Contribution to the theory of melting

Hans-Otto Carmesin
New York University, Courant Institute, 251 Mercer Street, New York, New York 10012
and Chemistry Department, State University of New York at Albany, Albany, New York 12222
(Received 2 October 1989)

An ensemble of particles with repulsive Yukawa-type interaction is solved at high dimension. The fluid exhibits a new static singularity at density $(\rho/T)_\infty$, which characterizes the supercooled-fluid branch and the glass transition; at equilibrium the system crystallizes at $\rho<\rho_\infty$. Thus, a unified picture of crystallization, supercooled fluid, glass formation, and melting is discovered. The theory remains exact for arbitrary potential as $\rho\rightarrow\rho_\infty$ and agrees qualitatively with experiments.

I. INTRODUCTION

While there is much known about the theory of fluids[1] and solids[2] there is less known about the theory of melting.[3–5] Recently the crystallization of hard spheres[6,7] and of charged particles[8] has been solved at infinite dimension D, which corresponds to the Kirkwood[4] instability. These calculations have two main shortcomings, namely they have not been extended to finite D and the respective transitions are continuous. Here an ensemble of particles with Yukawa-type potential[9,10] is solved for $1\ll D\leq\infty$. The respective fluid exhibits a singularity at density $\rho=\rho_\infty<\infty$. The system cannot exist at this singularity, since at equilibrium it undergoes a discontinuous phase transition into a crystalline phase at $\rho_f^{\text{eq}}<\rho_\infty$. On the other hand, if equilibrium is prohibited, the system may follow the local equilibrium of the fluid as $\rho_f^{\text{eq}}<\rho\rightarrow\rho_\infty$, however, a fluid state at ρ_∞ requires infinite pressure. Nevertheless, the fluid at $\rho_f^{\text{eq}}<\rho<\rho_\infty$ or $T>T_\infty(\rho)$, is the supercooled fluid, which is thereby solved. As the temperature is lowered, the supercooled fluid becomes nonergodic at $T>T_\infty(\rho)$; this transition corresponds to the dynamic singularity in the mode-coupling theory.[11] As the temperature is lowered further, the number of phases per particle increases and diverges at $T_\infty(\rho)$. The Kauzmann paradox[12] occurs at $T<T_\infty$ and is repaired by quantum corrections. The analogue of the Kirkwood instability is the singularity at ρ_∞. Thus a unified theory of crystallization, supercooled fluid, glass formation, and melting is presented. As $D\rightarrow\infty$ ($\rho\neq\rho_\infty$, $\rho\rightarrow\rho_\infty$ afterwards), the singularity vanishes and the Kirkwood instability is recovered. The special case of the Yukawa potential is generalized to an arbitrary potential asymptotically as $\rho\rightarrow\rho_\infty$. The results are compared with experiment.

II. POTENTIAL

The Fourier transform $\tilde g(k)$ of the Mayer function $g(r)$ of the potential under investigation is

$$\tilde g(k):=\frac{\tilde f(k)}{1-\tau\tilde f(k)}=\frac{-\sigma}{k^2+\tau\sigma}\ . \tag{1a}$$

Here τ is a parameter and

$$\tilde f(k)=-\sigma(k)k^{-2}\ ,$$
$$\sigma(k)=(2\pi)^{D/2}\frac{q^2}{T}b^{1-D/2}J_{D/2-1}(b)\ , \tag{1b}$$
$$b=k\left[\frac{q^2}{T(D-2)}\right]^{1/(D-2)}$$

is the Fourier transform of the Mayer function of the Coulomb potential $\phi=[q^2/(D-2)]r^{2-D}$, see Appendix A. Note that for the special case $\tau=\rho$, $\tilde g$ is the screened Coulomb potential.[10,13,14] Here the analogue of the screening length reads $\lambda^{-2}=\tau\sigma(k=0)$. If $D\gg1$, the mean interparticle distance is large compared to λ at the density, at which the simple hypercubic crystal becomes stable, see the following. At such densities the corresponding potential can be interpreted easily, namely it is a Yukawa[9] potential

$$\phi_g(r)=\frac{q^2}{D-2}r^{2-D}e^{-r/\lambda}\ . \tag{2}$$

III. DEBYE CHAIN

The activity coefficient[1] γ can be calculated in terms of the Debye-chain expansion[10,13] for the case of uniform density

$$\ln\gamma=-\rho\tilde g(k=0)-\frac{\rho^2}{2}\int d^Dk\frac{\tilde g^3}{1-\rho\tilde g} \tag{3a}$$

plus integrals corresponding to topologically more complicated diagrams than rings. If

$$\rho<\frac{0.27}{|\tilde g(k=0)|}=0.27\tau\ , \tag{3b}$$

Eq. (3a) truncates after the second term for large D, see Appendix B. The integrand can be discussed in the form

$$\frac{\tilde g^3}{1-\rho\tilde g}=-\sigma^3k^{-6}\tau^{-2}(\tau+\rho)^{-1}(\tau^{-1}+\sigma/k^2)^{-2}\times[(\tau+\rho)^{-1}+\sigma/k^2]^{-1}\ . \tag{4a}$$

IV. SINGULARITIES

Singularities can occur most easily at the most negative value of σ/k^2, say, $\sigma(k_0)/k_0^2$, see Appendix C. Since the potential shall not be singular at $\rho=0$ and $k\neq 0$, the parameter τ is restricted by

$$\tau^{-1}+\sigma(k_0)/k_0^2>0 \quad \text{or} \quad \tau<-k_0^2/\sigma(k_0)\ . \tag{4b}$$

Note that $=k_0^2/\sigma(k_0)$ is proportional to T, see Appendix C

$$-k_0^2/\sigma(k_0)=T\hat{\tau}_m=\tau_m\ . \tag{4c}$$

Thus also τ must be proportional to T

$$\tau=T\hat{\tau}\ , \tag{4d}$$

thus the screening length λ is independent of T.

There can be a singularity at nonzero density, say, ρ_∞, at any temperature T

$$(\tau+\rho_\infty)^{-1}+\sigma(k_0)/k_0^2=0 \quad \text{or} \quad \rho_\infty=T(\hat{\tau}_m-\hat{\tau})\ . \tag{5a}$$

At given density this singularity occurs at the temperature

$$T_\infty=\rho(\hat{\tau}_m-\hat{\tau})^{-1}\ , \tag{5b}$$

while it occurs at constant ratio

$$(\rho/T)_\infty=\hat{\tau}_m-\hat{\tau}\ . \tag{5c}$$

There is no real system at the singularity since either at $\rho<\rho_\infty$ the system crystallizes, or if the system remains a uniform fluid, it requires infinite pressure (see the following) to have $\rho=\rho_\infty$. Thus the singularity of the uniform fluid is fictive. At $\rho<\rho_\infty$ the integral in Eq. (3a) can be performed with the saddle-point method, see Appendix D, and reads up to corrections in $1/D$

$$\ln\gamma=\rho/\tau+{}^*\rho^2({}^*\tau+{}^*\rho)^{-1/2}(1-{}^*\rho)^{-1/2}\,{}^*\tau_m^{1/2}\Omega_D\ , \tag{6}$$

where

$${}^*\rho=\rho/\rho_\infty,\quad {}^*\tau=\tau/\rho_\infty,\quad {}^*\tau_m=\tau_m/\rho_\infty\ ,$$

$$\Omega_D=4.982D^{-7/6}(2e\pi^2)^{b/2}\,{}^*\tau_m^{1/2}\ .$$

Thus here first $\rho\to\rho_\infty$ and afterwards $D\to\infty$ is performed, which is the physical order of limits. In the opposite order of limits the fictive singularity vanishes at $D=\infty$, $\ln\gamma=\rho/\tau$; the second virial coefficient remains as in the Kirkwood instability.[5,7]

Three conditions have to be fulfilled if ρ_∞ shall exist, namely Eq. (3b) $\rho<0.27\tau$, Eq. (4c) $\tau<\tau_m$ and Eq. (5a) $\rho_\infty=\tau_m-\tau$. These conditions are fulfilled if

$$\frac{1}{1.27}\tau_m<\tau<\tau_m\ . \tag{7}$$

V. THERMODYNAMICS NEAR THE SINGULARITY

The following analysis concentrates on the vicinity of ρ_∞, $\rho\approx\rho_\infty$ and is performed at leading order in $\tilde{\rho}$, where $\ln\gamma$ takes the form

$$\ln\gamma=\rho/\tau+\tilde{\rho}^{-1/2}\Omega_D\ ,$$

where

$$\tilde{\rho}=1-{}^*\rho=1-T_\infty/T\approx T/T_\infty-1\ . \tag{8}$$

Pressure P_f and chemical potential μ_f of the fluid phase follow from the activity coefficient,[10] and read

$$P_f/T=\left[1+\frac{\rho}{2\tau}\right]\rho+\rho\tilde{\rho}^{-1/2}\Omega_D+\rho(\tilde{\rho}^{1/2}-1)2\Omega_D\ ,$$
$$\mu_f/T=\ln\rho+\rho/\tau+\tilde{\rho}^{-1/2}\Omega_D-\frac{D}{2}\ln(MT)\ ; \tag{9}$$

the compressibility is

$$\kappa_f=-\frac{1}{V}\frac{dV}{dP}=2\rho^{-1}\Omega_D^{-1}\tilde{\rho}^{3/2}\ ,$$

the free energy per particle is

$$f_f/T=\ln\rho+\frac{\rho}{2\tau}-D/2\ln(MT)-1-2\Omega_D(\tilde{\rho}^{1/2}-1)\ ,$$

the entropy per particle is

$$\sigma_f=-\ln\rho+D/2\ln(MT)+D/2-2\Omega_D+\Omega_D\tilde{\rho}^{-1/2}\ ,$$

and the specific heat per particle at fixed ρ is

$$c_f=D/2-\Omega_D/2\tilde{\rho}^{-3/2}\ ,$$

where M is the mass of the particle divided by the square of Planck's constant $\hbar$.

VI. SIMPLE HYPERCUBIC LATTICE

In order to allow the ensemble to exhibit nonuniform density, the special case of a simple hypercubic lattice is considered. The lattice is described crudely but sufficiently in the harmonic approximation at high temperature[6] and at leading order in $1/D$. The Helmholtz free energy reads

$$F_{hc}/N=\epsilon_0-DT\ln T+DT\ln h\omega$$

where

$$\epsilon_0=q^2\rho e^{-r_0/\lambda},\quad r_0^{-D}=\rho\ ,$$
$$h\omega=\left[\frac{2q^2\rho}{MD}\right]^{1/2}\frac{r_0}{\lambda}e^{-2r_0/\lambda}\ , \tag{10}$$

since $r_0/\lambda\gg D$.

The chemical potential $\mu_{hc}=dF/dN$ reads

$$\mu_{hc}/T=-D\ln T+D\ln q+\frac{D}{2}\ln\rho-\frac{D}{2}\ln M-\frac{D^2}{4} \tag{11a}$$

and the pressure is

$$P_{hc}/T=\rho\frac{r_0}{\lambda}\frac{1}{2}\ . \tag{11b}$$

At $D=\infty$ the crystal can be described in the framework of the Kirkwood transition[7] and exists at $\rho\geq\rho_\infty$.

VII. PHASE EQUILIBRIUM

At phase equilibrium the respective pressures and chemical potentials must be equal. At leading order the respective chemical potentials read at the same pressure P,

$$\mu_f/T = P/T\frac{1}{\rho_\infty} - \frac{D}{2}\ln(MT) ,$$
$$\mu_{hc}/T = D/2\ln(P/T) + D\ln\left[\frac{q}{T\sqrt{M}}\right] . \tag{12}$$

Since μ_f grows linearly and μ_{hc} logarithmically with P, the system is fluid at low and crystalline at high pressure. At high dimension the respective quantities at phase equilibrium read

$$P_{\mathrm{eq}}/T = \frac{D}{2}\rho_\infty\left[\frac{q^2}{T}D\rho_\infty\right] ,$$
$$\mu_{\mathrm{eq}}/T = \frac{D}{2}\ln\left[\frac{q^2}{T}D\rho_\infty\frac{1}{MT}\right] ,$$
$$\rho_{hc}^{\mathrm{eq}} = \rho_\infty\frac{\lambda}{r_0}D\ln\left[\frac{q^2}{T}D\rho_\infty\right] , \tag{13}$$
$$\tilde{\rho}_{\mathrm{eq}} = \left[\frac{D}{2\Omega_D}\ln\left[\frac{q^2}{T}D\rho_\infty\right]\right]^{-2} .$$

Since $\lambda \approx e^{-D/4}$, if e.g., $q^2/T \approx 1$ then the mean distance between neighboring particles is larger in the crystal than in the fluid by the factor $e^{1/4}$. On the other hand, the compressibility vanishes in the fluid phase at ρ_∞, while it is proportional to $1/\rho$ in the crystal. The possibility of a Wigner[15] crystal is discussed elsewhere.[8]

VIII. LOCAL EQUILIBRIUM

The phase diagram of the system is given in Fig. 1. Since the kinetics can be made extremely slow at low temperature, the system can be fixed in states of local equilibrium. While the existence of the fluid equilibrium states (feq) is proven already, the existence of the fluid local equilibrium states (fleq) is not yet proven and will be assumed in the following. Since $P_{\mathrm{eq}}(T)$ decreases as T decreases, a fluid state at fixed pressure, which is at equilibrium at high temperature $[P < P_{\mathrm{eq}}(T)]$ may be at local equilibrium at low temperature $[P > P_{\mathrm{eq}}(T)]$. Thus the fluid at local equilibrium can be identified at least approximately with a supercooled fluid. The fleq state will now be investigated in more detail.

IX. CORRELATION FUNCTION

The Fourier transform of the potential of mean force[1] reads[10] $\tilde{w} = -\tilde{g}/(1-\rho\tilde{g})$. The inverse transform can be calculated with the saddle-point method and reads

$$w(r) = (2\pi)^{(1-D)/2}(\tau+\rho)^{-1/2}\tilde{\rho}^{-1/2} \times \rho_\infty^{-1/2}k_0^{D-4}(k_0 r)^{-D/2+1}J_{D/2-1}(k_0 r) . \tag{14}$$

Thus the two-particle correlation function

$$g_2(r) = (\text{normalization constant})\exp[-w(r)/T]$$

oscillates with period $k_0^{-1} \approx 2/D$, and the maxima decay like $\exp(-r^{(1-D)/2})$ and diverge like $\exp(\tilde{\rho}^{-1/2})$.

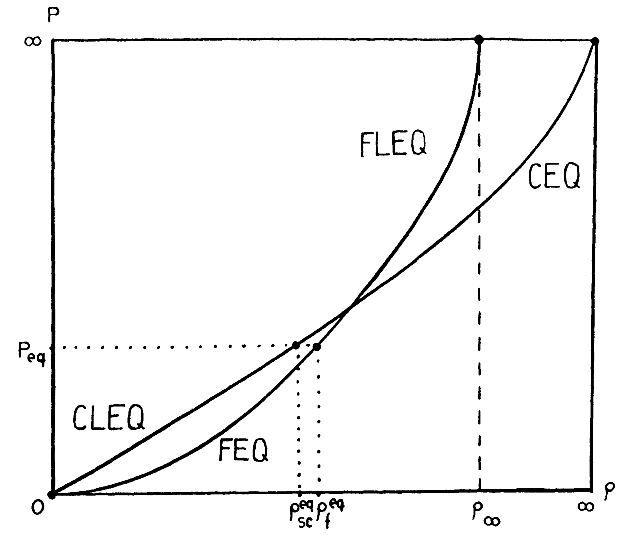

FIG. 1. Phase diagram in the ρ-P plane. Only one crystal structure is assumed for simplicity. The four possible branches are fluid in equilibrium (feq), fluid in local equilibrium (fleq), crystal in equilibrium (ceq) and crystal in local equilibrium (cleq).

X. KAUZMANN PARADOX (REF. 12)

At sufficiently low temperature, say, T_{Kauz}, the entropy σ_f [Eq. (9)] is zero. T_{Kauz} can be expressed as a function of ρ and $\tilde{\rho}$,

$$T_{\mathrm{Kauz}} = \rho^{2/D}\frac{1}{eM}\exp\left[\frac{2}{D}\Omega_D(2-\tilde{\rho}^{-1/2})\right] . \tag{15}$$

Since in experiments the pressure remains finite, mostly constant, $\tilde{\rho}$ is approximately constant and ρ decreases approximately proportional to T, see P_f Eq. (9). If $D > 2$, the change in ρ does not remove T_{Kauz}. Due to the exponential in Eq. (15), the Kauzmann temperature T_{Kauz} is zero at infinite dimension, but it is nonzero at $3 \le D < \infty$. Note that T_{Kauz} is reduced near ρ_∞. The Kauzmann paradox motivates the investigation of quantum corrections to the equation of state.

XI. QUANTUM CORRECTIONS

The free energy can be written as an expansion in $\hbar$. In this expansion, the leading correction to the classical free energy per particle reads[16]

$$f_{qm} = T^{-2}M^{-1}/24\langle(d\phi_g/dr)^2\rangle . \tag{16a}$$

Let us consider the forces $F_{ij} = -d\phi_g/dr(r_{ij})$. At states at which the quantum corrections become relevant, the solid phase virial theorem[17] is a sufficient approximation,

$$\sum_{i,j} r_{ij}F_{ij} = PV . \tag{16b}$$

At high dimension $r_0 \gg \lambda$ and thus only the interaction of immediate neighbors contributes significantly. At crude but sufficient approximation, the mean distance is

$\tau_0=\rho^{-1/D}$ and the number of immediate neighbors is D, thus

$$F_{ij}=2P\rho^{-1}D^{-1} . \tag{16c}$$

Inserting into Eq. (16a) yields

$$f_{qm}=T^{-2}M^{-1}P^2\rho^{-2}D^{-2}/6 . \tag{16d}$$

A. Small corrections

If the corrections are sufficiently small $P=P_f$ [Eq. (9)] can be inserted into Eq. (16d), thus at leading order in $\tilde{\rho}$,

$$f_{qm}=\phi\tilde{\rho}^{-1}, \quad \text{where } \phi=\Omega_D^2 D^{-2}M^{-1}/6 ,$$

$$\sigma_{qm}=\phi\tilde{\rho}^{-2}T^{-1} \tag{16e}$$

$$c_{qm}=-2\phi\tilde{\rho}^{-3}T^{-1}, \quad P_{qm}=\phi\rho\tilde{\rho}^{-2} .$$

This approximation is valid for $P_f \gg P_{qm}$, or

$$T\gg\Omega_D D^{-2}M^{-1}\tilde{\rho}^{-3/2}/6 . \tag{16f}$$

B. Large corrections

Since $P=\rho^2 df/d\rho$ and $f=f_f+f_{qm}$, Eq. (16d) takes the form

$$f=f_f+T^{-2}M^{-1}D^{-2}/6\rho^{-2}\left[\rho^2\frac{df_f}{d\rho}+\rho^2\frac{df_{qm}}{d\rho}\right]^2 . \tag{17a}$$

Inserting $P_f=\rho^2 df_f/d\rho$ and $f-f_f=f_{qm}$ and considering the vicinity of the singularity $P_f\approx T\rho\Omega_D\tilde{\rho}^{-1/2}$ yields the differential equation

$$\sqrt{f_{qm}}=A\tilde{\rho}^{-1/2}+B\frac{df_{qm}}{d\rho} ,$$

with

$$A=D^{-1}\Omega_D 6^{-1/2}$$

and

$$B=T^{-1}M^{-1/2}D^{-1}6^{-1/2}\rho . \tag{17b}$$

Only qualitative features of the solution f_{qm} of the preceding differential equation will be derived. Consider f_{qm} as a function of $\tilde{\rho}$, $\rho\approx$const, then

$$\sqrt{f_{qm}(\tilde{\rho})}=A\tilde{\rho}^{-1/2}-B/\rho_\infty\frac{df_{qm}}{d\tilde{\rho}} . \tag{17c}$$

Due to Eq. (16f); the construction of f_{qm} can be started at sufficiently large $\tilde{\rho}$ with Eqs. (16e). These approximate solution Eqs. (16e) can be inserted into the differential Eq. (17c) and thus increases the quantum correction. The increased approximate solution can again be inserted into Eq. (17c) and so forth. By this iteration the quantum corrections grow monotonically. Therefore the approximate solution Eqs. (16e) will be investigated further.

XII. REPARATION OF THE KAUZMANN PARADOX

The corrected entropy reads

$$\sigma=\sigma_f+\sigma_{qm}=-\ln\rho+\frac{D}{2}\ln MT+\frac{D}{2} -2\Omega_D+\Omega_D\tilde{\rho}^{-1/2}+\phi\tilde{\rho}^{-2}T^{-1} . \tag{18a}$$

The function $\sigma(T)$ diverges at infinite and zero temperature and exhibits a minimum at say, $T_{\min}$. At sufficiently high D or small $\tilde{\rho}$, $\sigma(T_{\min})>0$ and the Kauzmann paradox is thus repaired by the term due to the singularity, namely $\phi\tilde{\rho}^{-2}T^{-1}$.

For small $\tilde{\rho}$

$$T_{\min}/T_\infty-1=(\tfrac{2}{3}M^{-1}T^{-1}\Omega_D^2 D^{-3})^{1/3} ,$$
$$\sigma-\sigma_{\min}=\sigma_{qm}(1-\tilde{\rho}^2\tilde{\rho}_{\min}^{-2}) . \tag{18b}$$

XIII. IRREVERSIBILITY

Consider a decrease of temperature dT. Thereby occurs a decrease of heat dQ.

$$dQ\le T\,dS . \tag{19a}$$

The process is reversible if the equality holds. Thus if $d\sigma/dT<0$ only the inequality holds, thus that process is irreversible. Denote by T_{irrev} the highest temperature, at which an irreversible change of states occurs at T decreases. Thus.

$$T_{\min}\le T_{\text{irrev}} . \tag{19b}$$

An irreversible state exhibits a nonzero configurational entropy σ_{conf}, which is the logarithm of the number of its phases. This entropy σ_{conf} causes the increase of entropy at decreasing temperature. Since in reversible thermodynamics $d\sigma/dT>0$,

$$\sigma_{\text{conf}}\ge\sigma-\sigma_{\min} \quad \text{at } T\le T_{\min} . \tag{19c}$$

At $T\le T_{\text{irrev}}$ several states exist, thus the system is nonergodic, the longest relaxation time diverges, thus T_{irrev} marks a dynamic singularity[11] of the fluid and thereby a glass transition,[18] say, $G1$. As T decreases further below T_{irrev}, the number of phases grows continuously, Eqs. (16e), and diverges at T_∞. Thus in principle there occurs a transition of zeroth order, which is fictive, however, since at T_∞ the pressure diverges. Nevertheless it is conceivable that another glass phase occurs, say, G_∞. Since at T_∞ (or ρ_∞) $\tilde{g}(k_0)=1/\rho$, see Eq. (4a), that singularity is the analogue of the Kirkwood instability. Thus, if a transition into a phase G_∞ exists, it is the analogue of the Kirkwood transition.[5,7] Note that in the irreversible regime, the specific heats calculated in this paper are upper bounds of the true specific heats due to Eq. (19a).

XIV. MEAN FIELD THEORY

Consider the Fourier transform of the Mayer function of any two-particle potential say, $\tilde{h}(k)$. Then the activity coefficient can still be written in the form of Eq. (3a). In the following it will be assumed that the topologically more complicated diagrams than rings will neither compensate the singularity at ρ_∞, nor cause another singularity at $\rho<\rho_\infty$. Then the analysis of the singularity at ρ_∞ is asymptotically ($\tilde\rho\to 0$) exact. If truncation of [Eq. (3a)] is possible for $\tilde h(k)$ at sufficiently high dimension, then this high dimensional case can be regarded as the mean-field theory, which corresponds to the asymptotically ($\tilde\rho\to 0$) exact calculation.

The singularity occurs at [Eq. (3a)]

$$\rho_\infty(T)=\tilde h(k_0,T)^{-1}\ , \tag{20a}$$

where at k_0, $\tilde h$ is minimal and negative; potentials without such k_0 will not be discussed here. The integral in Eq. (3a) can still be performed by the saddle point method and is still proportional $\tilde\rho^{-1/2}$, see Appendix D, say, $\omega_D\tilde\rho^{-1/2}$.

Therefrom follows the thermodynamics of the supercooled fluid in mean-field theory (MFT). Here the asymptotic case $\tilde\rho\to 0$ is considered, and $\tilde h(k=0)=\hat h$ is abbreviated.

$$\begin{aligned}
P_f/T&=(1+\rho\hat h/2)\rho+\omega_D\rho\tilde\rho^{-1/2}+2\omega_D(\tilde\rho^{1/2}-1)\ ,\\
\mu_f/T&=\ln\rho+\hat h\rho+\omega_D\tilde\rho^{-1/2}-\frac{D}{2}\ln(MT)\ ,\\
\kappa_f&=2\omega_D^{-1}\rho^{-1}\tilde\rho^{3/2}\ ,\\
f_f/T&=\ln\rho+\rho\hat h/2-\frac{D}{2}\ln(\mathrm{MT})-1-2\omega_D(\tilde\rho^{1/2}-1)\ ,\\
\sigma_f&=-\ln\rho-\rho\hat h/2+\frac{D}{2}\ln(\mathrm{MT})-\frac{T}{2}\frac{d\hat h}{dT}\rho+\frac{D}{2}\\
&\quad-2\omega_D+\omega_D T\rho\rho_\infty^{-2}\frac{d\rho_\infty}{dT}\tilde\rho^{-1/2}\ ,\\
c_f&=-T\frac{d\hat h}{dT}\rho+\frac{D}{2}-T^2/2\frac{d^2\hat h}{dT^2}\rho\\
&\quad-\omega_D/2\left[T\rho\rho_\infty^{-2}\frac{d\rho_\infty}{dT}\right]^2\tilde\rho^{-3/2}\ .
\end{aligned} \tag{20b}$$

The Kauzmann paradox can be discussed analogously as it was done for the case of the Yukawa potential and so can the quantum corrections be discussed.

XV. COMPARISON WITH EXPERIMENT

Specific Heat (c). At $\tilde\rho\to 0$ the pressure reads $P=\omega_D T\rho\tilde\rho^{-1/2}$, thus at constant pressure $\tilde\rho^{-1/2}=P\omega_D^{-1}T^{-1}\rho^{-1}$, thus the specific heat reads as $\tilde\rho\to 0$ and at $P=$const,

$$\begin{aligned}
c&=\frac{D}{2}-T\frac{d\hat h}{dT}\rho-\frac{T^2}{2}\frac{d^2\hat h}{dT^2}\rho\\
&\quad-\tfrac{1}{2}P^3\omega_D^{-2}T^{-1}\rho^{-1}\rho_\infty^{-4}\left[\frac{d\rho_\infty}{dT}\right]^2 .
\end{aligned} \tag{21a}$$

It is conceivable, that $d\rho_\infty/dT$ does not compensate T^{-1}, and that $d^2\hat h/dT^2>0$. In this case the specific heat exhibits a maximum, as is observed[19] in glasses at relatively high temperature, which might correspond to the supercooled fluid or the first glass transition $G1$.

Thermal expansion: (α) As $\tilde\rho\to 0$ the pressure is given as above. That leads to a quadratic equation for ρ, which can be solved by

$$\rho_{1,2}=\tfrac{1}{2}P^2T^{-2}\omega_D^{-2}\rho_\infty^{-1}[1\pm(1+4P^{-2}T^2\omega_D^2\rho_\infty^2)^{1/2}]\ . \tag{21b}$$

Because of ω_D the second term in the root is large, thus $\rho\approx P\omega_D^{-1}T^{-1}$, thus

$$\alpha=\frac{1}{L}\frac{dL}{dT}=\rho\omega_0P^{-1}D^{-1}\ , \tag{21c}$$

where L is the length of the material. Experiments show,[19] that in glasses typically α is independent of temperature as is found here.

Compressibility: (κ) As $\tilde\rho\to 0$ the compressibility κ_f becomes a relatively small quantity in agreement with experiments (Ref. 19, p. 311) of glasses.

At constant pressure and as $\tilde\rho\to 0$ the compressibility reads

$$\kappa_f=2\omega_D^2T^3\rho^2P^{-3}\ . \tag{21d}$$

Thus $d\kappa_f/dP<0$ and $d\kappa_f/dT>0$, both in agreement with experiments on glasses (Ref. 19, p. 311).

A further comparison with experiment, especially with Eq. (14) is desirable.

ACKNOWLEDGMENTS

The work was partially supported by the Alexander von Humboldt Foundation. I thank K. Binder and K. Knorr for introducing me to the field of glasses, J. K. Percus for suggesting an investigation of charged particles, H. L. Frisch for introducing me to the statistical mechanics at high D, and M. Q. Zhang for interesting discussions.

APPENDIX A: FOURIER TRANSFORM OF COULOMB POTENTIAL

The Fourier transform of the Mayer function of the Coulomb potential reads after integration of angular space

$$\tilde f(k)=-\left[\frac{2\pi}{k^2}\right]^{D/2}\int_0^\infty[1-\exp(-Ab^{2-D})]\times b^{D/2}J_{D/2-1}(b)db\ , \tag{A1}$$

where

$$A=k^{2-D}\frac{q^2}{T(D-2)}\ .$$

Integration by parts yields

$$\tilde f=\left[\frac{2\pi}{k^2}\right]^{D/2}A(2-D)\times\int_0^\infty\exp(-Ab^{2-D})b^{1-D/2}J_{D/2}(b)db\ . \tag{A2}$$

Another integration by parts yields

$$\tilde{f}=-\left[\frac{2\pi}{k^2}\right]^{D/2} A^2(2-D)^2 \times \int_0^\infty \exp(-Ab^{2-D})b^{2-(3/2)D}J_{D/2-1}(b)db \ . \quad \text{(A3)}$$

The integral can be performed with the saddle-point method and thus reads

$$\tilde{f}(k)=\sigma(k)/k^2[1+O(1/D)] \ ,$$
$$\sigma(k)=(2\pi)^{D/2}\frac{q^2}{T}b^{1-D/2}J_{D/2-1}(b) \ , \quad \text{(A4)}$$
$$b=kR_{\text{eff}}, \quad R_{\text{eff}}=\left[\frac{q^2}{T(D-2)}\right]^{1/(D-2)} \ .$$

APPENDIX B: TRUNCATION OF THE EQUATION OF STATE

In order to prove the truncation of the equation of state, it is sufficient to show[20,21] that the ratio of the cluster integral of the single loop diagram with one root divided by the cluster integral of any topologically more complicated simply connected irreducible diagram with one root and the same number of particles diverges, as D diverges.

1. The Cluster Integrals P and Q

The topologically more complicated diagram will contain a point, one say, which is connected with at least three particles, and thus with at least three branches. Each of these branches will eventually and at the first time reach a point not equal to one, which is connected to at least three branches. Say these points of two of the branches are point M and point $m+l$.

Let the positions of points 1, M and $m+l$ be arbitrary and fixed and let the distance between 1 and M be shorter or equal to that between 1 and $m+l$. Let there be $m-1$ more particles on the branch between 1 and M and $l-1$ more particles on the branch between 1 and $m+1$.

Thus the corresponding cluster integral I will be proportional to

$$P=\int g_{1,2}g_{2,3}\cdots g_{m-1,M}d2d3\cdots d_{m-1} \times \int g_{1,m+1}\cdots g_{1,m+l}d_{m+1}d_{m+2}\cdots d_{m+l} \ , \quad \text{(B1)}$$

namely $I=cP$.

Let us now modify the cluster by bringing the $l-1$ particles of the branch connecting 1 and $l+m$ into the branch connecting 1 and M, and let us thereby annihilate the branch between 1 and $l+m$ completely. Since the rest of the cluster remains identical, the cluster integral J of the modified cluster reads

$$J=cQ \ ,$$
$$Q=\int g_{1,2}g_{2,3}\cdots g_{m+l-2,M}d2\,d3\cdots d_{m+l-2} \ . \quad \text{(B2)}$$

Thus it is sufficient to prove

$$\lim_{D\to\infty} Q/P=\infty \ . \quad \text{(B3)}$$

2. Zero distance

In order to calculate Q, let us write it in terms of Fourier transforms

$$Q=\int e^{i\mathbf{k}(\mathbf{r}_1-\mathbf{r}_M)}\tilde{g}(\mathbf{k})^{l+m-1}d^Dk(2\pi)^{-D} \ . \quad \text{(B4)}$$

Consider polar coordinates and let θ be the angle between $\mathbf{k}$ and $(\mathbf{r}_1-\mathbf{r}_M)$

$$Q=\int_0^\infty\int_0^\pi \sin^{D-2}\theta e^{ik|r_2-r_M|\cos\theta}\tilde{g}(k)^{l+m-1}k^{D-1}d\theta\, dkS_{D-1}(2\pi)^{-D} \ ,$$

or for the special case r_1-r_M

$$Q(r_1=r_M)=\int_0^\infty \tilde{g}(k)^{l+m-1}k^{D-1}dkS_D(2\pi)^{-D}=\hat{Q} \ . \quad \text{(B5)}$$

Analogously P reads for $r_1-r_M=r_{l+m}$

$$P(r_1=r_M=r_{l+M})=\int_0^\infty \tilde{g}^{\,l}(k)k^{D-1}dk\int_0^\infty \tilde{g}^{\,m}(k)k^{D-1}dkS_D^2(2\pi)^{-2D}=\hat{P} \ . \quad \text{(B6)}$$

We now investigate $\lim_{D\to\infty}Q/P$ for this special case. The integrals will be calculated by the saddle point method. The case $l=1$ will be discussed separately.

a. Location of the maximum

Consider the integral $I_l=\int_0^\infty \tilde{g}^{\,l}(k)k^{D-1}dk$, the derivative of its integrand reads

$$(D-1-2l)k^{D-2-sl}\sigma^l+l\frac{d\sigma}{dk}\sigma^{l-1}k^{D-1-2l} \ . \quad \text{(B7)}$$

Thus the maximum is determined by

$$(D-1-2l)J_{D/2-1}(k)=lkJ_{D/2}(k) \ . \quad \text{(B8)}$$

This equation will be solved at large D with (since $k<D/2$)

$$J_{D/2}(k)=\exp\left[\frac{D}{2}\tanh\alpha-\frac{D}{2}\alpha\right]\Big/(D\pi\tanh\alpha)^{1/2}\left[1+O\left[\frac{1}{D}\right]\right], \tag{B9}$$

where $D/2k=\cosh\alpha$.

Thus

$$k=\frac{1}{l}(D-1-2l)J_{D/2-1}(k)/J_{D/2}(k)\,, \tag{B10a}$$

or neglecting the correction $O(1/D)$, and approximating $D/k\approx e^{\alpha}$ and $\tanh\alpha\approx 1$,

$$k=\frac{1}{l}(D-1-2l)\exp\left[-1+\ln\frac{D}{k}+1\right],$$

or (B10b)

$$k_{\max}=l^{-1/2}D^{1/2}(D-1-2l)^{1/2}\,.$$

For the following it is sufficient to have an upper bound for $k_{\max}$, say

$$k_{\max}<l^{-1/2}D\,. \tag{B10c}$$

[Note that for the case $l=4$, Eq. (B10b) can be obtained without any approximation from a recursion relation for Bessel functions.]

b. Integration

It can be verified, that the width of the maximum is of order one. It can also be verified, that

$$\tilde{g}(k_{\max})=S_De^{-D/2}D^{D/2}k_{\max}^{-D/2}$$

times less singular terms . (B11)

Inserting yields for the integral

$$I_l=\left[e^{-1+l/2}\left[\frac{2\pi}{D}\right]^{l-1}e\right]^{D/2} \tag{B12}$$

For the case $l=2$ the integral can be evaluated exactly. (Note that the smaller l, the worse the approximation for $k_{\max}$.) Per definition

$$I_2=\int g^2(r)d^Dr=\text{ Fourier transform }\{g^2(r)\}|_{k=0}\,. \tag{B13a}$$

If

$$g_{D,\lambda}(r)=e^{-r/\lambda_D}r^{2-D}\,,$$

then (B13b)

$$g^2_{D,\lambda_D}(r)=g_{2D-2,\lambda_D/2}(r)\,.$$

Therefore if

$$\tilde{g}_D(k)=\frac{\sigma_D(k)}{k^2+\tau_D\sigma_D(k)}\,,$$

then

$$\tilde{g}_{2D-2}(k)=\frac{\sigma_{2D-2}(k)}{k^2+\tau_{2D-2}\sigma_{2D-2}(k)}\,,$$

with

$$\tau_{2D-2}=\tau_DS_D/S_{2D-2}\,. \tag{B13c}$$

Thus up to less singular factors,

$$\tilde{g}_{2D-2}(k=0)=S_{2D}/S_D=I_2\,. \tag{B13d}$$

c. Ratio

The ratio $\hat{Q}/\hat{P}$ from Eqs. (B5) and (B6) reads for $l,m\geq 3$

$$\hat{Q}/\hat{P}=I_{l+m-1}/(I_lI_m)\,,$$

or (B14)

$$\hat{Q}/\hat{P}=[e(l+m-1)^{l/2+m/2-3/2}/(l^{l/2-1}m^{m/2-1})]^{D/2}\,.$$

It can easily be verified, that the term in square brackets is larger than one.

For the case $m=2, l\geq 3$ the ratio reads

$$\hat{Q}/\hat{P}=\{l^{l/2-1}/[(l+1)^{l/2-1/2}4]\}^{D/2}\,. \tag{B15}$$

The term in curly brackets is larger than one. For the case $l=m=2$ the ratio reads

$$\hat{Q}/\hat{P}=(512/e)^{D/2}\,. \tag{B16}$$

Thus for zero distance the truncation is proven for $l,m\geq 2$.

3. Finite Distance

a. Monotonicity

For the case $l\geq 2$, the rest follows from monotonicity. Consider the integral

$$I(l,r)=\int e^{i\mathbf{k}\cdot\mathbf{r}}\tilde{g}(\mathbf{k})^l d^Dk(2\pi)^{-D}\,. \tag{B17}$$

If we denote $\mathbf{a}=\mathbf{r}_1-\mathbf{r}_M$ and $\mathbf{b}=\mathbf{r}_1-\mathbf{r}_{m+l}$ then the ratio Q/P reads

$$Q/P=I(l+m-1,a)/[I(l,a)I(m,b)]\,, \tag{B18}$$

where without loss of generality we choose $b\geq 0$. Since $I(l,r)$ must decay monotonically with r, we find $I(m,b)\leq I(m,a)$, thus

$$Q/P\geq I(l+m-1,a)/[I(l,a)I(m,a)]\,. \tag{B19}$$

Now $I(l,a)$ has the property, that the fewer particles l in the chain, the faster decays $I(l,a)$ with distance a, i.e., the smaller

$$I(l,a)/(l,0)\,. \tag{B20}$$

Thus

$$I(l,a)/I(l,0)<I(l+m-1,a)/I(l+m-1,0)\,. \tag{B21}$$

Since $I(m,a)/I(m,0)\leq 1$ we find

$$I(l,a)I(m,a)/[I(l,0)I(m,0)] < I(l+m-1,a)/I(l+m-1,0)\ ,$$

or

$$I(l+m-1,0)/[I(l,0)I(m,0)] < I(l+m-1,a)/[I(l,a)I(m,a)]\ ,$$

or

$$\hat{Q}/\hat{P} < Q/P\ . \tag{B22}$$

b. The case $l=1$

Let us first estimate the order of magnitude of the distance between two particles that contributes significantly to their cluster integral. Consider the integral

$$N_g=\int g(r)d^Dr=\tilde{g}(k=0)=1/\tau=O(1)\ . \tag{B23}$$

If the particles were hard spheres of diameter d and $h(r)$ the corresponding Mayer function, then the corresponding integral reads

$$N_h=\int h(r)d^Dr=S_D/Dd^D\approx(d^2 2\pi e/D)^{D/2}\ . \tag{B24}$$

The requirement $N_h=N_g$ yields

$$d\approx\sqrt{D/2\pi e}\ . \tag{B25}$$

Thus we conclude, that the distance between two particles is large compared to one.

If an additional bond is added to any given diagram, the integrand is multiplied by $g(r)$. Since $|g(r)|\leq 1$, and for $r>1$, $|g(r)|\leq O(r^{-D+2})$, and since $r=O(\sqrt{D})$, the ratio of the cluster integral of the diagram with the additional bond divided by the cluster integral without the additional bond vanishes as $D\to\infty$. Altogether the truncation of the equation of state is proven.

APPENDIX C: MINIMUM OF σk^{-2}

From Eq. (16) follows

$$\sigma(k)=D[R^D(2\pi)^{D/2}(kR)^{-D/2}J_{D/2}(kR)]\times\left[1+O\left[\frac{1}{D}\right]\right]\ , \tag{C1}$$

with

$$R=\left[\frac{q^2}{T(D-2)}\right]^{1/(D-2)}\ .$$

The first term in square brackets is the Fourier transform of the Mayer function of a hard sphere in D space of radius R.

Thus the minimum occurs[7] at

$$k_0R=D/2+O(D^{1/3})\ , \tag{C2}$$

and its value is at leading order in D

$$\sigma(k_0)k_0^{-2}=\frac{q^2}{T}\left[\frac{4\pi}{D}\right]^{D/2}\frac{0.7}{e}\times\exp[-z_0(D/2)^{1/3}](4/D)^{2/3}\ , \tag{C3}$$

with $z_0=1.8558$.

APPENDIX D: INTEGRATION OF THE GEOMETRIC SERIES

The integral

$$I=\int d^Dk\frac{\tilde{g}^3(b)}{1-\rho\tilde{g}(b)}\ ,$$

with

$$k^D=b^D\frac{TD}{q^2}\ , \tag{D1}$$

will be calculated for $\rho\to\rho_\infty$. In this case the relevant contribution is the singular contribution. The singular contribution is the integral between the first two zeros of σ, b_1 and b_2 say. The singular contribution will be calculated by the saddle-point method, thus slowly changing factors can be taken at the value of the saddle point, say, b_0.

Inserting for $\tilde{g}$ and substitution of k by b yields

$$I=-\frac{TD}{q^2}S_D\sigma(b_0)b_0^{D-7}\tau^{-2}(\tau+\rho)^{-1}(\tau^{-1}-\tau_m^{-1})^{-2}K\ , \tag{D2}$$

where

$$K=\int_{b_1}^{b_2}\frac{1}{\omega+\sigma/b^2}db,\quad \omega=(\tau+\rho)^{-1}\ ,$$

The maximum of the integrand is determined by $b\sigma'=2\sigma$, or by

$$-J_{D/2}b^{-D/2}=2b^{1-D/2}J_{D/2-1}b^{-2}\ . \tag{D3}$$

Since the relative maxima of $J_{D/2}b^{-D/2}$ are of order S_D, and since $O(S_{D-2})=O(DS_D)$, and since $b=O(D)$, the right-hand side is negligible compared to the left-hand side. Thus b_0 is given by the zero of $J_{D/2}$, or by the first minimum of σ.

Let us now calculate the width of the saddle. Denote

$$\mathcal{L}=-\ln(\omega+\sigma/b^2)\ . \tag{D4}$$

Thus at $(\sigma'b=2\sigma)$ the saddle

$$\mathcal{L}''(b_0)=(\omega b^4+\sigma b^2)^{-1}(2\sigma-b^2\sigma'')\ . \tag{D5}$$

Let us now discuss σ'' at dimension D, say, σ_D''. Since σ_D is of the form

$$\sigma_D=cJ_{D/2-1}b^{1-D/2}\ ,$$

thus

$$\sigma_D''=c(J_{D/2+1}b^{1-D/2}-J_{D/2}b^{-D/2})\ . \tag{D6}$$

At b_0, the second term vanishes,

$$\sigma_D''(b_0)=cJ_{D/2+1}b^{1-D/2}=b^2\sigma_{D+4} . \quad \text{(D7)}$$

Since the loci of the zeros and the extrema of σ_{D+4} are the same as those of σ_D, and the absolute values of the extrema of σ_D are b^2 times as large as those of σ_{D+4}.

$$\sigma_{D+4}=-\sigma_D b^{-2} . \quad \text{(D8)}$$

Thus

$$\sigma_D''(b_0)=-\sigma_D(b_0) . \quad \text{(D9)}$$

Thus

$$\mathcal{L}''(b_0)=b_0^{-2}\sigma(b_0)(\omega+\sigma(b_0)/b_0^2) . \quad \text{(D10)}$$

From the saddle point integration

$$K=\sqrt{2\pi}[-\mathcal{L}''(b_0)]^{-1/2}[\omega+\sigma(b_0)/b_0^2]^{-1}$$

and therefrom follows

$$K=\sqrt{2\pi}[\omega+\sigma(b_0)/b_0^2]^{-1/2}|\sigma(b_0)|^{-1/2}b_0 , \quad \text{(D11)}$$

and therefrom Eq. (6).

[1]J. P. Hansen, *Theory of Simple Liquids* (Academic, London, 1986).

[2]C. Kittel, *Einfuehrung in die Festkoerperphysik* (Oldenbourgh, Muenchen, 1980).

[3]L. Onsager, Chem. Phys. **13**, 73 (1933).

[4]J. G. Kirkwood and E. Montroe, J. Chem. Phys. **3**, 300 (1935).

[5]J. G. Kirkwood, in *Phase Transformation in Solids,* edited by R. Smoluchwski, J. E. Mayer, and W. A. Weyl (Wiley, New York, 1951).

[6]D. Wyler, N. Rivier, and H. L. Frisch, Phys. Rev. A **36**, 2422 (1987).

[7]H. L. Frisch and J. K. Percus, Phys. Rev. A **35**, 4696 (1987).

[8]H.-O. Carmesin, H. L. Frisch, and J. K. Percus (to be published).

[9]N. Pistoor and K. Kremer, in *Dynamics of Disordered Materials,* edited by D. Richter, A. J. Dianoux, W. Petry, and J. Teixeira (Springer, Berlin, 1989).

[10]E. E. Salpeter, Ann. Phys. (N.Y.) **5**, 183 (1958).

[11]L. Sjoegren and W. Goetze, in *Dynamics of Disordered Materials,* edited by D. Richter, A. J. Dianoux, W. Petry, and J. Teixeira (Springer, Berlin, 1989).

[12]W. Kauzmann, Chem. Rev. **43**, 219 (1948).

[13]J. E. Mayer, J. Chem. Phys. **18**, 1426 (1950).

[14]P. Debye and E. Hueckel, Phys. Z **24**, 305 (1923).

[15]E. Wigner, Trans. Faraday Soc. **34**, 678 (1938).

[16]L. D. Landau and E. M. Lifschitz, *Lehrbuch der Theoretischen Physik V Teil I* (Akademie-Verlag, Berlin, 1979).

[17]W. G. Hoover, *Molecular Dynamics* (Springer, Berlin, 1986).

[18]J. Jaeckle, Rep. Prog. Phys. **49**, 171 (1986).

[19]N. P. Bansal and R. H. Doremus, *Handbook of Glass Properties* (Academic, New York, 1986).

[20]H. -O. Carmesin (unpublished).

[21]H.-O. Carmesin (unpublished).