

Dislocation-mediated melting: The one-component plasma limit

Leonid Burakovsky* and Dean L. Preston†

Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 13 March 2000; revised manuscript received 21 December 2000; published 25 May 2001)

The melting parameter Γ_m of a classical one-component plasma is estimated using a relation between the melting temperature, density, shear modulus, and a crystal coordination number that follows from our model of dislocation-mediated melting. We obtain $\Gamma_m = 172 \pm 35$, in good agreement with the results of numerous Monte Carlo calculations.

DOI: 10.1103/PhysRevE.63.067402

PACS number(s): 52.25.Kn, 52.65.-y, 61.72.Bb, 64.70.Dv

I. INTRODUCTION

The classical one-component plasma (OCP) is an idealized system of mobile ions of charge Ze , number density n , and temperature T , immersed in a neutralizing background of uniform charge density $-Zne$. The OCP is realized in nature only at the enormous densities occurring in white dwarfs and neutron stars. The thermodynamics of the classical OCP is completely described in terms of the dimensionless coupling parameter [1]

$$\Gamma = \frac{(Ze)^2}{ak_B T}, \quad (1)$$

where $a = (3/4\pi n)^{1/3}$ is the Wigner-Seitz radius. In the quantum regime, one more parameter, a or T , is needed to characterize the system. Melting of a classical OCP occurs at a fixed value Γ_m of the plasma coupling parameter. When $\Gamma > \Gamma_m$, an OCP is either a glass [2] or it has a bcc crystal structure, provided that it is subject to only hydrostatic stress. The evaluation of Γ_m for melting from the bcc structure has been the subject of extensive Monte Carlo (MC) calculations [3–16] employing the Ewald potential, which yields data pertinent to an infinite system from simulations using only a finite number of particles confined to a cubic computational cell with periodic boundary conditions. By fitting simple functional forms, guided by theory, to the measured excess potential energy per particle for both liquid and solid phases of the OCP, it is possible to obtain the Helmholtz free energy as a function of Γ . The intersection of the liquid and solid free-energy curves gives the value of the melting parameter Γ_m . In their pioneering study [3], Brush, Sahlin, and Teller observed melting in a 32-particle system at $\Gamma_m \approx 125$. Subsequently Hansen [4] and Pollock and Hansen [5] followed with an improved calculation and found $\Gamma_m = 155 \pm 10$. Van Horn [6] used the empirical Lindemann melting criterion to obtain $\Gamma_m = 170 \pm 10$. Other MC studies resulted in the following values of Γ_m : 144 [7], 168 ± 4 [8], 178 ± 1 [9], 180 ± 1 [10], 178 [11], 172 [12], and 173 [13]. Values of very similar magnitude have been obtained in MC simulations of a strongly coupled screened Coulomb (Yukawa) system in the limit of zero screening: 171 [14] and 171.8 [15]. Recent

path-integral MC simulations of the OCP [16] give $\Gamma_m = 175$. Hence, numerous MC studies suggest that $\Gamma_m \approx 170 - 180$ for the classical bcc OCP.

In this paper we calculate Γ_m using a melting relation obtained from our model of dislocation-mediated melting [17,18]. Before proceeding with the calculation of Γ_m , we briefly recapitulate the main ideas and assumptions of our melting model. As first proposed by Mott [19], dislocations are assumed to be the basic degrees of freedom underlying the melting transition. Dislocation interactions beyond a distance of order of the mean dislocation separation are assumed negligible because of screening, and steric interactions are ignored. Accordingly, dislocations are taken to be noninteracting and therefore uncorrelated, and are modeled as lines lying along the nearest-neighbor links of the lattice. The links coincide with the shortest perfect-dislocation Burgers vectors, which have magnitude b . The dislocation configurations (Brownian, self-avoiding, open, closed, etc.) are parametrized by a single parameter $q > 1$, in terms of which the mean dislocation length is given by $\langle L \rangle = 4qb/(q-1)$. In addition to q , the partition function depends on the temperature-dependent effective dislocation line tension, that is, the energy cost to create unit length of dislocation at temperature T . The effective line tension vanishes at the critical temperature $k_B T_{cr} = \sigma b / \ln(z-1)$. Here z is the coordination number of the lattice and σ , which we discuss in more detail below, is the ρ -dependent self-energy per unit length, ρ being the dislocation density. Dislocations proliferate as T_{cr} is approached from below, while at temperatures just above T_{cr} the partition function diverges, an indication that a new phase appears. So T_{cr} corresponds to a phase transition, namely melting, and we identify T_{cr} with the melting temperature T_m . A full defect theory of melting, a version of which is presently available [20], would have to include the effects of both dislocations and disclinations. In our model we ignore the effects of disclinations under the assumption that they will produce only small changes of the order of 10% to the melting temperature.

Crystal anisotropy was assumed to be a small correction to our model of dislocation-mediated melting. We recently reconsidered anisotropy and found that it introduces a correction to our melting relation which we estimate to be only 10%. Interestingly, the same correction factor to the melting temperature vanishes precisely when the crystal loses its structural stability, as expected. We also found that taking into account anisotropy explicitly in our melting relation

*Email address: BURAKOV@LANL.GOV

†Email address: DEAN@LANL.GOV

would lead to the $\xi^{0.5}$ behavior of the melting temperature for small ξ , consistent with Kleinert's finding of $T_m \sim \xi^{0.6}$ [20], as discussed in more detail below.

Under the assumption that dislocation strain fields are screened away at distances beyond the mean dislocation spacing [21], the self-energy per unit length in an anisotropic cubic crystal is

$$\sigma = \frac{1 - \nu(\hat{\mathbf{b}} \cdot \hat{\mathbf{l}})^2}{1 - \nu} \frac{Gb^2}{4\pi} \phi(c_{11}, c_{12}, c_{44}, \hat{\mathbf{b}}, \hat{\mathbf{l}}) \ln\left(\frac{\alpha R}{b}\right), \quad (2)$$

where $2R \approx 1/\sqrt{\rho}$ is the mean distance between dislocations, $\hat{\mathbf{l}}$ is the unit dislocation sense vector, $\hat{\mathbf{b}} = \mathbf{b}/|\mathbf{b}|$, ν is the Poisson ratio, and α accounts for nonlinear effects in the dislocation core. Kröner's [23] cubic equation for the shear modulus of macroscopic polycrystals defines G , and therefore ν , as a function of the single crystal elastic constants. We must have $\phi \rightarrow 1$ when the crystal anisotropy ratio

$$\xi = \frac{c_{11} - c_{12}}{2c_{44}}, \quad (3)$$

equals one, i.e., in a perfectly isotropic crystal. The general form of the function ϕ is unknown. However, we estimated the mean value of ϕ using expressions for the line energies of $\langle 110 \rangle$ and $\langle 111 \rangle$ screw dislocations in anisotropic cubic materials [22] in conjunction with the Kröner cubic equation for G and single crystal data on 31 elements [24] and found $\phi = 0.90 \pm 0.09$. This anisotropy correction shifts the critical dislocation density downward from $0.61b^{-2}$, determined under the assumption of isotropy, to $0.53b^{-2}$.

The line energies of both $\langle 110 \rangle$ and $\langle 111 \rangle$ screw dislocations have $\sqrt{\xi}$ behavior near the origin that gives way to a slow variation of ϕ above $\xi \approx 0.2$ [25]. In our melting model T_m is proportional to the average of σ in the dislocation ensemble near melt, hence $T_m \sim \langle \phi \rangle$. Approximately equal amounts of edge and screw dislocations are present in the ensemble, and if $\phi_{\text{edge}}(\xi)$ behaves like $\phi_{\text{screw}}(\xi)$ then $T_m \sim \xi^{0.5}$ as $\xi \rightarrow 0$ and T_m will be insensitive to ξ for $\xi \geq 0.2$. The vanishing of T_m with ξ is to be expected because of the loss of cubic crystal stability when $c_{11} = c_{12}$. Kleinert's three-dimensional lattice model of defect melting [20] predicts very similar behavior, specifically $T_m \sim \xi^{0.6}$.

Many authors [26] have successfully used the $\ln(1/\rho)$ form for σ , as in Eq. (2), so we chose it as well, even though it has not been thoroughly investigated theoretically. Careful derivations [27] have been carried out only for nearly parallel dislocations. However, the $\ln(1/\rho)$ form is expected to hold in a three-dimensional ensemble of nondirected dislocations provided the mean dislocation length is much larger than the mean distance between dislocations, that is, $\langle L \rangle \sqrt{\rho} \gg 1$. In our model the $\ln(1/\rho)$ self-energy leads to a dislocation free energy $F = -a_1 \rho \ln \rho - a_2 \rho - a_3 \rho^{a_4}$, and the $\rho \ln \rho$ term results in a first-order melting transition.

We obtain the following melting relation:

$$k_B T_m = \frac{1 - \nu/2}{1 - \nu} \frac{\lambda G(T_m) v_{WS}(T_m)}{8\pi \ln(z-1)} \langle \phi \rangle \ln\left(\frac{\alpha^2}{4b^2 \rho(T_m)}\right). \quad (4)$$

Here the factor $(1 - \nu/2)/(1 - \nu)$ results from averaging over φ , $\cos \varphi = \hat{\mathbf{b}} \cdot \hat{\mathbf{l}}$, v_{WS} is the Wigner-Seitz volume, $\lambda \equiv b^3/v_{WS}$ is a geometric factor characterizing the lattice, and $\rho(T_m)$ is the dislocation density at melt. Note that the factor $\ln(z-1)$ explicitly accounts for the influence of crystal structure on melting. This melting relation plus experimental data on over half the elements in the Periodic Table give $b^2 \rho(T_m) = 0.61 \pm 0.20$ [18].

In Ref. [17] we applied Eq. (4) (with $\langle \phi \rangle \equiv 1$) to the zero-pressure elemental data for more than half of the periodic table and found that it is accurate to 17%. Here we investigate the validity of this relation in the OCP limit by using it to calculate the value of Γ_m , which is then compared to the available MC data.

Calculation of Γ_m from Eq. (4) requires that we make the reasonable assumption that $\alpha^2/b^2 \rho(T_m)$ is a pressure-independent constant. Then we can estimate this quantity for the OCP from zero-pressure data on the alkali metals. It is well known that the deviations of alkali-metal Fermi surfaces from perfect spheres are of order 1% or less, clear evidence that the valence electrons are very nearly free. In addition, the ratio of ionic radius to half the interatomic distance increases from 0.4 in Li to only 0.7 in Cs [28], hence the overlap between alkali ions is small, and so to a good approximation the ions are effectively point charges. With respect to many of its physical properties (third-order elastic constants are one exception [29]), an alkali metal can be regarded as a bcc lattice of point positive ions in a uniform background of free electrons, i.e., a one-component plasma.

II. ANALYSIS OF ALKALI METAL DATA

Let us first discuss the temperature dependencies of G and v_{WS} , since their values to be used in Eq. (4) should be those at $T = T_m$, not the measured values at room temperature. The fixed-pressure ratio of Wigner-Seitz volumes at T_m and $T = 0$ is equal to $1 + \beta T_m$, where β is the volume expansivity. At $p = 0$, β is typically of order 10^{-5} K^{-1} , and melting temperatures are at most about 4000 K, so v_{WS} changes by only a few percent between $T = 0$ and T_m . We can therefore always use room-temperature values for v_{WS} .

In contrast to v_{WS} , the dependence of G on T is not necessarily weak. Its T dependence involves two characteristic temperatures, namely the Debye temperature T_D and the melting temperature. G is always monotonically decreasing with T , and is nonlinear for $T \leq T_D$ and linear from T_D to T_m . An accurate representation of $G(T)$ at fixed density is achieved by ignoring the low-temperature nonlinearity and approximating $G(T)$ as a linear function of the reduced temperature T/T_m with the correct value $G(0)$ at $T = 0$ [30],

$$G(T) = G(0) \left(1 - \gamma \frac{T}{T_m}\right). \quad (5)$$

This straight-line representation turns out to be quite accurate: the maximum deviation of the data from the corresponding fitted lines is $\sim 11\%$ for the 22 metals analyzed in [30].

Hence, as follows from Eqs. (4) and (5),

$$\frac{1}{\lambda \langle \phi \rangle \ln[\alpha^2/4b^2\rho(T_m)]} = \frac{1-\nu/2}{1-\nu} \frac{1-\gamma}{2} \frac{G(0)v_{WS}}{4\pi k_B T_m \ln 7}, \quad (6)$$

where we have taken $z=8$. For our analysis, we use Li, Na, K, Rb, and Cs, and omit Fr for which lattice constant data are not available. For the remaining five alkali metals, $v_{WS} = a^3/2$, where the values of the lattice constant a are taken from [31]. The values of both $G(0)$ and T_m come from [32]. We take the values of γ from Ref. [30] for Na, K, and Rb, and for Li and Cs we use $\gamma=0.23$, which is the average value over the 22 metals analyzed in [30]. The corresponding values of ν are taken from Ref. [32]. Averaging over the five alkali metals gives

$$\frac{1}{\lambda \langle \phi \rangle \ln[\alpha^2/4b^2\rho(T_m)]} = 0.385 \pm 0.052, \quad (7)$$

where the error is the root-mean-square deviation.

III. OCP MELTING PARAMETER Γ_m

We first consider the Poisson ratio in the OCP limit. In terms of G and the bulk modulus, B , the Poisson ratio is given by [32]

$$\nu = \frac{3B-2G}{2(3B+G)}. \quad (8)$$

We approximate B^{OCP} by the bulk modulus of the electron gas since the negative electrostatic (Madelung) contribution never exceeds 10% of the bulk modulus of the gas. The variation of B^{OCP} with density changes from a $n^{5/3}$ dependence in the nonrelativistic case to a $n^{4/3}$ dependence in the extreme relativistic limit, whereas the OCP shear modulus always varies as $n^{4/3}$. Hence, in a nonrelativistic gas, $B/G \sim n^{1/3} \gg 1$, so $\nu \rightarrow 1/2$, as seen from Eq. (8). Although B and G both vary as $n^{4/3}$ in the extreme relativistic limit, we find $B/G \approx 1000Z^{-2/3}$, so again $B/G \gg 1$ and $\nu \approx 1/2$.

Hence, as follows from Eqs. (1), (4), and (7) with $\nu = 1/2$, the OCP melting parameter is given by

$$\Gamma_m = (0.385 \pm 0.052) 8\pi \ln 7 \frac{2}{3} \frac{(4\pi/3)^{1/3} (Ze)^2 n^{4/3}}{G^{\text{OCP}}(\Gamma_m)}, \quad (9)$$

where we have used $v_{WS} = 1/n$.

The bcc OCP elastic constants were recently obtained by Ogata and Ichimaru, using MC simulations [33] as functions of Γ . However, the formula for the effective shear modulus used in Ref. [33],

$$G_{\text{eff}} = \frac{c_{11} - c_{12} + 3c_{44}}{5}, \quad (10)$$

TABLE I. The elastic constants and shear modulus, in units of $(4\pi/3)^{1/3} (Ze)^2 n^{4/3}$.

Γ	$(c_{11} - c_{12})/2$	c_{44}	ξ	G^{OCP}
∞	0.02454	0.1827	0.1343	0.0930
800	0.024(2)	0.174(1)	0.138(11)	0.089(12)
400	0.025(2)	0.167(1)	0.150(12)	0.087(11)
300	0.025(3)	0.157(4)	0.159(19)	0.084(19)
200	0.019(3)	0.12(1)	0.158(28)	0.064(28)

is in fact the Voigt (upper) bound [34] on the shear modulus, and therefore does not give the correct value of G , which is known to always lie between the Voigt and the Reuss (lower) [35] bounds.

An analysis by Kröner [23] shows that successively narrower bounds can be placed on the shear modulus as the degree of disorder in grain orientation increases. In the limit of perfect disorder, the shear modulus can be obtained as the root of a cubic equation with coefficients that depend on the single-crystal elastic constants. In the case of the OCP, where the shear modulus is down by a factor of $n^{1/3}$ from the bulk modulus, the cubic equation reduces to a quadratic with only one positive real root,

$$G = \frac{1}{6} [c_{44} + \sqrt{c_{44}^2 + 12(c_{11} - c_{12})c_{44}}]. \quad (11)$$

In Table I we present the values of the elastic constants from Ref. [33] and the correct values of G^{OCP} as calculated from Eq. (11). The value of ξ for the OCP, as given in Table I, 0.158 ± 0.028 (this value embraces all five values of ξ in Table I), is consistent with the average value of ξ that we calculated for five alkali metals Li, Na, K, Rb, and Cs, 0.157 ± 0.044 , where the error is the root-mean-square deviation.

Let us again assume a linear temperature dependence of G^{OCP} on $T \propto 1/\Gamma$,

$$G^{\text{OCP}}(\Gamma) = G^{\text{OCP}}(\infty) \left(1 - \frac{\eta}{\Gamma} \right). \quad (12)$$

Fitting the values in Table I to this linear formula, and taking into account their uncertainties, we obtain [36]

$$\eta = 36.7 \pm 30.4. \quad (13)$$

Finally, we evaluate the OCP melting parameter Γ_m in the framework of melting as a dislocation-mediated phase transition. As follows from Eqs. (9), (12), and (13) with the value of $G^{\text{OCP}}(\infty)$ from Table I,

$$\Gamma_m = 172 \pm 35. \quad (14)$$

This value is in good agreement with the available data from MC simulations, albeit with 20% uncertainty. We note that most ($\approx 2/3$) of this uncertainty comes from the uncertainty in the value of η .

The OCP value of the parameter γ defined in Eq. (5) is simply related to η and Γ_m ,

$$\eta \equiv \gamma^{\text{OCP}} \Gamma_m. \quad (15)$$

From Eqs. (13) and (14) we get $\gamma^{\text{OCP}} = 0.21 \pm 0.18$, which is consistent with the value of γ at $p \sim 0$, namely 0.23 [30].

IV. CONCLUDING REMARKS

Our central value for Γ_m , that is 172, agrees well with the more recent MC results. Two-thirds of the 20% uncertainty in this value is attributable to the error in the MC-calculated temperature dependence of the OCP single-crystal elastic constants.

Our previous study of the melting curves of 24 elements

[37] revealed that the melting relation (4) is in good agreement with data up to pressures $\sim 100\text{--}200$ GPa. Here we have demonstrated that Eq. (4) also holds in a classical OCP. These successful comparisons of Eq. (4) with experimental data and MC calculations suggest, but of course do not by themselves prove, that melting is a dislocation-mediated phase transition.

ACKNOWLEDGMENTS

We wish to thank T. Goldman and R. R. Silbar for very valuable discussions during the preparation of this work, and M. M. Brisudová for her help with a least-squares fitting.

-
- [1] M. Baus and J.P. Hansen, Phys. Rep. **59**, 1 (1980); S. Ichimaru, Rev. Mod. Phys. **54**, 1017 (1982); S. Ichimaru, H. Iyetomi, and S. Tanaka, Phys. Rep. **149**, 91 (1987).
- [2] S. Ichimaru, H. Iyetomi, S. Mitake, and N. Itoh, Astrophys. J. **265**, L83 (1983).
- [3] S.G. Brush, H.L. Sahlin, and E. Teller, J. Chem. Phys. **45**, 2102 (1966).
- [4] J.P. Hansen, Phys. Rev. A **8**, 3096 (1973).
- [5] E.L. Pollock and J.P. Hansen, Phys. Rev. A **8**, 3110 (1973).
- [6] H.M. Van Horn, Phys. Lett. **28A**, 706 (1969).
- [7] H.E. DeWitt, Phys. Rev. A **14**, 1290 (1976).
- [8] H.E. DeWitt and Y. Rosenfeld, Phys. Lett. **75A**, 79 (1979).
- [9] W.L. Slattery, G.D. Doolen, and H.E. DeWitt, Phys. Rev. A **21**, 2087 (1980); **26**, 2255 (1982).
- [10] S. Ogata and S. Ichimaru, Phys. Rev. A **36**, 5451 (1987).
- [11] G.S. Stringfellow, H.E. DeWitt, and W.L. Slattery, Phys. Rev. A **41**, 1105 (1990).
- [12] D.H.E. Dubin, Phys. Rev. A **42**, 4972 (1990).
- [13] R.T. Farouki and S. Hamaguchi, Phys. Rev. E **47**, 4330 (1993).
- [14] R.T. Farouki and S. Hamaguchi, J. Chem. Phys. **101**, 9885 (1994).
- [15] S. Hamaguchi, R.T. Farouki, and D.H.E. Dubin, Phys. Rev. E **56**, 4671 (1997).
- [16] M.D. Jones and D.M. Ceperley, Phys. Rev. Lett. **76**, 4572 (1996).
- [17] L. Burakovsky and D.L. Preston, Solid State Commun. **115**, 341 (2000).
- [18] L. Burakovsky, D.L. Preston, and R.R. Silbar, Phys. Rev. B **61**, 15 011 (2000).
- [19] C. Mott, Proc. R. Soc. London, Ser. A **215**, 1 (1952).
- [20] H. Kleinert, *Gauge Fields in Condensed Matter* (World Scientific, Singapore, 1989), Vol. II.
- [21] J. P. Hirth and J. Lothe, *Theory of Dislocations*, 2nd ed. (Krieger, Malabar, FL, 1992).
- [22] Y.Q. Sun and A.H.W. Ngan, Philos. Mag. Lett. **74**, 175 (1996).
- [23] E. Kröner, Z. Phys. **151**, 504 (1958); Eng. Mech. Div. Amer. Soc. Civ. Eng. **108**, 899 (1980); B.K.D. Gairola and E. Kröner, Int. J. Eng. Sci. **19**, 865 (1981).
- [24] P. Sisodia and M.P. Verma, J. Phys. Chem. Solids **50**, 223 (1989).
- [25] An example of such a function is $\phi(\xi) = 6\sqrt{\xi}/(1 + \sqrt{1 + 24\xi})$, which is realized in the OCP limit for a $\langle 110 \rangle$ screw dislocation in a cubic crystal.
- [26] S. Mizushima, J. Phys. Soc. Jpn. **15**, 70 (1960); R.M.J. Cotterill, J. Cryst. Growth **48**, 582 (1980); J. Kierfeld and V. Vinokur, e-print cond-mat/9909190.
- [27] T. Yamamoto and T. Izuyama, J. Phys. Soc. Jpn. **57**, 3742 (1988); G.F. Sarafanov, Fiz. Tverd. Tela (St. Petersburg) **39**, 1575 (1997) [Phys. Solid State **39**, 1403 (1997)].
- [28] K. Fuchs, Proc. R. Soc. London, Ser. A **153**, 622 (1936).
- [29] T. Suzuki, A.V. Granato, and J.F. Thomas, Jr., Phys. Rev. **175**, 766 (1968).
- [30] D.L. Preston and D.C. Wallace, Solid State Commun. **81**, 277 (1992).
- [31] *Numerical Data and Functional Relationships in Science and Technology*, Landolt-Börnstein, New Series, Group III, edited by K.-H. Hellwege and O. Madelung (Springer-Verlag, Berlin, 1971), Vol. 7; Vol. 14 (1988); Vol. 25 (1991).
- [32] K. A. Gschneidner, Jr., in *Solid State Physics, Advances in Research and Applications*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1965), Vol. 16, p. 275.
- [33] S. Ogata and S. Ichimaru, Phys. Rev. A **42**, 4867 (1990).
- [34] W. Voigt, *Lehrbuch der Kristallphysik* (Teubner, Leipzig, 1928), p. 962.
- [35] A. Reuss, Z. Angew. Math. Mech. **9**, 55 (1929).
- [36] M. M. Brisudová (private communication).
- [37] L. Burakovsky, D.L. Preston, and R.R. Silbar, J. Appl. Phys. **88**, 6294 (2000).