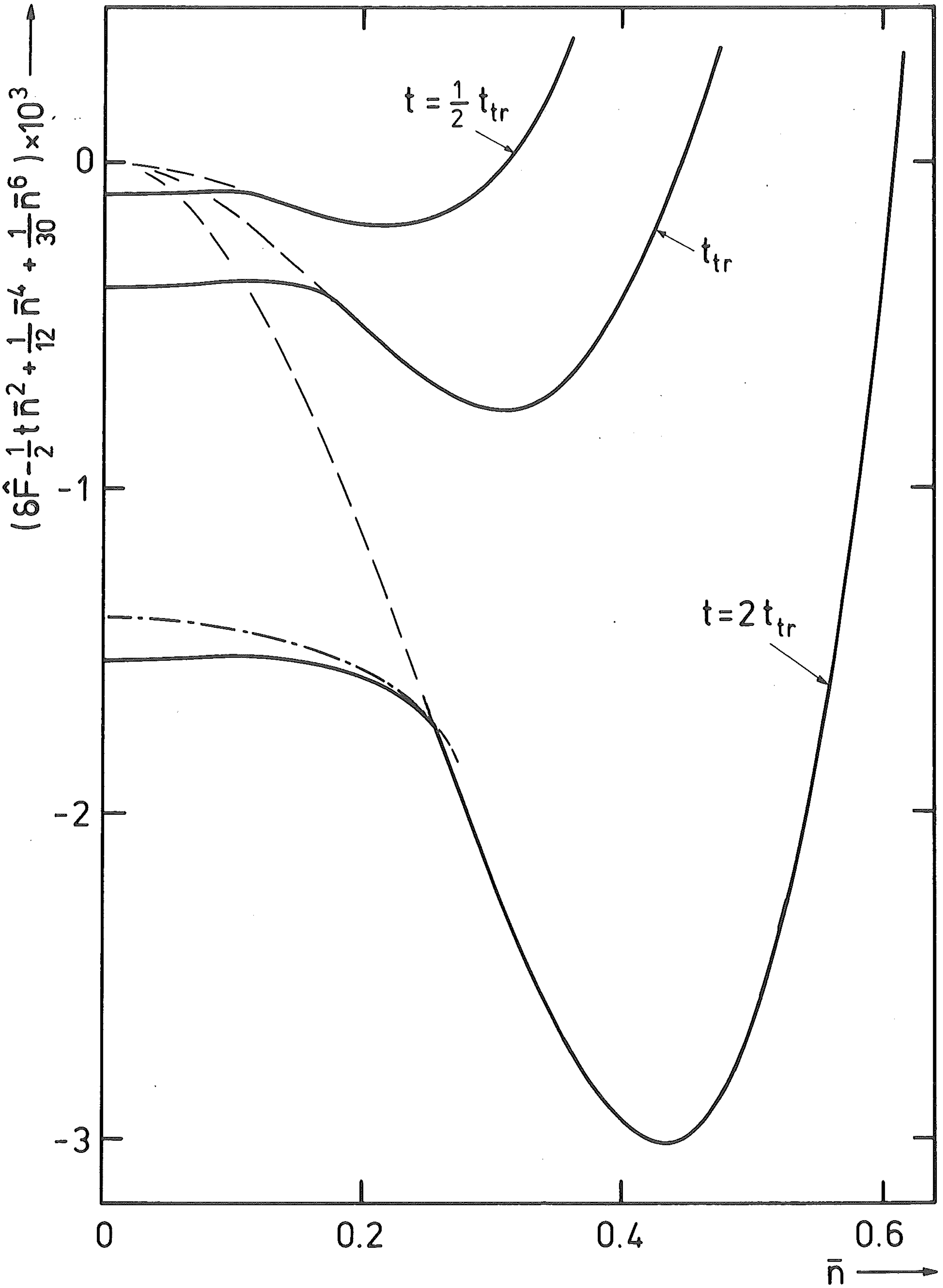
$(\delta\hat{F}-\frac{1}{2}t\bar{n}^2+\frac{1}{12}\bar{n}^4+\frac{1}{30}\bar{n}^6)\times10^3$
0
-1
-2
-3
0
0.2
0.4
0.6
$\bar{n}$
$t=\frac{1}{2}t_{tr}$
t_{tr}
$t=2t_{tr}$

Fig. 8

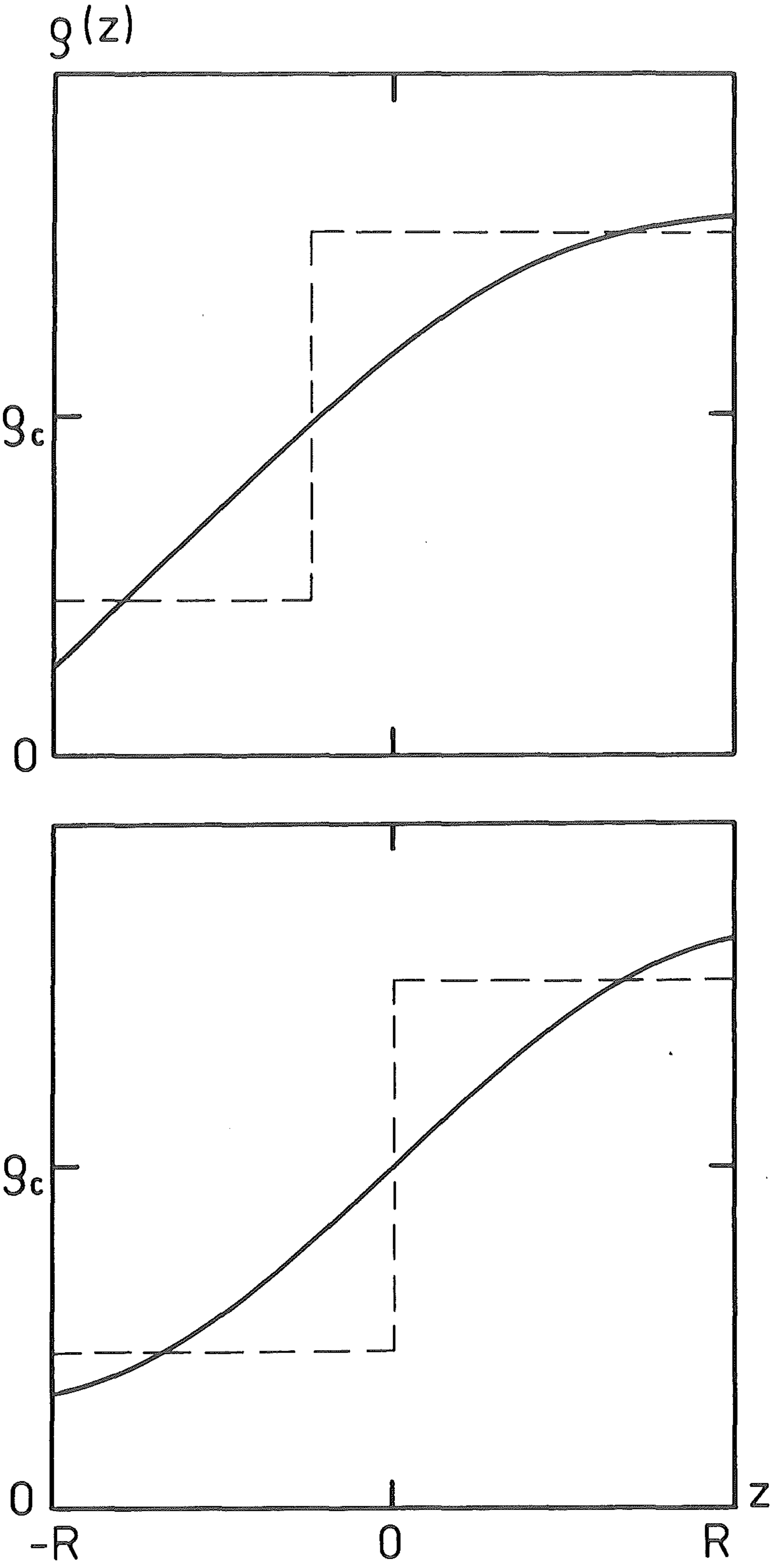

Fig. 9

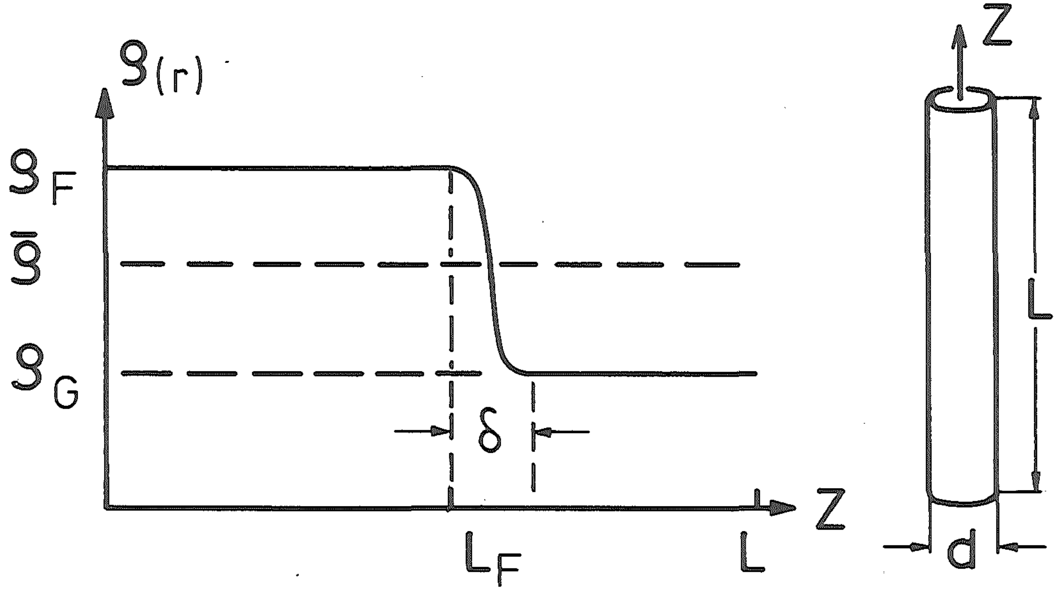

Fig. 10