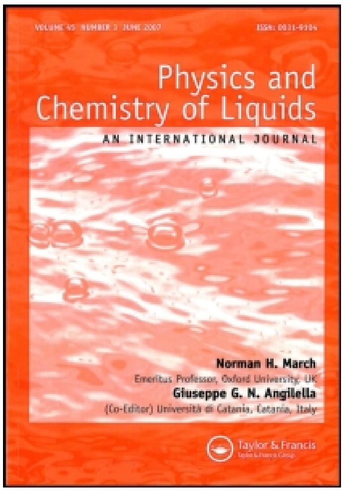

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Thermodynamic Behaviour of a Simple Liquid—MFA with non-additive Lateral Interactions

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The thermodynamic functions of a simple liquid are expressed in terms of analytical expressions within the framework of the Mean Field Approximation (MFA), whereby the classical model is improved in the following aspects:

i) It is shown that accounting for nonadditive forces between molecules in the liquid improves considerably the quantitative predictions of the theory.

ii) An analytical formula for the free volume on density dependence is derived on the ground of harmonic oscillator approximation.

iii) A partition function is suggested which properly describes the state of motion of a single atom at various temperatures and densities.

It appears that a proper qulitative description of melting necessarily requires a different lattice for the fluid—and for the solid phase. Only under this assumption the temperature course of the thermodynamic functions of the undercooled melt closely resembles existing experimental evidence.

I INTRODUCTION

It is widely accepted at present, that a proper description of the thermodynamical properties of a liquid could be obtained in two principally differing ways, namely, the method of pair correlation functions and the various modifications of the lattice gas model of a liquid. The former method, although rigorous in its foundations, yields results which are obtained at the expense of huge computational efforts and are thus difficult to operate with. Moreover, this method seems practically limited within the scope of simple nonassociated liquids with additive pair interactions between the particles.

The authors intention in the present paper, however, is to suggest analytical formulae for the thermodynamic functions which could provide a deeper insight into the physics of a simple liquid and, moreover, bridge the gap between simple- and polymer liquids, so that an extension of the present consideration over polymer and associated melts could be feasible.

Model descriptions of the properties of simple liquids have been intensively developed recently whereby also the thermodynamical behaviour of some associated liquids, e.g. of glassforming melts, has gained importance within the scope of theoretical research. Most of these investigations are based on various modifications of the cell- and lattice gas models of a simple liquid while elements allowing for the complex structure of polar, orientationally dependent associated liquids are taken additionally into account.[1,2]

However, there is no liquid state theory at present which could provide a satisfactory description of the properties of the system within the whole liquid range and even such a common physical phenomenon as the process of melting at a microscopical level still remains a mystery. Below the melting point T_m the thermodynamic behaviour of a simple undercooled melt which preserves its metastable equilibrium has not been theoretically treated due to the lack of experimental data over this hardly accessible region.

In the present work we suggest a transparent model of a simple liquid whereby predominantly the following aspects of the problem have been considered:

I) The Mean Field Approximation (MFA)[4] has been extended in order to deal with varying strength of the lateral interactions between the atoms (nonadditivity of the energy bonds) in dependence on the number of nearest neighbours which are actually present in the first coordination sphere of any deliberately chosen atom. Thus a certain degree of long-range disorder may be introduced despite the use of a periodic lattice in the statistical treatment of the lattice gas.

II) An analytical expression for the "free volume" as well as for the non-configurational partition function which describes a gradual transition in the state of motion of a single particle from quantum into classical oscillations and further into free translational movement with growing temperature.

III) Results for the critical parameters obtained in the framework of the present model are compared with those of earlier treatments and then some important conclusions are suggested on the ground of detailed investigation of the thermodynamic functions of undercooled melts at $0 \leq T \leq T_m$.

During the thirties some attempts to suggest an atomistic picture of the melting transition gained prominence although they can be hardly accepted in view of the new information available at present. Born's conjecture of vanishing shear modulus[5] at the melting point has been subsequently disproved by careful measurements of this parameter as function of temperature, right up to the melting point. The lattice gas theories of Frenkel,[6] Bresler[3] and Lennard-Jones and Devonshire[7] appear inadequate since the first can be interpreted as yielding a second-order phase transition while the second and the third predict the existence of a critical point of melting which contradicts recent results of both theoretical and experimental research.[8] Moreover, generally lattice gas models predict no more than one phase transition which in fact is identified as that of condensation. In the present approach after the validity of the theory is verified in the region of the liquid-gas transition the "missing" solid-liquid phase transition is introduced *ad hoc* by equating the Gibbs free energy of an Einstein crystal to that of a liquid described in the framework of the model. Similar methods of such somewhat artificially fixing of the melting temperature T_m have been used earlier by several authors.[9–11]

II DESCRIPTION OF THE THEORETICAL MODEL

1 Lattice gas statistics with nonadditive energy bonds

In line with the basic idea of the model used in this paper, namely that the liquid is formed from a hypothetical crystalline lattice by the introduction of certain amount of crystal defects (holes), one may determine the degree of disorder in the system considering only the immediate surrounding of a given molecule. It has long been known from X-ray diffraction studies that liquids exhibit a certain order within small ranges, i.e. that the pair distribution functions which give the probability density of finding another molecule in a certain volume element at some distance from a given molecule in a solid or in its melt do not differ considerably for small distances.[12] Since the most probable distances of the nearest neighbours lie within a very narrow interval one may introduce also for liquids the concept of coordination spheres. The number of neighbouring molecules whose centers lie within the coordination sphere is given by the coordination number Z. In an ideal crystal the coordination number Z is fully defined by the geometry of the lattice, whereas for the melt of the same crystal this value has only statistical meaning. Evidently, in the liquid one may observe in principle a variety of a coordination numbers: $Z, Z-1, Z-2, \ldots$ (cf. Fig. 1) although the probability of finding an atom whose nearest neighbours are far less than Z should be extremely small. A coordination number $Z+1$ appears impossible since an additional atom may be inserted in the coordination sphere of a dense (hexagonal) packing only at the expense of a considerable extension of the latter and this demands a great amount of energy. Consequently the degree of

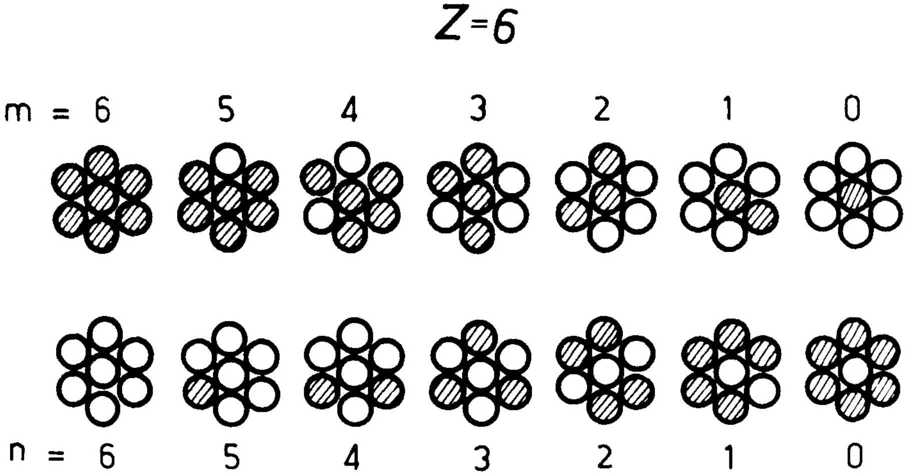

FIGURE 1 Various possible degrees of occupation of the first coordination sphere of a particle ●, resp. of a hole ○ in a 2D-hexagonal lattice.

order in such a system is expressed by the probability for a certain atom to be surrounded by Z nearest neighbours and this probability tends to unity for the state of ideal order when the temperature T goes to zero.

It is an easy task to find the probability distribution of the various coordination numbers to be met in a simple liquid, provided the excess of the melt volume over the crystal volume is known. In the lattice gas model where the liquid volume is divided into cells such that the number of cells is larger than the number of particles, and each cell is centered at one site of a lattice, the ratio $V_{\mathrm{liq}}/V_{\mathrm{sol}}$ is simply related to the average concentration of N particles over the M sites of the lattice: $\theta = N/M$, that is $V_{\mathrm{sol}}/V_{\mathrm{liq}} = \theta$. If now, according to the MFA, one assumes that the probability of a single site to be occupied by a particle does not depend on whether the adjacent sites are occupied or free, the probability P_m for a certain atom to have only m of Z possible nearest neighbours actually present at their sites should be given by:

$$P_m(\theta) = \binom{Z}{m} \cdot \theta^m \cdot (1 - \theta)^{Z-m} \tag{1}$$

where θ is the probability of a site to be occupied, $1 - \theta$—to be empty, and $\binom{Z}{m}$ yields the number of ways such a coordination sphere can be filled. For a typical nonassociated liquid such as liquid argon one has at the melting point $\theta = V_{\mathrm{sol}}/V_{\mathrm{liq}} = 0{,}88$ and for solid Ar $Z = 12$.

In Figure 2 the probability P_m of different coordination numbers as well as the total probability distribution $\sum_{1=m}^{Z} P_1$ are plotted for liquid Ar near the melting point and thus a mean coordination number $\bar{m} = 10.6$ is ob-

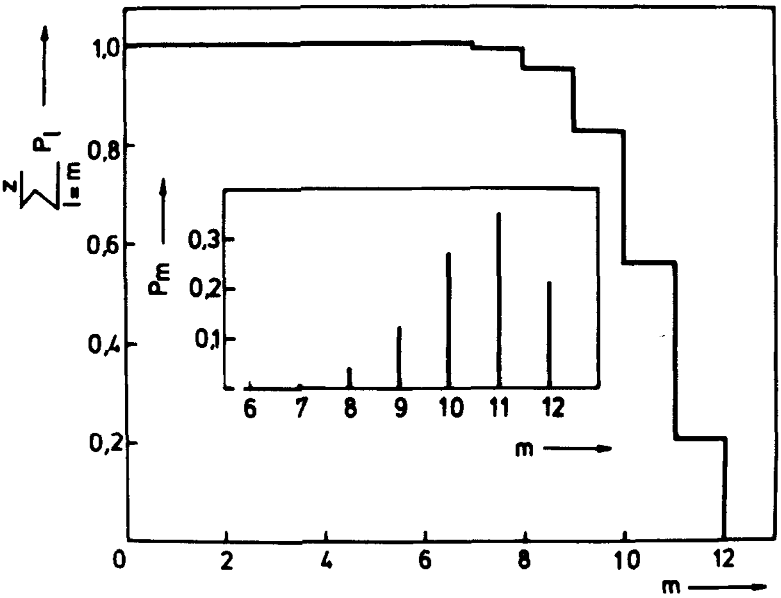

FIGURE 2 Coordination number distribution P_m in liquid Ar near the melting point (see inset). The integral probability distribution $\Sigma_{n=m}^{Z} P_n$ vs. actual coordination number m is also shown.

tained in close agreement with the experimental result of 10.5[13] and with the values 10.7[14] and 10.8[15] used earlier by other investigators. From Figure 2 it is also evident, that coordination numbers less than eight do not practically occur, in line with what was said at the beginning of this section.

Consider now the partition function $Q(N, M, T)$ of N atoms which may occupy M sites and suppose only nearest neighbours interactions are taken into account. One has in this case[16]

$$Q(N, M, T) = q(T)^N\left[\cdot g_1 \exp\left(-\frac{E_1}{kT}\right) + g_2 \exp\left(-\frac{E_2}{kT}\right) + \cdots + g_l \exp\left(-\frac{E_l}{kT}\right) + \cdots\right] \tag{2}$$

(where E_l is the energy of the lth configuration, g_l is the number of degeneracy and $q(T)$ is the partition function of a single atom at temperature T). In the MFA (2) is replaced by:

$$\begin{aligned} Q(N, M, T) &= q(T)^N(g_1 + g_2 + \cdots + g_l + \cdots)\exp\left(-\frac{E_c}{kT}\right) \\ &= q(T)^N \cdot G(N, M) \cdot \exp\left(-\frac{E_c}{kT}\right) \end{aligned} \tag{3}$$

Here $G(N, M)$ is the total number of configurations that the system may possess $G(N, M) = M!/N!(M - N)!$ and E_c is the average value of the energies E_1.

In order to calculate the mean configurational energy E_c for a certain density θ one should notice first that all N particles are in principle subdivided into several fractions N_m (exactly $Z + 1$) of particles with an actual coordination number $m = 0, 1, 2, \ldots, Z - 1, Z$. These fractions are given by the binomial distribution (1):

$$N_m = N \cdot \binom{Z}{m} \cdot \theta^m \cdot (1 - \theta)^{Z-m} \tag{4}$$

Suppose further that generally the strength W_m of an energy bond which connects a certain atom of the mth fraction with the nearest neighbours in the first coordination sphere depends on the degree of filling m. The configurational energy $E_c(\theta)$ becomes then simply:

$$E_c(\theta) = \frac{1}{2} \sum_{m=0}^{Z} m \cdot W_m \cdot N_m = \frac{N}{2} \sum_{m=0}^{Z} m W_m \binom{Z}{m} \theta^m (1 - \theta)^{Z-m} \tag{5}$$

where W_m labels the energy bond in the m-fold occupied coordination sphere ($W_0 = 0$—no bonds existing) and a factor of $\frac{1}{2}$ emerges because each bond has been counted twice.

It is an easy task to prove that in the case of equal bonds where $W_m = W$ ($m = 1, 2, \ldots, Z$) Eq. (5) yields a familiar result for the configurational energy $E_c(\theta)$ in terms of the MFA:

$$E_c(\theta) = \frac{NW}{2} \sum_{m=0}^{Z} m \binom{Z}{m} \theta^m (1 - \theta)^{Z-m} = \frac{NZW\theta}{2} = -\lambda_s \cdot \theta \tag{6}$$

where λ_s is taken to be the sublimation heat of a system with first neighbour interactions.

Equation (5) may be easily transformed into a more suitable form

$$E_c(\theta) = \frac{N}{2} \sum_{k=1}^{Z} \alpha_k \cdot \theta^k \tag{7}$$

with

$$\alpha_k = \sum_{m=1}^{k} (-1)^{k-m} \binom{Z - m}{Z - k} m W_m \tag{7'}$$

Equation (7) is the final expression for the configurational energy which should be inserted in the partition function (1) and further dealt with, provided the values of W_m are known. However, a major simplification of (7) may be achieved if one assumes a linear dependence of W_m on m as a first correction to a constant lateral bond energy. In this case all coefficients in (7′), but α_1 and α_2, vanish and one obtains:

$$E_c(\theta) = \frac{ZN}{2}[(Z - 1)(W_2 - W_1)\theta^2 + W_1\theta] \tag{8}$$

where for $W_2 = W_1 = W$ again expression (6) follows.

A question which immediately arises is to what extent the bond energy between two nearest neighbours in a lattice depends on whether neighbouring sites around are occupied or free, or otherwise, is a single energy bond in the bulk of the condensed matter the same as in the gas phase. Theoretical investigations of the stability of very small crystals show, that the mean bond energy W in a crystal where the configurational energy is represented in terms of first neighbour interactions is essentially smaller than the dissociation energy D_2 of a diatomic gas molecule of the same substance.[17] For the ratio D_2/W one obtains the value 2.85 which agrees favourably with the experimental data of 2.21 ÷ 4.07 for metals.[17] At the same time the distance between nearest neighbours in crystals is about 15% larger than the interatomic distance in the diatomic molecule. It is also generally known, that the distance between the surface lattice plane and the next lattice plane is smaller than the distance between the second and the third ones, the latter distance being practically the same as in the bulk of the crystal.[18] As a plausible explanation of these effects one could argue that in the diatomic molecule both atoms interact with each other only and their valence electrons are concentrated to form only one bond, whereas when an atom is connected with more than one partner, as it is in the crystal, then the same number of valence electrons take part in the formation of a larger number of bonds.

Within the framework of the present lattice-gas model such variable (nonadditive) bonds between the constituents of the system in dependence of their actual surrounding at any density θ is used to account for the distortion in the long-range order, i.e. for the actual displacements of the atoms with respect to the regular arrangement of their sites in a periodic grid. It is clear that lattice gas statistics may be developed only on the ground of a (hypothetical) periodic lattice imposed on the system so as to provide a coordinate system while the state of distorted long range order is reflected by the modification (7) of the formula (6) for the configurational energy E_c.

As a convenient measure of how rapidly W_m descends with increasing m the ratio $\tilde{p} = W_1/W_z$ may serve which in the following consideration will be briefly called a parameter of nonaddivitity. With the help of $\tilde{p}$ and W_z, as well as with W_m linearly dependent on m, Eq. (8) converts to

$$E_c(\theta) = \frac{ZNW_z}{2}[(1 - \tilde{p})\theta^2 + \tilde{p}\theta] \tag{9}$$

which is the form we shall use throughout in this paper.

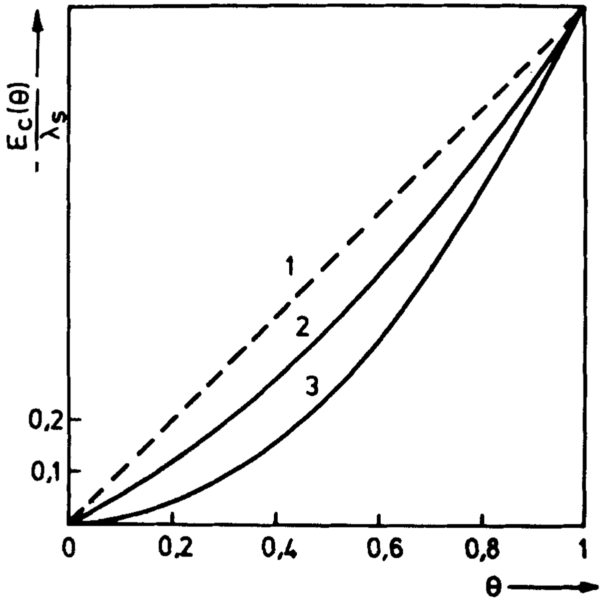

FIGURE 3 Dependence of configurational energy E_c on relative density θ in a system with: additive ($\tilde{p} = 1$)—1; and nonadditive ($\tilde{p} = 1.5$)–2, ($\tilde{p} = 2$)–3 pair interactions within the framework of MFA.

In Figure 3 the configurational energy $E_c(\theta)$ of the system for additive ($\tilde{p} = 1$)—and nonadditive ($\tilde{p} > 1$) energy bonds is shown. We shall like to point out here that the plot of Eq. (9) practically coincides with that of the more general Eq. (7), provided $\tilde{p}$ is kept the same, i.e. for a certain degree of nonadditivity the configurational energy is highly insensitive to the genuine W_m on m relationship. From the quite general demand that the configurational energy remains negative ($W < 0$) within the whole density interval $0 \leq \theta \leq 1$ the maximal value of $\tilde{p}$ may be determined. In particular for the case of W_m linearly dependent on m one readily obtains from (9) $\tilde{p}_{\max} = 2$ which agrees reasonably with the ratio D_2/W quoted above. Evidently $\tilde{p}_{\min}$ is equal to unity thus reflecting the case of full additivity of the energy bonds. Although one could in principle estimate $\tilde{p}$ by means of quantum mechanical computations in the present work we use it as an adjusting parameter.

2 The nonconfigurational partition function q(T)

Dealing with the configurational statistics we have so far neglected the influence of $q(T)$ in Eq. (1) on the thermodynamic characteristics of our system, i.e. we have assumed the state of each particle within its own cell to be independent of the density θ. It is intuitively clear, however, that at high densities ($\theta \approx 1$) each particle will behave as an oscillator in the potential well of the nearest neighbours, while at very low densities ($\theta \approx 0$) the particle is expected to move freely in its cell. The most widely accepted theory of the liquid state at present which accounts for the change in the state of motion of a single particle is the free volume theory of Lennard-Jones and Devonshire[19] which has been modified to allow for empty cells and has been used by several authors.[20–26] In all investigations so far a variety of linear interpolation formulae has been used in order to approximate the complex free volume V_f on θ dependence as revealed by the tables of Lennard-Jones and Devonshire.[19] In the present paper a simple analytical expression for the free volume is derived which accounts for the density θ at any temperature and properly describes the transitions from harmonic vibrations into free movement with the variation of θ and T.

The free volume which the atom actually occupies within the cell is defined by:[26]

$$V_f(\theta) = \int_{\Delta} \mathrm{d}\mathbf{r} \exp\left\{-\frac{\psi(\mathbf{r}) - \psi(0)}{kT}\right\} \qquad (10)$$

where

$$\psi(\mathbf{r}) = 4W\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{5}\right]$$

is the pair interaction potentials and Δ denotes the volume of the cell. Summing the Lennard–Jones potential over $\theta \cdot Z$ nearest neighbours which are smeared on a sphere with radius a ($\frac{4}{3}\pi a^3 = \Delta$), and differentiating twice with respect to r, one obtains for the force constant f of a simple harmonic oscillator[27]

$$f = \frac{2ZW\theta}{2^{1/3}\sigma^2}\left[22{,}106\left(\frac{N\sigma^3}{V_s}\right)^4 - 10{,}559\left(\frac{N\sigma^3}{V_s}\right)^2\right] \cdot \left(\frac{N\sigma^3}{V_s}\right)^{2/3} \qquad (11)$$

where the following approximation is made:

$$\theta \cdot Z[\psi(\mathbf{r}) - \psi(0)] = \tfrac{1}{2} \cdot f \cdot r^2 \qquad (12)$$

In (11) σ is the "hard core" radius of the Lennard–Jones potential and for hexagonal close packing $V_s = N\sigma^3$. Hence, one has

$$f = \frac{18{,}32972 \cdot Z \cdot \theta \cdot W}{\sigma^2} \qquad (13)$$

With the help of (13) the characteristic temperature θ_E of an Einstein crystal may be immediately determined as:

$$\theta_E = \frac{h}{k} \cdot \frac{1}{2\pi} \left(\frac{f}{m}\right)^{1/2} \tag{14}$$

Inserting (12) into (10) and performing the integration one readily obtains for the free volume V_f:

$$V_f(\theta) = \left(\frac{2\pi kT}{f}\right)^{3/2} \left[\mathrm{Erf}\left(\frac{fa^2}{2kT}\right) - \frac{2}{\sqrt{\pi}} \sqrt{\frac{fa^2}{2kT}} \cdot \exp\left(-\frac{fa^2}{2kT}\right)\right] \tag{15}$$

where

$$\mathrm{Erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} \cdot \mathrm{d}t.$$

It may be directly proved, that for strong lateral bonds ($W/kT \gg 1$) and at high densities $\theta \approx 1$ Eq. (15) gives $V_f = (2\pi kT/f)^{3/2}$ which is just the volume occupied by a 3D harmonic oscillator (classical case), while for high temperatures and low densities $\theta \approx 0$ each particle moves freely within the cell volume $V_f = \Delta = \frac{4}{3}\pi a^3$. In Figure 4 the dependence of the ratio $\ln (V_f(\theta)/\Delta)$ on θ is shown at $kT/W = 1.3$.

From Figure 4 it is seen, that the plot of Eq. (15) closely resembles the tabulated V_f on θ relationship of Lennard-Jones and Devonshire.[19] At high temperature ($T \approx T_{cr}$), however, Eq. (15) predicts a greater free volume, than that which follows from the Lennard-Jones and Devonshire theory, i.e. the particle may come closer to the cell borders which seems more realistic and is due to the finite potential barrier between neighbouring cells in the oscillator approximation. With (15) the partition function q_{class} of a single particle at not too low (not "quantum") temperatures is expressed as:

$$q_{\text{class}}(T) = \frac{1}{\Lambda^3} V_f(\theta) \tag{16}$$

where $\Lambda = h/(2\pi mkT)^{1/2}$ denotes the de Broglie thermal wavelength.

Our final step should be to construct a more general expression for the configurational partition function $q(T)$ which would be valid also at very low temperatures, thus reflecting the transition from classical to quantum behaviour of the particle. A very convenient interpolation formula, employed previously in the theoretical treatment of hindered rotation,[16]

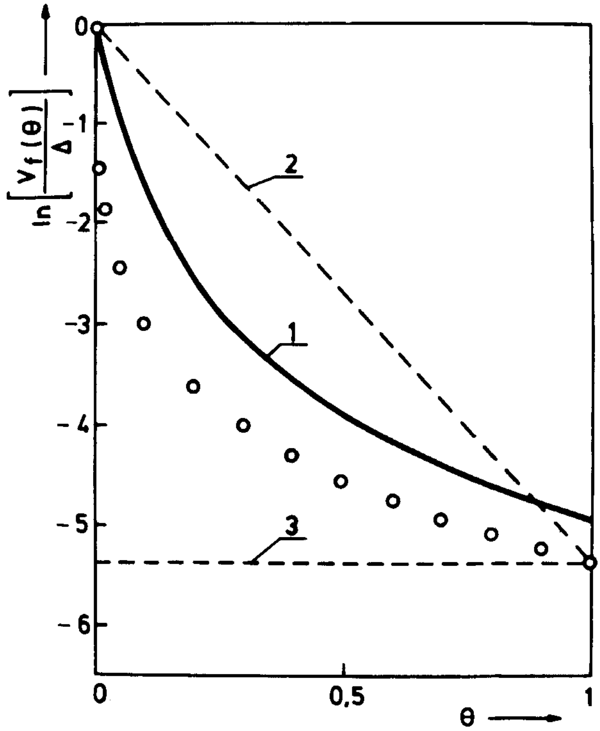

FIGURE 4 Dependence of the free volume V_f on density of the system: 1-acc. to Eq. (15) of this paper, 2-linear interpolation formula of Ono (1947), 3-acc. to Cernuschi and Eyring (1939), o-tabulated results of Lennard-Jones and Devonshire (1937).

is used in the present paper to serve for this purpose. We set

$$q(T) = q_{\text{class}} \cdot \frac{q_{\text{quant. osc.}}}{q_{\text{class. osc.}}} \tag{17}$$

where

$$q_{\text{quant. osc.}} = \frac{\exp(-3\theta_E/2T)}{(1-\exp(-\theta_E/T))^3},$$

and $q_{\text{class. osc.}} = (T/\theta_E)^3$. At high temperatures the ratio $q_{\text{quant. osc.}}/q_{\text{class. osc.}}$ tends to unity and therefore $q(T) \approx q_{\text{class.}}$ with the vibrations gradually converting into translational degrees of freedom (cf. Eq. (15)), whereas for $T \approx 0$ $q_{\text{class.}} \approx q_{\text{class. osc.}}$ and $q(T)$ approaches the partition function of the 3D Einstein crystal. With (17) which is the central statement in this section, some important theoretical consequences may be derived. For the non-configurational internal energy E_{vib}, specific heat C_{vib} and entropy S_{vib} one obtains from (17) and (16):

$$\frac{E_{\text{vib}}}{R} = \frac{kT^2}{R}\left(\frac{\partial \ln q^N}{\partial T}\right)_{N,M}$$

$$= \frac{3}{2}\theta_E \operatorname{cth}\frac{\theta_E}{2T} - \frac{t\theta_E^2}{\sqrt{\pi}/2\sqrt{(T/t\theta_E^2)}\exp(t\theta_E^2/T)\cdot \operatorname{Erf}\sqrt{(t\theta_E^2/T)} - 1} \tag{18}$$

$$\frac{C_{\text{vib}}}{R} = \left(\frac{\partial E_{\text{vib}}}{\partial T}\right)_{N,M} = 3\left(\frac{\theta_E/2T}{sh(\theta_E/2T)}\right)^2$$

$$+ \frac{\sqrt{\pi}/2(1-2t\theta_E^2/T)\exp(t\theta_E^2/T)\operatorname{Erf}\sqrt{(t\theta_E^2/T)}/\sqrt{(t\theta_E^2/T)} - 1}{[\sqrt{\pi}/2\sqrt{(T/t\theta_E^2)}\cdot\exp(t\theta_E^2/T)\cdot \operatorname{Erf}\sqrt{(t\theta_E^2/T)} - 1]^2}\cdot\frac{t\theta_E^2}{2T} \tag{19}$$

$$\frac{S_{\text{vib}}}{R} = \kappa\frac{\partial}{\partial T}[T\cdot \ln q^N]_{N,M}$$

$$= \ln\left\{\frac{1}{8\, sh^3(\theta_E/2T)}\left[\operatorname{Erf}\sqrt{\frac{t\theta_E^2}{T}} - \frac{2}{\sqrt{\pi}}\sqrt{\frac{t\theta_E^2}{T}}\cdot\exp(-t\theta_E^2/T)\right]\right\}$$

$$+ 3\frac{\theta_E/2T}{\operatorname{th}\theta_E/2T} - \frac{t\theta_E^2/T}{\sqrt{\pi}/2\exp(t\theta_E^2/T)\cdot\sqrt{(T/t\theta_E^2)}\cdot \operatorname{Erf}\sqrt{(t\theta_E^2/T)} - 1} \tag{20}$$

where $R = kN$ and $t = 2m\pi^2 \cdot a^2 \cdot k/h^2$ is used for abbreviation.

In Figure 5 the nonconfigurational specific heat $C_{\text{vib}}(T)$ is plotted against the reduced temperature T/T_c while the degree of coverage of the lattice θ is kept as a constant parameter. The curves in Figure 5 show the contribution of harmonic oscillations of the system of particles to the heat capacity $C_{\text{vib}}(T)$ to depend sharply on the density parameter θ. Consequently one could maintain that the validity of the various theoretical models neglecting the $q(T)$ on θ dependence (e.g. as in [20] and similar expressions) is reduced to a very narrow temperature interval where the heat capacities for, say, $\theta \approx 0$ and $\theta \approx 1$ do not greatly differ.

From Figure 6 which represents the $S_{\text{vib}}(T)$ on T relationship for various θ it becomes evident that the entropy gain produced by the introduction of holes is twofold. Firstly there is a configurational entropy of mixing (cf. Eq. (3) $G(N, M)$) between particles and holes and secondly—a nonconfigurational contribution, due to an increase of the volume available for individual particle motion if a particle is located besides holes.

It is also seen from Figure 6 that at temperatures below the critical one $T/T_c < 1$ the configurational and vibrational contributions to the entropy of vapourization $\Delta S_{\text{ev}} = \Delta S_{\text{conf}} + \Delta S_{\text{vib}}$ have the same order, as far as for simple liquids $\Delta S_{\text{ev}}/R \approx 9.2$ (Trouton's rule).

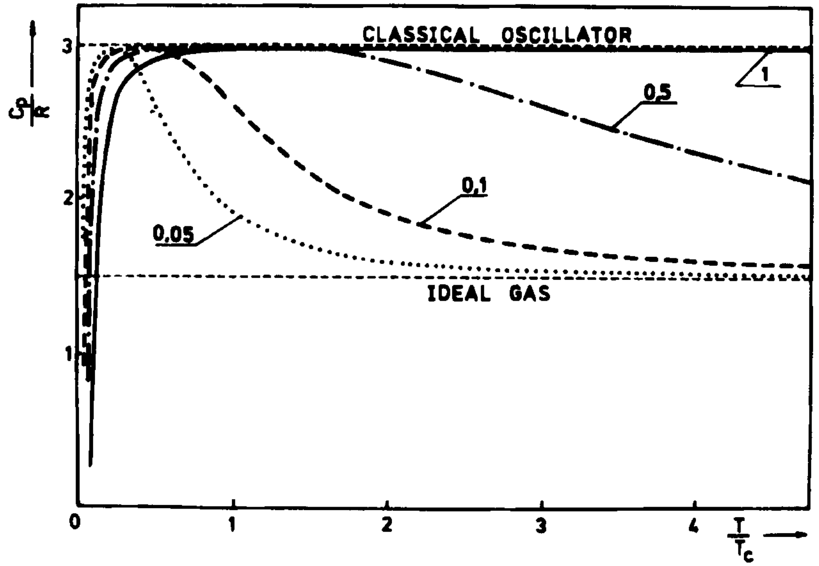

FIGURE 5 Dependence of the nonconfigurational heat capacity C_p on reduced temperature T/T_c at various densities 0 of the system.

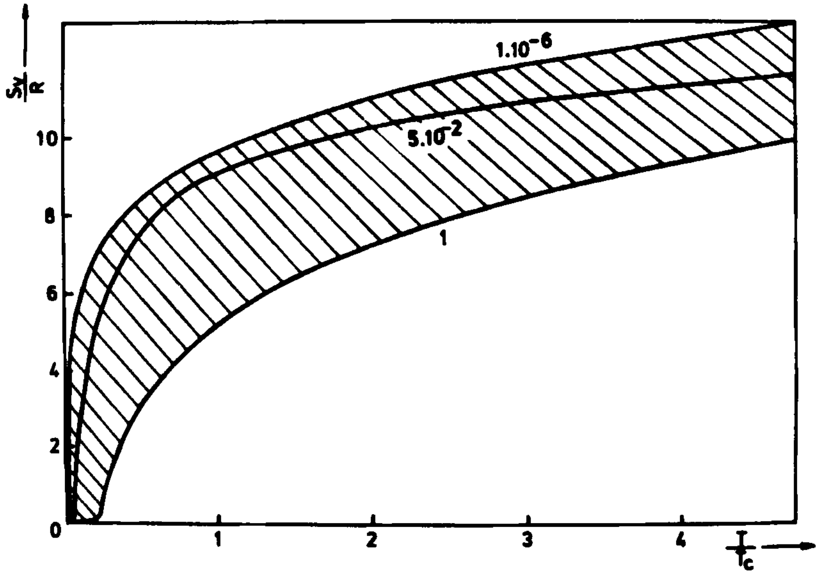

FIGURE 6 Dependence of the nonconfigurational entropy S_v on reduced temperature T/T_c (the density 0 of the system is given as a parameter).

3 Equations of state and critical data

From the partition function (3) and making use of (9), (16) and (17) all thermodynamical functions of the system may be readily obtained. The internal pressure P is given by

$$\begin{aligned}\frac{P\Delta}{kT_c} &= \frac{T}{T_c}\left(\frac{\partial \ln Q}{\partial M}\right)_{N,T}\\ &= \frac{\theta}{2}\left[\frac{3}{2}\cdot\frac{\theta_E}{T_c}\operatorname{cth}\frac{\theta_E}{2T} + \frac{2t\theta_E^2/T_c}{\sqrt{\pi}/2\sqrt{(T/t\theta_E^2)}\exp(t\theta_E^2/T)\operatorname{Erf}\sqrt{(t\theta_E^2/T)} - 1}\right]\\ &\quad + \frac{ZW}{2kT_c}[2(1-\tilde{p})\theta^3 + \tilde{p}\theta^2] - \frac{T}{T_c}\cdot\ln(1-\theta). \qquad (21)\end{aligned}$$

and for the chemical potential μ one has

$$\begin{aligned}\frac{\mu}{kT_c} &= -\frac{T}{T_c}\left(\frac{\partial \ln Q}{\partial N}\right)_{M,T} = \frac{T}{T_c}\ln\frac{8\,sh^3(\theta_E/2T)}{\operatorname{Erf}\sqrt{(t\theta_E^2/T)} - 2/\sqrt{\pi}\sqrt{(t\theta_E^2/T)}\exp(-t\theta_E^2/T)}\\ &\quad - \frac{\theta_E}{2}\left[-\frac{3}{2T_c}\operatorname{cth}\frac{\theta_E}{2T} + \frac{2t\theta_E/T}{\sqrt{\pi}/2\exp(t\theta_E^2/T)\sqrt{(T/t\theta_E^2)}\operatorname{Erf}\sqrt{(t\theta_E^2/T)} - 1}\right]\\ &\quad + \frac{ZW}{2kT_c}[3(1-\tilde{p})\theta^2 + 2\tilde{p}\theta] + \frac{T}{T_c}\ln\frac{\theta}{1-\theta} \qquad (22)\end{aligned}$$

In the Table I the theoretical predictions concerning the critical behaviour of our model liquid are compared in the case of Ar with theoretical critical data following from the conventional MFA, as well as from some other models developed so far.

TABLE I

Reduced critical constants

	v_c/σ^3	kT_c/W	$P_c\sigma^3/W$
Experiment[14]	3.15	1.28	0.12
van der Waals[16]	8.88	0.30	0.01
Lennard-Jones & Dev.[7]	1.77	1.30	0.43
Cernuschi & Eyring[20]	2.00	2.74	0.47
Bragg and Williams[4]	2.00	3,00	0.58
MFA—nonadditiv and $q(\theta)$ = const.	3.15	2.67	0.30
MFA—additive and $q(\theta)$ dependence	1.63	1.80	1.11
MFA—nonadditive and $q(\theta)$ dependence	3.15	1.33	0.37

It is evident that the improvement of the conventional MFA due to the use of nonadditive interactions (Eq. (9)) leads to critical values which are even better than those obtained in the highly superior quasichemical approximation.[20] Preliminary estimations of the effect of nonadditivity indicate that the improvement of the critical values is even more pronounced in terms of the quasichemical approximation. The additional inclusion of q on θ dependence brings the critical temperature T_{cr} to nearly coincide with the experimental value, whereas the agreement of P_{cr} with the experimental data, although somewhat deteriorated, remains better than in all the models listed above. Hence the only phase transition produced by this model should be undoubtedly referred to as a gas-liquid one while like in all models of lattice gas statistics with only attractive interactions included, no changes in the thermodynamical functions witness the existence of a second phase transition which could be identified with the process of melting.

III THE CRYSTAL-MELT TRANSITION

Attempts to tackle fusion in terms of configurational statistics have so far either predicted the existence of a critical point T_{cr} for this phase transition[7] or lead to more realistic results ($T_{cr} = \infty$) at the expense of an extremely sophistication of the mathematical treatment.[8] Meanwhile it seems illuminating, that a critical point may be connected with a phase transition only between phases which can be distinguished on purely quantitative basis, e.g. both gas- and liquid-phases differ on the more or less important role which intermolecular interactions play. On the other hand such phases like the liquid and the solid reveal a qualitative difference in what concerns their internal symmetry. As far as a certain type of symmetry may be either present or not, it could be argued that there can be no continuous transition between them.[28] As far as all attempts to construct an atomic scale picture of the melting transition have failed so far to win universal acclaim[29] one may invoke instead a well-known thermodynamic approach. In this paper we fix the crystal-melt phase transition at the interception point of the chemical potential of our model liquid and that of a perfect Einstein crystal which is assumed to represent adequately the properties of the solid phase. We show below that in spite of the extreme simplicity and, to some extent, artificialness of such approach some important conclusions about the thermodynamic behaviour of simple undercooled melts follow which are qualitatively consistent with earlier experimental results on glassforming melts.

Consider first the chemical potential μ_{cryst} of an ideal Einstein solid in which no configurational degeneracy exists, i.e. the number of locked lattice vacancies present in solids at finite temperatures is negligibly smaller than the number of holes in the respective liquid. Using (3) and (6) at $\theta = 1$, one has in this case

$$\frac{\mu_{\text{cryst}}(T)}{kT_c} = \frac{ZW}{2kT_c} + 3\frac{T}{T_c}\cdot\ln\left(2sh\frac{\theta_E}{2T}\right) \tag{23}$$

In order to plot the μ_{liq}/kT_c dependence on temperature at constant pressure one must first determine from Eq. (21) the θ on T relationship for a certain pressure and then insert these data into Eq. (22). In Figure 7 both the chemical potential μ_{liq}/kT_c (22) and the total entropy $S = S_{\text{conf}} + S_{\text{vib}}$ of our model liquid are plotted in dimensionless units versus reduced temperature T/T_{cr} at nearly atmospheric pressure (for Ar $P/P_{\text{cr}} = 1/400$). Consider first the μ_{liq}/kT_c curve. There are two stable branches of this curve, namely AOB which corresponds to the condensed liquid phase and COD corresponding to the gaseous phase whose interception point 0 determines the boiling temperature T_b at normal pressure. As shown in Figure 7 one obtains for liquid Ar approximately $T_b/T_c \approx 0.37$ which lies considerably below the experiment value of 0.58.[12] One may argue that such a discrepancy reflects the fact that P_{cr} which follows from the present model is also considerably

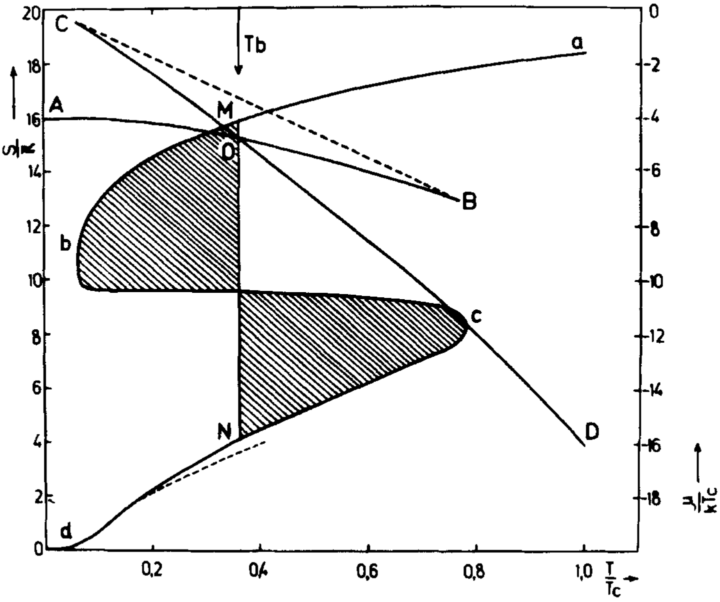

FIGURE 7 Dependence of the total entropy S-curve abcd, and of the chemical potential μ/kT_c-curve ABCD—on reduced temperature T/T_c at constant pressure $P/P_c = 1/400$. The dashed line dN represents the entropy of the respective perfect crystal.

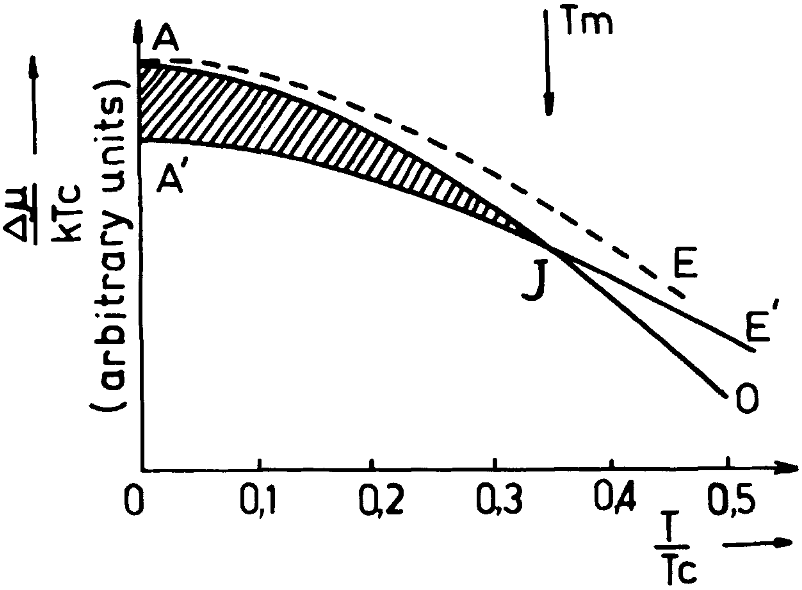

FIGURE 8 Dependence of the chemical potential μ/kT_c on reduced temperature T/T_c in the case of a model liquid-curve AO, and of a perfect crystal with $W_{\text{cryst.}} = W_{\text{liq.}}$-curve AE and with $|W_{\text{cryst.}}| > |W_{\text{liq.}}|$ -curve $A'E'$.

higher than its experimental value (cf. Table I). Looking further at the entropy S/R dependence on temperature one may verify from Figure 7 that the entropy has a characteristic S-shaped form at the liquid-gas phase transition. The entropy of vaporization appears equal to $S_{ev} \approx 11.5R$ which, as mentioned earlier, is due to changes both in the configurational- and vibrational-components of the entropy and overestimates only slightly the empirically established average value of the Trouton's rule. It is also evident from Figure 7 that the entropy vanishes when T goes to zero in line with the requirement of the Third Law of Thermodynamics (Nernst's theorem) and that Maxwell's rule of equal areas at the phase transition holds also for the entropy as function of temperature.†

Consider next in more detail the process of melting. Although no dramatic changes in the behaviour of the thermodynamic functions mark the temperature T_m of the phase transition crystal-melt one may look rather for the interception point between the graphs AE of Eq. (23) and AO of Eq. (22) in Figure 8. The point A which is thus the only common point between the

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† The latter may be easily proved if one integrates the total differential of enthalpy $dH = T \cdot dS$ (at constant pressure) over the closed path MNcbM.

melt branch AOB (Figure 7) and that of the respective crystal appears at the origin and leads to the rather absurd result of $T_m/T_c = 0$. On the other hand, one may reasonably *ad hoc* determine T_m either from the experimentally established ratio T_m/T_b ($T_m/T_b = 0.96$ for Ar) or independently from the excess of the melt volume over the crystal one $V_{\text{cryst}}/V_{\text{liq}} = 0.88$. Both methods lead unanimously to a finite melting temperature which in the present consideration is fixed at $T_m/T_c = 0.35$, that is, Eq (23) should properly intercept the liquid branch AOB at point J where $T_m/T_c = 0.35$. Consequently the only way out of the deadlock is to suppose that the energy bonds W_{liq} of an undercooled melt, provided it might be kept in metastable equilibrium even down at $T = 0$ where $\theta = 1$, are averagely weaker than those in the corresponding solid phase, i.e. $W_{\text{liq}} < W_{\text{cryst}}$ is the necessary and sufficient condition to move down the curve AE to a new position $A'E'$ (cf. Figure 8).

Therefore as a first major conclusion which follows from the present consideration one may claim that the zero enthalpy H (at $T = 0$) of an undercooled melt must be higher than that of the respective crystal at $T = 0$. In Figure 8 the change in the Gibbs free energy $\Delta\Phi = N(\mu_{\text{liq}} - \mu_{\text{cryst}})$ is represented by the ordinata difference of the shaded area AJA'. A rough estimation gives in this case the value of $W_{\text{cryst}}/W_{\text{liq}} \approx 1.01$. A further consequence which immediately follows concerns the zero volume V°_{liq} of the undercooled melt. As far as a stronger attraction between the nearest neighbours inevitably leads to an additional contraction of the lattice, one should expect the zero volume of the undercooled melt V°_{liq} to exceed the volume of the crystal at $T = 0$. This conclusion is additionally supported by the fact that the extrapolation of excess densities of simple undercooled liquids at $T = 0$ appear to be nearly 3% lower than the packing density (0.7405) of f.c.c. or h.c.p. lattices of equal spheres.[30]

One is thus forced to imagine the state of an undercooled melt in internal equilibrium at $T \to 0$ as a perfectly ordered one ($S_{\text{conf}} = 0$ according to Nernst's theorem), but with lattice parameters which necessarily differ from those of the respective perfect crystal so that at $T \to 0\lambda$, $V_{\text{liq}} - V_{\text{cryst}} > 0$ and $\Delta H = H_{\text{liq}} - H_{\text{cryst}} > 0$. Consequently it is also evident that the description of melt to crystal transition should inevitably involve two different lattices: one for the liquid (from $T = 0$ up to T_{cr}) and a second, corresponding to the crystal (from $T = 0$ up to T_m). It appears difficult for the authors at present to suggest any reasonable picture of the nature of this fictive undercooled melt in internal equilibrium at $T = 0$, however, one should stress here, that the generality of this paradoxal result which, as discussed below, follows also from experimental thermodynamic evidence on typical glassforming melts is independent of the particular model employed in this paper.

In Figure 9A we show the differences in the chemical potential and in the enthalpy of the melt over that of the crystal, as calculated from Eqs. (22) and

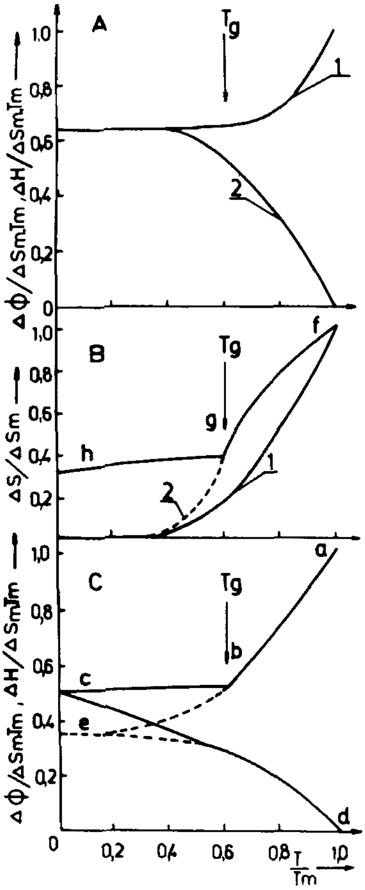

FIGURE 9 A–theoretically determined course of the differences in enthalpy–1, and in Gibbs free energy–2 of an undercooled melt over that of a crystal acc. to the present calculations. B–entropy difference between undercooled melt and crystal: experimental results for glycerol (Simon, 1931)–curve–fgh, extrapolated behaviour of an equilibrium melt under vitrification temperature Tg–2, and acc. to the present model–1. C–experimentally determined course of the thermodynamic functions for a typical glass-forming system (glycerol), as measured by Simon (1931)—full line, and extrapolated by himself for the case of an undercooled melt in internal equilibrium–dashed line.

(23) of the present model. The same is done in Figure 9B with the excess entropy of the melt over that of the crystal. On the same figure—Figure 9C are shown in dimensionless coordinates the classical investigations of Simon[31,32] over the temperature course of S, $\Delta\Phi$, ΔH which have been measured for a typical glassforming substance (Glycerol). Obviously there is a qualitative coincidence in the course of the respective thermodynamic

functions for both our model undercooled melt and for the extrapolated behaviour, proposed by Simon himself, of the fictive undercooled glycerol melt at $T \rightarrow 0$. The only qualitative difference concerns the shape of the $S(T)/T$ curve (cf. Figure 9*B*) which in the case of a simple model liquid is convex contrary to the concave form of the experimental S on T relationship which is typical for all glassforming melts. It is to be expected, as argued in Ref. 33, that this difference is caused by the more complex structure of typical glassforming melts in which effects of aggregation, polymerization, etc., are to be allowed for in the partition function.

Quantitatively the entropy difference for the calculated curve at T_m is only 25% of the respective experimental value which undoubtedly is a shortcoming of the employed model. Nevertheless, the qualitative behaviour of the thermodynamic properties of the system in the temperature interval $0 \leq T \leq T_m$ is correct and obeys strictly the requirements of the Third Law of Thermodynamics, that is, at $T \rightarrow 0$, $S \rightarrow 0$ and $\Delta H(T)$, $\Delta\Phi(T)$ have a common tangent parallel to the T/T_c axis.

It is generally known, that typical glassforming systems vitrify at $T = T_g \approx (0.5 \div 0.7)T_m I$, according to the Beaman–Kauzmann's rule $T_g/T_m \approx 2/3$. Vitrification is in fact a kinetic process whereby at $T = T_g$ the respective equilibrium structure of the melt is frozen in. Therefore under T_g the thermodynamic differences between glass and crystal are practically constant with varying T, as shown for glycerol in Figure 9B, C. Although it is not possible in the framework of a purely thermodynamic treatment to determine the temperature of vitrification T_g of our model liquid, it is evident, that if the Beaman–Kauzmann's rule is obeyed a considerably lower entropy should be frozen in a substance similar to Ar. The lower excess entropy frozen in at $T = T_g$ in the case of simple liquid, such as Ar, results in a higher energy differences (cf. Eq. 9A, C) between the hypothetical vitrified melt and the respective crystal which may be interpreted as thermodynamic explanation for the unsuccessful attempts to vitrify a genuine simple liquid, such as rare gases.

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