

Individual and Collective Aspects of the Microfield Distribution

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Starting from the exact formulation of the electric microfield distribution in an electron gas the question is investigated of whether collective phenomena are correctly included in previous calculations. Application of Bohm and Pines' procedure yields a separable expression for the total microfield distribution: the collective component is represented by a Gaussian distribution, the individual component is similar to the high-frequency profile of Baranger and Mozer. Both components vary with the cut-off parameter of the spectrum of the collective modes. For realistic values of this cut-off parameter the total distribution may differ from the high-frequency profile as much as ten per cent for systems close to the critical density. With increasing plasma parameter Λ the distribution approaches that of Holtsmark.

1. Introduction

The electric microfield distribution for systems in thermodynamic equilibrium was originally calculated by HOLTSMARK¹ for a one-component model of uncorrelated ions. Consequently the applicability of this model is restricted to the limit of $\Lambda^{-1} \rightarrow 0$, where Λ is the well-known plasma parameter (proportional to the number of particles in the Debye sphere). The influence of correlations in a system of electrons and ions was first included in calculations by ECKER and MÜLLER² and by BARANGER and MOZER³, who introduced different "Dressed Particles"-models⁴ to account for interactions. Their calculations yielded deviations from the Holtsmark distribution depending only on the value of Λ .

The theories accounting for correlation effects do so within the frame of the well-known pair approximation. They consequently neglect long-range collective interactions. There have been claims in the literature⁵ that such collective effects can change the distribution function substantially, so that even in the limit $\Lambda^{-1} \rightarrow 0$ no Holtsmarkian behaviour results.

Under these aspects it is the *aim of this paper* to establish the effect of collective phenomena on the microfield distribution.

2. Model

For the sake of transparency we restrict ourselves to a one-component model of N electrons in thermodynamic equilibrium at a temperature T with an immobile smeared-out neutralizing positive background charge. We consider only Coulomb interactions and calculate the microfield distribution at a neutral point of observation non-relativistically. The system is studied in the limit $N \rightarrow \infty$, $V \rightarrow \infty$, $n = N/V = \text{const.}$ Density and temperature are restricted to the range below the critical density.

3. Outline

To check the influence of the collective modes we apply the procedure of BOHM and PINES⁶ to the calculation of the electric microfield distribution. We give preference to this procedure because it allows to treat individual and collective phenomena simultaneously, an advantage not sheared by other theories⁷.

In Sec. 4 we calculate the field function, the Hamiltonian, and with these the microfield distribution of our system in terms of individual and collective variables.

In Sec. 5 we sketch the mathematical details of the evaluation procedure.

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¹ J. HOLTSMARK, Ann. Phys. 58, 577 [1919].

² G. ECKER and K. G. MÜLLER, Z. Phys. 153, 317 [1958].

³ M. BARANGER and B. MOZER, Phys. Rev. 115, 521 [1959]; 118, 626 [1960].

⁴ G. ECKER and K. G. FISCHER, Forschungsber. NRW 1949 [1968].

⁵ K. HUNGER and R. W. LARENZ, Z. Naturforsch. 23 a, 1488 [1968].

⁶ D. BOHM and D. PINES, Phys. Rev. 82, 625 [1951], in the following referred to as BP I. — D. BOHM and D. PINES, Phys. Rev. 92, 609 [1953], in the following referred to as BP II. — D. PINES, Phys. Rev. 92, 626 [1953], in the following referred to as BP III.

⁷ D. TER HAAR, Introduction to the Physics of Many-Body Systems, Interscience, New York 1958, Chapter VI.



In Sec. 6 we present our results and compare them with the microfield distributions quoted in the introductory section.

4. The Microfield Distribution

Expressed in Terms of Individual and Collective Variables

According to Markoff's method the probability density for the electric microfield is given by

$$W(\mathbf{E}) = \int \delta(\mathbf{E} - \sum_i \mathbf{E}_i) P_N(H) d\mathbf{r}_1 \dots d\mathbf{p}_N \quad (1)$$

where P_N is the well-known Gibbs-factor and H is the Hamiltonian

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (2)$$

\mathbf{E}_i is the electric field exerted by the i -th particle at the neutral point of observation

$$\mathbf{E}_i = e(\mathbf{r}_i/r_i^3). \quad (3)$$

To improve the approximate evaluation^{2,3} of the exact description contained in Eqs. (1) to (3) we apply the collective approach.

The basic idea of this approach is the understanding that the individual coordinates are not appropriate for the description of long-range collective effects. One therefore aims to transform to a new set of variables consisting of two groups: the one suitable for the description of short-range, the other of long-range effects.

We start with the Fourier representation of the potential energy in the *Hamiltonian* yielding

$$H = \sum_i \frac{p_i^2}{2m} + \frac{2\pi e^2}{V} \sum_{\mathbf{k}, k \leq k_c} \frac{\exp\{i\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)\}}{k^2} + \frac{2\pi e^2}{V} \sum_{\mathbf{k}, k > k_c} \frac{\exp\{i\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)\}}{k^2} \quad (4)$$

where we have chosen to subdivide the total interaction by the parameter k_c into two parts which — as Bohm and Pines demonstrated — are suitable to represent collective and individual interactions.

The prime excluded the term $\mathbf{k} = 0$ from the summation to account for the over-all charge neutrality of our system.

We introduce in addition to the $2N$ variables $\{\mathbf{r}_i, \mathbf{p}_i\}$ a set of $2N_c$ variables $\{\mathbf{Q}_k, \mathbf{P}_k\}$, $|\mathbf{k}| \leq k_c$.

We transform to new variables $\{\mathbf{r}'_i, \mathbf{p}'_i, \mathbf{Q}'_k, \mathbf{P}'_k\}$ with the generating function

$$S(\mathbf{p}', \mathbf{r}, \mathbf{P}', \mathbf{Q}) = \sum_{\mathbf{k}, k \leq k_c} \mathbf{P}'_k (\mathbf{Q}_k + \boldsymbol{\xi}_k) + \sum_j (\mathbf{p}'_j \mathbf{r}_j) \quad (5)$$

where $\boldsymbol{\xi}_k$ is determined by the Fourier components of the density fluctuations

$$\boldsymbol{\xi}_k = \left(\frac{4\pi e^2}{V} \right)^{1/2} \sum_j \hat{\mathbf{k}} \frac{\exp\{-i\mathbf{k} \mathbf{r}_j\}}{k}, \quad k \leq k_c, \quad (6)$$

and $\hat{\mathbf{k}} = \mathbf{k}/k$ is the unit vector in the \mathbf{k} -direction.

The transformed Hamiltonian is given by the sum of the following three contributions

$$H_{\text{ind}} = \sum_i \frac{p_i'^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2 \exp\{-k_c |\mathbf{r}'_i - \mathbf{r}'_j|\}}{|\mathbf{r}'_i - \mathbf{r}'_j|}, \quad (7)$$

$$H_{\text{coll}} = \frac{1}{2} \sum_{\mathbf{k}, k \leq k_c} (\mathbf{Q}'_k \mathbf{Q}'_k^* + \omega_p^2 \mathbf{P}'_k \mathbf{P}'_k^*), \quad (8)$$

$$H_{\text{inter}} = -i \left(\frac{e}{m} \right) \left(\frac{4\pi}{V} \right)^{1/2} \sum_{\mathbf{k}, k \leq k_c} (\mathbf{P}'_k \mathbf{p}'_i) \exp\{-i\mathbf{k} \mathbf{r}'_i\} \quad (9)$$

where ω_p is the plasma frequency. In arriving at the Hamiltonian Eqs. (7) – (9) we had to introduce the Fourier components Eq. (6) into Eq. (4) thereby introducing implicitly the self-energy part of the interaction. Accordingly we should subtract this self-energy part explicitly from the final Hamiltonian, but we omitted it because it is not of interest here. Moreover we already neglected mode-mode coupling within the frame of the random phase approximation.

The Hamiltonian Eqs. (7) – (9) is not satisfactory because of the nonnegligible term H_{inter} , which causes mode-particle coupling.

To eliminate this unwanted term Bohm and Pines apply a second canonical transformation⁸ — the new variables will be denoted by $\{\mathbf{r}''_i, \mathbf{p}''_i, \mathbf{Q}''_k, \mathbf{P}''_k\}$ — and a perturbation expansion⁹ in terms of the parameter

$$\varepsilon = \left\langle \left(\frac{\mathbf{k} \mathbf{p}''}{m \omega_k} \right)^2 \right\rangle_{\text{Av}} \ll 1. \quad (10)$$

The average is taken over the particle momenta and the wave vectors \mathbf{k} with $k \leq k_c$. ω_k is the k -dependent frequency of the collective oscillations determined through the dispersion relation

⁸ The generating function may be derived from BP II, Eq. (47), using the corresponding relationship between BP I, Eq. (45) and BP I, Eqs. (11) and (12).

⁹ Compare BP II, Eq. (48) and the following argumentation.

$$1 = \frac{4\pi e^2}{mV} \sum_i \frac{1}{(\omega_k - (\mathbf{k}\mathbf{p}_i''/m))^2}. \quad (11)$$

For the details of this rather involved second transformation and expansion procedure we refer the reader to the cited equations of the original works and give here only the final result¹⁰

$$H = \sum_i \frac{p_i'^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2 \exp\{-k_c |\mathbf{r}_i'' - \mathbf{r}_j''|\}}{|\mathbf{r}_i'' - \mathbf{r}_j''|} + \frac{1}{2} \sum_{\mathbf{k}, k \leq k_c} (|\mathbf{Q}_k''|^2 + \omega_k^2 |\mathbf{P}_k''|^2). \quad (12)$$

We now turn to express the *field function* \mathbf{E} in terms of collective and individual variables. We Fourier transform the field and perform the first canonical transformation. The result is given by

$$\sum_i \mathbf{E}_i = \sum_i \frac{e}{r_i'^3} \mathbf{r}_i' (1 + k_c r_i') \exp\{-k_c r_i'\} + \left(\frac{4\pi}{V}\right)^{1/2} \sum_{\mathbf{k}, k \leq k_c} \mathbf{Q}_k' \exp\{i\mathbf{k}\mathbf{r}'\} \quad (13)$$

where the first term results from the summation over the individual contributions and represents a Debye-Hückel field type with the screening length k_c^{-1} . The second term represents the collective field contributions. \mathbf{r}' denotes the spatial variable of the neutral point of observation after the first canonical transformation.

The application of the second canonical transformation to Eq. (13) within the frame of the approximations described above produces the field presentation¹¹

$$\sum_i \mathbf{E}_i = \sum_i \frac{e}{r_i''^3} \mathbf{r}_i'' + \left(\frac{4\pi}{V}\right)^{1/2} \sum_{\mathbf{k}, k \leq k_c} \mathbf{Q}_k'' \exp\{i\mathbf{k}\mathbf{r}''\} \quad (14)$$

where \mathbf{r}'' denotes the correspondingly transformed spatial variable of the neutral point of observation.

with

$$\mathcal{W}_{\text{ind}}(\mathbf{q}) = \frac{\int \exp\left\{-i\mathbf{q} \sum_i \frac{e}{r_i^3} \mathbf{r}_i - \frac{e^2}{2\kappa T} \sum_{i \neq j} \frac{\exp\{-k_c |\mathbf{r}_i - \mathbf{r}_j|\}}{|\mathbf{r}_i - \mathbf{r}_j|}\right\} d\mathbf{r}_1 \dots d\mathbf{r}_N}{\int \exp\left\{-\frac{e^2}{2\kappa T} \sum_{i \neq j} \frac{\exp\{-k_c |\mathbf{r}_i - \mathbf{r}_j|\}}{|\mathbf{r}_i - \mathbf{r}_j|}\right\} d\mathbf{r}_1 \dots d\mathbf{r}_N} \quad (18)$$

and

$$\mathcal{W}_{\text{coll}}(\mathbf{q}) = \frac{\int \exp\left\{-i\mathbf{q} \left(\frac{4\pi}{V}\right)^{1/2} \sum_{\mathbf{k}, k \leq k_c} \mathbf{Q}_k \exp\{i\mathbf{k}\mathbf{r}\} - \frac{1}{2\kappa T} \sum_{\mathbf{k}, k \leq k_c} Q_k^2\right\} d\mathbf{Q}_{k_1} \dots d\mathbf{Q}_{k_c}}{\int \exp\left\{-\frac{1}{2\kappa T} \sum_{\mathbf{k}, k \leq k_c} Q_k^2\right\} d\mathbf{Q}_{k_1} \dots d\mathbf{Q}_{k_c}}. \quad (19)$$

Of course, since we introduced $2N_c$ additional variables subsidiary conditions are necessary to keep the total number of degrees of freedom constant. The ratio of the number of collective modes to the number of individual modes is of the order of Λ^{-1} . As we are well below the critical density it follows that the number of collective degrees of freedom is small compared with the number of individual degrees of freedom. Consequently, it is common use¹² to neglect the subsidiary conditions.

Thus, the microfield distribution is given by the general formula

$$\mathcal{W}(\mathbf{E}) = \int \delta(\mathbf{E} - \sum_i \mathbf{E}_i) P_N(H) d\mathbf{r}_1'' \dots d\mathbf{P}_{k_c}'' \quad (15)$$

where the Gibbs factor is

$$P_N(H) = \frac{\exp\{-H/\kappa T\}}{\int \exp\{-H/\kappa T\} d\mathbf{r}_1'' \dots d\mathbf{P}_{k_c}''.} \quad (16)$$

The Hamiltonian follows from Eq. (12), and the field contributions are determined through Eq. (14). The integrations extend over individual and collective variables.

For the sake of simplicity we will omit from here on the double prime at the variables. However, we want to keep in mind in the following that the $\{\mathbf{r}_i'', \mathbf{p}_i'', \mathbf{Q}_k'', \mathbf{P}_k''\}$ are neither identical with the original variables nor related to them in a simple way.

5. Evaluation Procedure

Fourier transformation of Eq. (15) using Eqs. (12) and (14) yields the separable spectral function

$$\mathcal{W}(\mathbf{q}) = \int \exp\{-i\mathbf{q}\mathbf{E}\} \mathcal{W}(\mathbf{E}) d\mathbf{E} = \mathcal{W}_{\text{ind}}(\mathbf{q}) \mathcal{W}_{\text{coll}}(\mathbf{q}) \quad (17)$$

¹⁰ Compare BP III, Eqs. (2) – (5) and BP II, Eq. (41).

¹¹ Compare especially BP II, Eqs. (47) – (51), Eq. (41), Eq. (57), Eq. (65) and BP III, Eq. (41).

¹² D. BOHM, K. HUANG, and D. PINES, Phys. Rev. **107**, 71 [1957].

Introducing reduced fields and reduced configuration space variables with the help of the average particle distance r_0 via

$$\beta = E/E_0, \quad E_0 = e/r_0^2, \quad \frac{A}{15} (2\pi)^{1/2} r_0^3 n = 1, \\ x = q E_0; \quad z_i = r_i/r_0 \sqrt{x} \quad (20)$$

and normalizing k_c with the Debye length

$$A = k_c \lambda_D, \quad \lambda_D^2 = 1/\kappa_D^2 = \kappa T/4\pi n e^2 \quad (21)$$

we find for the individual component of the microfield distribution

$$W_{\text{ind}}(\beta) = \frac{2\beta}{\pi} \int_0^\infty \sin(\beta x) \cdot \exp\{-x^{1/2}(1-\psi_2(x, A))\} x dx \quad (22)$$

where ψ_2 is given by¹³

$$\psi_2(x, A) = -\frac{15}{64\pi^2 \sqrt{2}\pi} x (\kappa_D r_0)^2 \iint (e^{i\eta_1 \cos \Theta_1} - 1) \cdot (e^{i\eta_2 \cos \Theta_2} - 1) \frac{\exp\{-\sqrt{1+A^2} \kappa_D r_0 \sqrt{x} |\mathbf{z}_1 - \mathbf{z}_2|\}}{|\mathbf{z}_1 - \mathbf{z}_2|} \cdot d\mathbf{z}_1 d\mathbf{z}_2 \quad (23)$$

with $\cos \Theta_i = \mathbf{z}_i \cdot \mathbf{q}/z_i q$ and $\eta_i = 1/z_i^2$.

The calculation of the collective part $W_{\text{coll}}(\mathbf{q})$ yields a Gaussian distribution

$$W_{\text{coll}}(\beta) = (\beta^2/2 \sqrt{\pi} c^3) \cdot \exp\{-\beta^2/4 c^2\}, \\ c^2 = (5 A^3 \kappa_D r_0)/\sqrt{2}\pi. \quad (24)$$

The total microfield distribution follows from the convolution of the collective and individual components.

The theory⁶ does not provide a specific value for the cut-off A . However, on the one hand, the condition $A^2 \ll 1$ is necessary to secure the validity of the perturbation expansion following the second canonical transformation. On the other hand, if we want maximal improvement through the collective variables, we have to choose A as large as possible.

Obeying these requirements we consider the cut-off parameters in the range $0.5 \leq A \leq 0.6$

6. Results and Discussion

In Fig. 1 we present the results of the numerical evaluation of ψ_2 defined in Eq. (23). In addition we show the case $A=0$ which includes no collective

description at all and should consequently be identical with the high-frequency result of Baranger and Mozer. Actually our results show small deviations which confirm the findings of PFENNIG and TREFFTZ (l. c.¹⁴).

In Fig. 2 the individual component of the microfield distribution is shown as calculated from Eq. (22) for $0.5 \leq A \leq 0.6$ for the value $\kappa_D r_0 = 0.6$

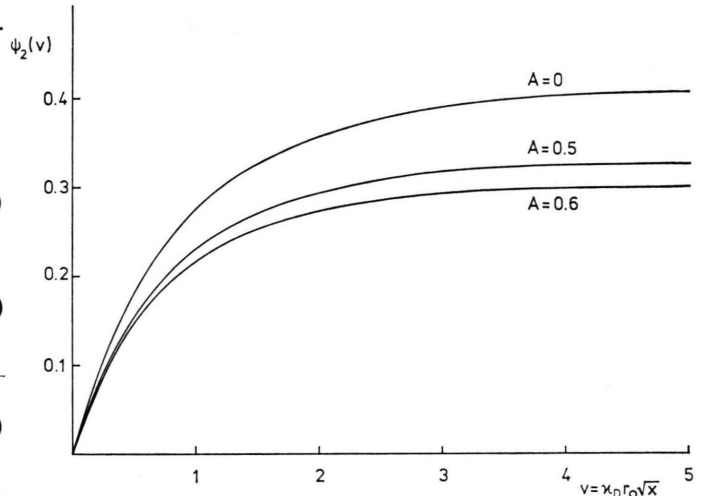


Fig. 1. The function ψ_2 , Eq. (23).

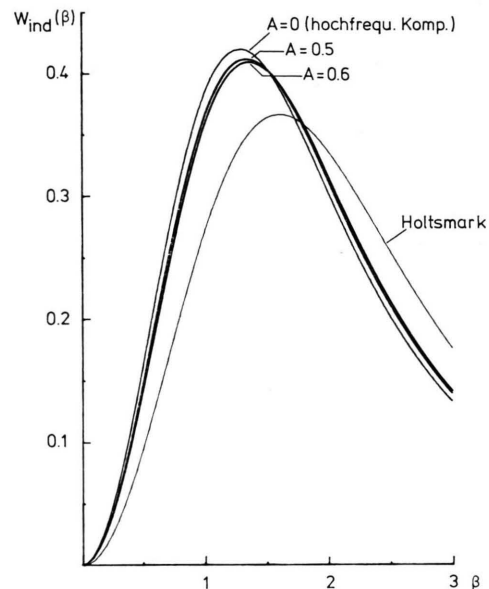


Fig. 2. Individual component of the microfield distribution ($\kappa_D r_0 = 0.6$).

¹³ Compare H. PFENNIG and E. TREFFTZ, Z. Naturforsch. **21a**, 697 [1966], Eqs. (C 39), (C 36) and (C 37).

¹⁴ H. PFENNIG and E. TREFFTZ, Z. Naturforsch. **21a**, 697 [1966].

of the characteristic parameter (this corresponds to ~ 5 particles in the Debye region). For reasons of comparison we also include the correlationfree Holtsmark distribution and the high-frequency component of Baranger and Mozer corresponding to $A=0$. Obviously the deduction of the contribution reserved for the collective description moves the distribution towards the Holtsmark result. This is not surprising since due to Eq. (12) it effectively means a weaker interaction energy.

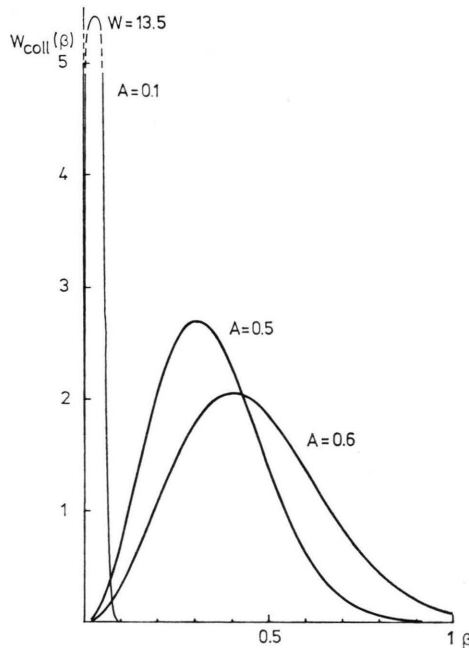


Fig. 3. Collective component of the microfield distribution ($\kappa_D r_0=0.6$; varying cut-off parameter A).

Figure 3 shows the collective distributions for the same values as in Fig. 2 with the exception that the Baranger-Mozer result ($A=0$) was replaced by the curve for $A=0.1$. The case $A=0$ corresponds to a Dirac function at the origin, the curve for $A=0.1$ is meant to demonstrate how with decreasing A this Dirac function is approached so that the collective effects become negligible.

In Fig. 4 we show the collective distribution for a constant cut-off parameter $A=0.6$ and varying number of particles in the Debye region. The purpose of this demonstration is to show that with increasing number of particles in the Debye region the change introduced by the collective phenomena gradually disappears.

The final result of the convolution of the individual and collective contribution is shown in Fig. 5 again together with the Holtsmark- and the Baranger-Mozer high-frequency profile. The convolution obviously emphasizes the tendency to shift the dis-

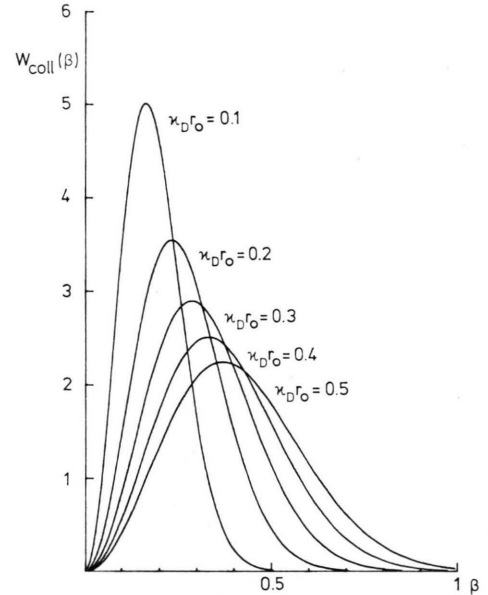


Fig. 4. Collective component of the microfield distribution [$A=0.6$, varying number of particles in the Debye sphere $(\kappa_D r_0)^{-3}$].

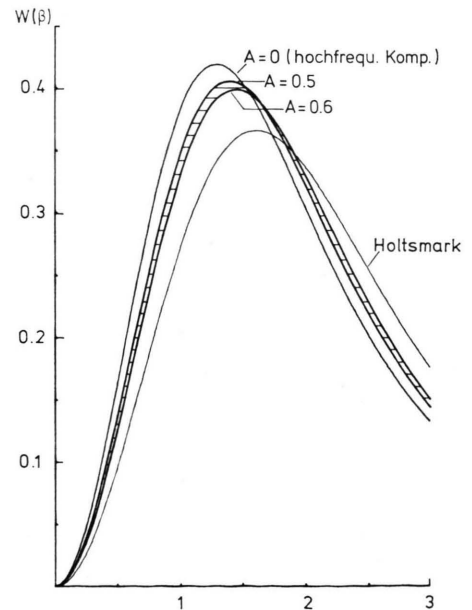


Fig. 5. Total microfield distribution ($\kappa_D r_0=0.6$). The shaded area corresponds to the realistic range $0.5 \leq A \leq 0.6$ of cut-off parameters.

tribution in the direction of the correlationfree Holtsmark result.

In judging the magnitude of this effect we want to remember that we have chosen the cut-off at its maximum possible value¹⁵.

Summary

The inclusion of collective long-range effects in the calculation of the electric microfield distribution shifts previous results calculated on the individual variable basis towards the correlationless Holtsmark distribution. For high values of the cut-off parameter and systems close to the critical density the effect may reach 10 per cent. With increasing number of

particles in the Debye region the effect disappears. In particular the distribution is little affected in the high field range.

Our findings can therefore not corroborate results which claim decisive effects of the collective phenomena even for high fields and in the far sub-critical region⁵.

We are presently studying the analytical interrelations of the procedure and results presented here to similar findings of HOOPER¹⁶ who used an essentially different approach.

¹⁵ L. J. CAROFF and R. L. LIBOFF, *J. Plasma Phys.* **4**, 83 [1970].

¹⁶ C. F. HOOPER, JR., *Phys. Rev.* **149**, 77 [1966].

Predictable Low Enrichment of Methane Isotopes by Clusius-Dickel Thermal-Diffusion Columns for Use in Radiocarbon Dating Technique*

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By means of the Clusius-Dickel thermal-diffusion column the range of the radiocarbon dating method may be extended by 20 000 years. It is shown in this work that the total sample amount required is reasonably low, if column dimensions are suitably chosen. The enrichment run time and the length of the thermal-diffusion column will allow sample enrichment in routine operation. Optimal values of column dimensions and operation conditions are calculated.

With an all metal thermal-diffusion column that has been carefully constructed, a high reproducibility is found. The stationary as well as the non-stationary state operation are in agreement with column theory within 1%, concerning the enrichment both of $C^{13}H_4$ and $C^{14}H_4$ in methane. The theory has been evaluated by numerical methods.

1. Introduction

In radiocarbon dating technique the lowest C^{14} activity that can be detected significantly by gas counting methods corresponds to a maximum Libby-age of about 50.000 years B.P. (before present). An outermost limit of about 60.000 years B.P. seems to have been reached by GEYH¹. In order to extend the radiocarbon dating limit further — especially for establishing a chronology of the interstadials of

early WÜRM ice age — we took up anew the problem of enrichment of the C^{14} isotope by known amounts. An enrichment procedure developed earlier in Groningen^{2,3} did not enter routine dating work because the amount of carbon needed and the enrichment time were too high for continuous laboratory work. Therefore we started to develop a more advantageous enrichment plant. In connection with this, the enrichment factors had to be predicted under various conditions of operation.

* This work is part of a doctoral dissertation at the University of Kiel, 1971.

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¹ M. A. GEYH, Dissertation, Bergakademie Clausthal 1966.

² A. HARING, A. E. DE VRIES, and H. DE VRIES, *Science* **128**, 472 [1958].

³ A. E. DE VRIES and A. HARING, *Peaceful Uses of Atomic Energy* **2**, 249 [1958].