

1176.3 keV. The energy of the isomeric transition in ^{73}As was measured to be 360.4 ± 0.4 keV. The isomeric level at 427.3 ± 0.4 keV is fed by the 7 h ^{73}Se .*

The authors wish to express their sincere thanks to the linear accelerator crew and in particular to Dr. A. MOREIRA for their willing co-operation. Financial support from B.N.D.E., C.N.E.N. and C.N.Pq. is also acknowledged. One of us (P.R.M.) would like to thank the members of the Centro Brasileiro de Pesquisas Fisicas for their kind hospitality.

* *Note added in proof:* Very recently MURRAY et al. (Nucl. Phys. A **130**, 563, June 1969) published the energies and relative intensities of the gamma-rays following the decays of 7.1 h ^{73}Se and 42 min ^{73m}Se produced by $^{70}\text{Ge}(\alpha, n)$ reaction. The gamma-rays of 253.8 keV, 320.1 keV, 392.3 keV, 401.1 keV, 577.5 keV, 1002.6 keV and 1076.6 keV observed by us were confirmed. The lines of 84.3 keV, 848.8 keV and 992.1 keV were also present in our spectra. They are associated to the decay of ^{73m}Se by MURRAY et al. — The absence of some conspicuous peaks observed in our spectra obtained by irradiating natural selenium among the transitions reported by MURRAY et al. forced us on a

revision of some conclusions concerning the origin of those peaks. Thus, the 649.5 keV transition is now attributed to the decay of ^{81}Se in agreement with previously reported results of PRAWIROSOEHARDJO (Phys. Rev. **157**, 995 [1967]). Another transition to be attributed to the same decay is that of 260.2 keV, as suggested by YTHIER et al. (Physica **34**, 559 [1967]). The relative intensities of these lines are 0.40 ± 0.07 and 1.05 ± 0.13 , respectively. However, five gamma-ray, namely those with 976.2 keV, 986.2 keV, 1104.6 keV, 1171 keV and 1176.3 keV, remain without definite assignment.

The Functional Method in the Theory of Real Gases

E. LUX

Institut für Theoretische Physikalische Chemie der Universität Frankfurt/Main

(Z. Naturforsch. **24 a**, 1405—1408 [1969]; received 21 June 1969)

The relations of the theory of real gases which have first been derived by Mayer and his co-workers can be obtained in a simple way by the functional method. In this case the assumption of the pairwise additivity of the intermolecular potential can be dropped. Apart from some new relations for distributions functions the expansion of the direct correlation functions is obtained as a power series in density with coefficients consisting of integrals over Husimi functions.

In a series of papers¹ the functional method has been analysed to derive integral equations for molecular distribution functions. In (I) we have shown that successive applications of functional operations lead to hierarchies of functions and their interrelations. In particular we have found that the Ursell and the Husimi expansions can be expressed in terms of appropriate functional derivatives which in turn generate relations between different hierarchies of integral equations. As these expansions are also used in the theory of real gases developed by MAYER and his coworkers²⁻⁵ one may suspect

that the functional method yields a simple derivation of the MAYER theory.

In the following sections we want to present this derivation showing that it is by far less complicated than that given by Mayer himself. Furthermore, the intermolecular potential is restricted only by the properties required for the existence of the relevant integrals. Moreover, this method leads to some new relations for distribution functions and the density expansions of the direct correlation functions. The coefficients in this power series are cluster integrals over Husimi functions.

Sonderdruckerfordernungen erbeten an Dr. E. LUX, Institut für Theoretische Physikalische Chemie der Universität Frankfurt/Main, D-6000 Frankfurt, Gräfstr. 38.

¹ J. K. PERCUS, Phys. Rev. Letters **8**, 462 [1962]. — J. L. LEBOWITZ and J. K. PERCUS, J. Math. Phys. **4**, 116, 1495 [1963]. — J. K. PERCUS, The Equilibrium Theory of Classical Fluids, W. A. Benjamin, Inc., New York-Amsterdam 1964. — L. VERLET, Physica **30**, 95 [1964]; **32**, 304 [1966]. — E. LUX and A. MÜNSTER, Z. Phys. **199**, 465 [1967], hereafter referred to as I. — E. LUX and A. MÜNSTER, Z. Phys. **213**, 46 [1968].

² J. E. MAYER and E. W. MONTROLL, J. Chem. Phys. **9**, 2 [1941].

³ G. E. UHLENBECK and G. W. FORD, in: Studies in Statistical Mechanics, vol. I, North-Holland Publ. Co., Amsterdam 1962.

⁴ J. E. MAYER and M. G. MAYER: Statistical Mechanics, J. Wiley & Sons Inc., New York 1959. — J. E. MAYER, in: Encyclopedia of Physics, vol. XII Springer-Verlag, Berlin-Göttingen-Heidelberg 1958.

⁵ A. MÜNSTER, Statistical Thermodynamics, Springer Academic Press, Berlin-New York 1969.

1. Distribution Functions as Power Series in Fugacity

Consider the generalized grand canonical partition function (1) which is a functional of φ

$$\Xi(\varphi) = \sum_{N \geq 0} \frac{z^N}{N!} \int \prod_{i=1}^N \varphi(i) P(1, \dots, N) d1 \dots dN. \quad (1)$$

The $\varphi(i) \equiv \varphi_i$ are differentiable functions which in addition have the properties required for the existence of the integral. For the functional derivatives with respect to $z\varphi_i$ at $\varphi_i = 0$ we have

$$\left. \frac{\delta^n \Xi(\varphi)}{\prod_{i=1}^n \delta z \varphi_i} \right|_{\varphi=0} = P(1, \dots, n), \quad (2a)$$

whereas for $\varphi_i \neq 0$ we get

$$\frac{\delta^n \Xi(\varphi)}{\prod_{i=1}^n \delta z \varphi_i} = \Xi(\varphi) \frac{\varrho(1, \dots, n, \varphi)}{\prod_{i=1}^n z \varphi_i}. \quad (2b)$$

Here $\varrho(1, \dots, n, \varphi)$ is the generalized n -particle molecular distribution function, corresponding to Eq. (1).

We now define the logarithmic functional derivatives of $\Xi(\varphi)$

$$\left. \frac{\delta^n \ln \Xi(\varphi)}{\prod_{i=1}^n \delta z \varphi_i} \right|_{\varphi=0} = U(1, \dots, n) \quad (3a)$$

and

$$\frac{\delta^n \ln \Xi(\varphi)}{\prod_{i=1}^n \delta z \varphi_i} = \frac{l(1, \dots, n, \varphi)}{\prod_{i=1}^n z \varphi_i}, \quad (\varphi_i \neq 0). \quad (3b)$$

Using the functional chain rule we find that the P - and the U -functions as well as the ϱ - and the l -functions are related to each other by the Ursell expansion [theorem 1a of (I)]

$$\begin{aligned} P(1) &= U(1) \\ P(1, 2) &= U(1, 2) + U(1)U(2) \\ &\text{etc.}, \end{aligned} \quad (4a)$$

$$\begin{aligned} \varrho(1) &= l(1) \\ \varrho(1, 2) &= l(1, 2) + l(1)l(2) \\ &\text{etc.} \end{aligned} \quad (4b)$$

Thus (3a) defines the well-known Ursell functions whereas the l -functions are apart from normalisation the total correlation functions.

Next we expand $\ln \Xi$ and the right hand side of (3b) into a functional Taylor series at $\varphi = 0$

$$\ln \Xi(\varphi) = \sum_{N \geq 0} \frac{z^N}{N!} \int \prod_{i=1}^N \varphi_i U(1, \dots, N) d1 \dots dN, \quad (5a)$$

$$\begin{aligned} \frac{l(1, \dots, n, \varphi)}{z^n \prod_{i=1}^n \varphi_i} &= U(1, \dots, n) \\ &+ \sum_{N > n} \frac{z^{N-n}}{(N-n)!} \int \prod_{i=n+1}^N \varphi_i U(1, \dots, N) dn + 1 \dots dN. \end{aligned} \quad (5b)$$

With the relation $\ln \Xi = PV/kT$ ^{4,5} we have for $\varphi_i = 1$

$$PV/kT = V \sum_{l \geq 1} b_l z^l \quad (6a)$$

and

$$\begin{aligned} \frac{l(1, \dots, n)}{z^n} &= U(1, \dots, n) + \sum_{N > n} \frac{z^{N-n}}{(N-n)!} \\ &\cdot \int U(1, \dots, N) dn + 1 \dots dN \end{aligned} \quad (6b)$$

where the coefficient b_l are the reducible cluster integrals^{4,5}. Note that the first Eq. of (6b) is the well-known fugacity expansion of the density:

$$\varrho/z = 1 + \sum_{n \geq 2} n b_n z^{n-1} \quad (7)$$

because of

$$\frac{1}{(n-1)!} \int U(1, \dots, n) d2 \dots dn = n b_n.$$

Equations (6a), (6b) and (7) have first been derived by MAYER and MONTROLL² in a completely different and complicated way.

2. Conversion to Power Series in Density

From the functional method we obtain density expansions in a most simple way. To solve this so-called elimination problem^{3,4} we simply make use of an appropriate functional operation which

1) is related to Eqs. (3) since they introduce the fugacity expansions,

2) employs $\varrho(i, \varphi)$ as independent function.

Because of

$$\frac{\delta \ln \Xi(\varphi)}{\delta z \varphi_1} \cdot z \varphi_1 = \frac{\varrho(1, \varphi)}{z \varphi_1} \cdot z \varphi_1 = \varrho(1, \varphi),$$

$\varrho(1, \varphi)/z \varphi_1$ or $\ln \varrho(1, \varphi)/z \varphi_1$ can be used as functionals, and theorems 2a resp. 4a as well as theorems 3a resp. 5a of (I) can be applied.

2.1. The functional $\varrho(1, \varphi)/z\varphi_1$

Defining

$$\left. \frac{\delta^n[\varrho(1, \varphi)/z\varphi_1]}{\prod_{i=2}^{n+1} \delta\varrho(i, \varphi)} \right|_{\varphi=0} = R(1, \dots, n+1) \quad (8a)$$

and

$$\frac{\delta^n[\varrho(1, \varphi)/z\varphi_1]}{\prod_{i=2}^{n+1} \delta\varrho(i, \varphi)} = \frac{\varrho_1}{z\varphi_1} k(1, \dots, n+1, \varphi), \quad (\varphi \neq 0), \quad (8b)$$

the functional chain rule leads to the intermediate expansion of U -functions into R -functions [theorem 2a of (I)]

$$\begin{aligned} U(1, 2) &= R(1, 2), \\ U(1, 2, 3) &= R(1, 2, 3) \\ &\quad + U(2, 3)(R(1, 2) + R(1, 3)) \\ &\quad \text{etc.} \end{aligned} \quad (9a)^6$$

and to the intermediate integral expansion of h -into k -functions [theorem 4a of (I)]

$$\begin{aligned} h(1, 2) &= k(1, 2) \\ &\quad + \int \varrho_3 k(1, 3) h(2, 3) d3, \quad (\varphi = 1), \\ &\quad \text{etc.} \end{aligned} \quad (9b)$$

with

$$h(1, \dots, n) = l(1, \dots, n) / \prod_{i=1}^n \varrho_i.$$

In the same way as in part 2 we expand the right hand side of (8b) into a functional Taylor series at $\varphi = 0$ and put then $\varphi = 1$. Because of $\varrho(i, \varphi = 0) = 0$ and $\varrho(i, \varphi = 1) = \varrho_i$ we find the relations

$$\frac{\varrho_1}{z} = 1 + \sum_{m \geq 1} \frac{\varrho^m}{m!} \int R(1, \dots, m+1) d2 \dots dm + 1, \quad (10)$$

$$\frac{\varrho_1}{z_1} k(1, \dots, n) = R(1, \dots, n) + \sum_{m \geq 1} \frac{\varrho^m}{m!} \int R(1, \dots, n+m) dn + 1 \dots dn + m.$$

The left hand side of (10) still contains the fugacity. On differentiating the functional $\ln[\varrho(1, \varphi)/z\varphi_1]$ instead of (8), z is automatically eliminated.

⁶ When $P(1, \dots, n) = \exp\{-\beta \sum_{i < j} u_{ij}\}$

where u_{ij} is the pair potential, the R -functions can be expressed in terms of Mayer- f -functions

$$\begin{aligned} R(1, 2) &= f_{12}; \\ R(1, 2, 3) &= f_{12}f_{13}f_{23} + f_{12}f_{13}; \\ R(1, 2, 3, 4) &= f_{12}f_{13}f_{24}f_{34}(f_{14}f_{23} + f_{14} + f_{23} + 1) + \\ &\quad + f_{12}f_{23}f_{14}f_{34}(f_{13} + f_{24} + 1) + \\ &\quad + f_{13}f_{23}f_{14}f_{24}(f_{12} + f_{34} + 1) + \\ &\quad + f_{12}f_{13}f_{14}(f_{23} + f_{24} + f_{34} + 1); \end{aligned}$$

For the expansion of the U - and the later defined V -functions see³.

2.2. The functional $\ln[\varrho(1, \varphi)/z\varphi_1]$

Defining

$$\left. \frac{\delta^n \ln[\varrho(1, \varphi)/z\varphi_1]}{\prod_{i=2}^{n+1} \delta\varrho(i, \varphi)} \right|_{\varphi=0} = V(1, \dots, n+1) \quad (11a)$$

and

$$\frac{\delta^n \ln[\varrho(1, \varphi)/z\varphi_1]}{\prod_{i=2}^{n+1} \delta\varrho(i, \varphi)} = c(1, \dots, n+1, \varphi), \quad (\varphi \neq 0), \quad (11b)$$

the functional chain rule yields the Husimi expansion of the U -functions into V -functions [theorem 3a of (I)]

$$\begin{aligned} U(1, 2) &= V(1, 2), \\ U(1, 2, 3) &= V(1, 2, 3) + U(2, 3)(V(1, 2) + V(1, 3)) \\ &\quad + V(1, 2)V(1, 3) \\ &\quad \text{etc.} \end{aligned} \quad (12a)$$

and the Husimi integral expansion of the h -function into c -functions [theorem 5a of (I)]

$$h(1, 2) = c(1, 2) + \int \varrho_3 c(1, 3) h(2, 3) d3 \quad \text{etc.} \quad (12b)$$

Thus we see that (11a) defines the Husimi functions and (11b) the direct correlation functions (for $\varphi = 1$). The right hand side of (11b) is now expanded into a functional Taylor series at $\varphi = 0$. If we then put $\varphi = 1$ we obtain

$$\ln[\varrho/z] = \sum_{m \geq 1} \beta_m \varrho^m, \quad (13a)$$

where β_m are the irreducible cluster integrals^{4,5} and

$$c(1, \dots, n) = V(1, \dots, n) + \sum_{m \geq 1} \frac{\varrho^m}{m!} \int V(1, \dots, n+m) dn + 1 \dots dn + m. \quad (13b)$$

Here we see for the first time that for the direct correlation functions $c(1, \dots, n)$ a power series in density exists, the coefficients being integrals over Husimi functions. If (13b) is introduced into (12b) we find the density expansion of the total correlation functions h . Together with (4b) we have the density expansion of the molecular distribution functions g . Under the general assumptions underlying this work they are both rather complicated and will therefore not be given explicitly⁷.

From

$$\varrho/z = \partial(P/kT)/\partial z \quad (14)^{4,5}$$

⁷ For pair potentials they reduce to well-known expansions^{3,5}.

the virial form of the equation of state is obtained using (13a)

$$\begin{aligned} \frac{P}{kT} &= \int (1 - \sum_{n \geq 1} n \beta_n \varrho^n) d\varrho \\ &= \varrho (1 - \sum_{n \geq 1} \frac{n}{n+1} \beta_n \varrho^n). \quad (15) \end{aligned}$$

3. Conclusion

In the present derivation of relations for the imperfect gas the only restrictions on the intermolec-

ular potential are those required by the existence of the thermodynamic limit⁵. Combinatorial or equivalent considerations as well as the use of the theory of functions have been avoided. Furthermore, we have been able to derive the density expansion of the direct correlation functions.

Acknowledgement

I wish to thank Professor Dr. A. MÜNSTER for his continued interest and help during the course of this work.

Abhängigkeit des optischen Bandabstandes von der molaren Zusammensetzung bei Zinksulfid-Kadmiumsulfid-Mischkristallen

Y. KOTERA und T. SEKINE

Staatliche Institute der Chemischen Industrie, Tokio

Herrn Professor Dr.-Ing. H. GOBRECHT zum 60. Geburtstag gewidmet

(Z. Naturforsch. **24 a**, 1408—1410 [1969]; eingegangen am 7. Juli 1969)

The optical band gap was determined for powder samples of $(Zn_xCd_{1-x})S$ by absorption measurements using a microspectrophotometer. Whereas the lattice constants (measured by X-ray lattice analysis) are linear functions of the components, the band gap is smaller than expected from the molar composition. The relation between band gap and composition was found to be linear, with a break at the equimolar composition. Possible reasons of this phenomenon are discussed.

1. Einleitung

Der Bandabstand von Zinksulfid-Kadmiumsulfid-Mischkristallen $(Zn_xCd_{1-x})S$ wurde zuerst von CURIE¹ durch Messung der diffusen Reflexion an pulverförmigen Proben ermittelt. Er fand einen linearen Zusammenhang zwischen dem Bandabstand und der molaren Zusammensetzung, allerdings bei erheblichen Streuungen der Meßwerte. Wir haben die Abhängigkeit des Bandabstandes von der Zusammensetzung mit einer wesentlich genaueren Methode erneut bestimmt. Dazu wurden die Transmissionskurven für Kristallire unterschiedlicher Zusammensetzung mit einem Mikrospektralphotometer gemessen und die energetische Lage der Absorptionskanten bestimmt, da diese dem Bandabstand entsprechen. Zum Vergleich wurde außerdem die Abhängigkeit der Gitterkonstanten von der Zusammensetzung der Mischkristalle röntgenographisch untersucht.

Sonderdruckanforderungen erbeten an Dr. Y. KOTERA, Government Chemical Industrial Research Institute Tokyo, *Tokyo-Hatagaya*, Japan.

¹ D. CURIE, *Luminescence in Crystals*, Methuen, London 1963.

2. Experimentelle Methode

Die Mischkristalle wurden durch einstündiges Glühen der aus lumineszenzreinem Zink- und Kadmiumsulfid hergestellten Ausgangssubstanz gewonnen. Für zusätzliche Lumineszenzmessungen, über die in der vorliegenden Arbeit jedoch nur orientierende Angaben gemacht werden, wurden alle Proben mit 10^{-4} Ag dotiert. Die genauen Zink-Kadmium-Verhältnisse der verschiedenen Proben wurden durch chemische Analyse der Phosphore bestimmt. Die Kristallstruktur wurde mit einem Röntgen-Diffraktometer (Rigaku Denki GmbH) gemessen.

Die Transmissionskurven der Kristallite wurden mit einem Universal-Mikro-Spektralphotometer (Typ UMSP I, Carl Zeiss) registriert. Dieses Gerät ermöglicht spektral-photometrische Messungen an mikroskopischen Präparaten im sichtbaren und ultravioletten Spektralbereich nach einem Zweistrahlverfahren.

Abbildung 1 zeigt den prinzipiellen Aufbau des Photometers. Zwei synchron rotierende Spiegelräder teilen das monochromatische Licht in einen Meß- und einen Vergleichsweg auf. Beide Strahlengänge enthalten ein vollständiges UV-Mikroskop. Das Licht des Meß- und des Vergleichsweges wird in schnellem Wechsel dem gleichen Lichtempfänger zugeführt. Ein über einen Verstärker angeschlossener Kompensationsschreiber zeichnet das Verhältnis zwischen Meß- und Vergleichsstrahl auf. Das Vergleichssignal wird über eine an den Verstärker angeschlossene automatische Spaltverstellung auch bei variabler Wellenlänge konstant gehalten. Das Meßsignal ändert