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Thermodynamic perturbation theory in studies of metal melts

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The review concerns methods of the thermodynamic perturbation theory (TPT) used to study liquid metals and alloys. Basic relations of the TPT are presented. Various reference systems are analyzed, their advantages and drawbacks are described. The results of calculations of the structure and thermodynamic properties of metal melts by various methods are discussed. Promising avenues of research in the title field are outlined.
The bibliography includes 272 references.

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I. Introduction

The thermodynamic perturbation theory (TPT) is based on Zwanzig's approach which treats a liquid that obeys the laws of classical statistical mechanics as the sum of two subsystems.[1] One of them, called 'reference system', mainly includes the forces of repulsion between molecules, whereas the other, called 'perturbation', mainly includes the forces of intermolecular attraction. In the text below, the quantities characterizing the reference system and perturbation will be labeled with the subscripts '0' and '1', respectively. Taking into account this separation, classical statistical mechanics gives the following exact relation [1]

$$\exp(-\beta F_1) = \langle \exp(-\beta U_1) \rangle_0 \qquad (1)$$

where $\beta = \dfrac{1}{k_B T}$

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k_B is the Boltzmann constant, T is absolute temperature, F is the Helmholtz free energy and U is the potential energy.

When calculating the structure functions and macroscopic properties of a liquid with a specified pair interaction potential $[\varphi(r)]$, the TPT helps to avoid computational problems connected with solution of the Ornstein – Zernike (OZ) integral equation.[2] This is of particular importance for calculations of the thermodynamic properties of metals. Indeed, on the one hand, metallic state is usually described using complex pair potentials. On the other hand, calculations of thermodynamic properties require additional numerical operations. Taken altogether, these features make direct calculations of the thermodynamic properties of metals using the OZ integral equation difficult.

In this review, we will consider the classical version of the TPT of simple liquids, because most liquid metals are correctly described within the framework of this theory.

In the theory of simple liquids, the potential energy of an equilibrium homogeneous system is written as the sum of central, spherically symmetrical pair interactions between particles (hereafter, all thermodynamic functions are given per particle)

$$U = \frac{1}{N} \sum_{k=1}^{N-1} \sum_{l=k+1}^{N} \varphi(r_{kl}) \qquad (2)$$

where N is the number of particles in the system and r_{kl} is the distance between the particles k and l.

Using the separations

$$U = U_0 + U_1 \tag{3}$$

and

$$\varphi(r) = \varphi_0(r) + \varphi_1(r), \tag{4}$$

the approximation (2) is transformed to

$$U_0 = \frac{1}{N}\sum_{k=1}^{N-1}\sum_{l=k+1}^{N}\varphi_0(r_{kl}) \tag{5}$$

$$U_1 = \frac{1}{N}\sum_{k=1}^{N-1}\sum_{l=k+1}^{N}\varphi_1(r_{kl}) \tag{6}$$

Zwanzig,[1] who developed the foundations of the TPT, also elaborated a high-temperature approximation (HTA) of this theory and proposed to use the model of hard spheres (HS) as the reference system. Then, exact analytical expressions for the structure functions of the HS model[3,4] in the Percus–Yevick (PY) approximation[5] were derived. This made the HS reference system not only physically substantiated but also mathematically convenient and favoured rapid progress in the TPT.

Studies of liquid metals within the framework of the TPT began in the early 1970s and since then became an integral part of the physics of condensed matter. It is of importance that the TPT can be applied to metals without imposing any additional restrictions compared to the theory of simple liquids. In fact, to use the TPT instead of integral-equation theories of liquids means to search for some integral-equation approximation for the reference system rather than the entire system under study.

The authors of the reviews[6,7] on theoretical studies of metal melts paid considerable attention to the TPT. However, these reviews were published long ago, while recent reviews and monographs, either entirely devoted to the TPT[8–11] or concerned with particular problems in the TPT,[12–21] pay little attention, if any, to metals. This is the main reason for writing the present review.

II. Basic relations

In the high-temperature approximation of TPT, F_1 is represented by a power series in β (see Ref. 1)

$$F_{\mathrm{HTA}} = F_0 + \sum_{n=1}^{\infty}\frac{\omega^{(n)}}{n!}(-\beta)^{n-1} \tag{7}$$

where

$$F_0 = \frac{3}{2}k_{\mathrm{B}}T + U_0 - TS_0 \tag{8}$$

and S is entropy. From expression (1) Zwanzig[1] derived

$$\omega^{(n)} = n!\sum_{\left(\sum sm_s = n\right)}(-1)^{\sum m_s - 1}\left(\sum m_s - 1\right)!\prod_{s=1}^{\infty}\frac{1}{m_s!}\left(\frac{\langle\alpha^s\rangle_0}{s!}\right)^{m_s} \tag{9}$$

where

$$\langle\alpha^s\rangle_0 = k!\sum_{\left(\sum nm_n = k\right)}\prod_{n=1}^{\infty}\frac{1}{m_n!}\left(\frac{\langle\omega^{(n)}\rangle_0}{n!}\right)^{m_n},$$

and showed that

$$F_{\mathrm{HTA}} = F_0 + \omega^{(1)} - \frac{\omega^{(2)}\beta}{2} + O(\beta^2), \tag{10}$$

where

$$\omega^{(1)} = \langle U_1\rangle_0\,;\ \omega^{(2)} = \langle U_1^2\rangle_0 - \langle U_1\rangle_0^2 \tag{11}$$

Usually, the contribution $\omega^{(2)}\beta/2$ in expansion (10) is neglected and thus the Helmholtz free energy to be considered ($F^{(1)}_{\mathrm{HTA}}$) includes at most the first-order perturbation

$$F^{(1)}_{\mathrm{HTA}} = F_0 + \langle U_1\rangle_0 \tag{12}$$

Withn the framework of the approximation (6) one has

$$\langle U_1\rangle_0 = 2\pi\rho\int_0^{\infty}\varphi_1(r)g_0(r)r^2\mathrm{d}r \tag{13}$$

where ρ is the mean atomic density and $g(r)$ is the pair correlation function.

Equality (12) holds at $\beta\varphi_1(r) \ll 1$;[14] therefore, the HTA can be applied to liquid metals at temperatures above their melting points.

The HTA methods differ in reference systems and in procedures for the determination of their parameters. They are used in studies of the structure and thermodynamic properties of metal melts. The most widely utilized HTA methods include the Weeks–Chandler–Andersen (WCA) method[22] and the variational approach. They will be considered separately below.

From expressions (7)–(13) it follows that in the HTA the entropy and structure functions of the entire system are respectively equal to those of the reference system. Within the framework of the TPT, general expressions for these quantities can be derived by going beyond the HTA.

In terms of the perturbation theory, the Fourier transform of the direct correlation function [$c(r)$] is

$$c(q) = c_0(q) + c_1(q) \tag{14}$$

Combining expression (14) with the definition of the structure factor [$S(q)$]

$$S(q) = \frac{1}{1 - \rho c(q)} \tag{15}$$

one gets

$$S(q) = \frac{1}{1 - \rho c_0(q) - \rho c_1(q)} \tag{16}$$

From Eqn (15) it follows that

$$c(q) = \frac{S(q) - 1}{\rho S(q)} \tag{17}$$

Applying Eqn (17) to the reference system and substituting into relationship (16), one gets the general expression for the structure factor in the TPT:

$$S(q) = \frac{S_0(q)}{1 - \rho S_0(q)c_1(q)} \tag{18}$$

The expression for the Helmholtz free energy going beyond the HTA can be obtained within the framework of

the diagram technique or field theory (FT). A general expression derived by Itoh [23] has the form

$$F = F_{\mathrm{HTA}} - \frac{1}{4\pi^2}\int_0^\infty \left\{\varphi_1(q)S_0(q) + \right.$$
$$\left. + \frac{\varphi_1(q)}{\rho c_1(q)}\ln\left[1-\rho S_0(q)c_1(q)\right]\right\}q^2\mathrm{d}q \qquad (19)$$

where $\varphi(q)$ is the Fourier transform of the potential $\varphi(r)$. The second term on the right side of Eqn (19) is the entropy contribution to F, *i.e.*, the perturbation written in terms of entropy within the framework of the TPT–FT approach is as follows:

$$S_1 = \frac{1}{4\pi^2 T}\int_0^\infty \left\{\varphi_1(q)S_0(q) + \right.$$
$$\left. + \frac{\varphi_1(q)}{\rho c_1(q)}\ln\left[1-\rho S_0(q)c_1(q)\right]\right\}q^2\mathrm{d}q \qquad (20)$$

The particular kind of method in the TPT–FT approach depends on the approximation for $c_1(q)$ and, in some cases, on the additional requirements for structure or thermodynamic functions.

The simplest TPT–FT method is called the random phase approximation (RPA) [24]

$$c_{\mathrm{RPA}}(r) = c_0(r) - \beta\varphi_1(r) \qquad (21)$$

Since $c(r)$ asymptotically tends to $-\beta\varphi(r)$ at $r\to\infty$, the correlation function $c_{1\mathrm{RPA}}(r)$ in this limit is exact.

With Eqn (21) written in the reciprocal space

$$c_{\mathrm{RPA}}(q) = c_0(q) - \beta\varphi_1(q), \qquad (22)$$

in the RPA, expressions (18) and (20) are respectively transformed to

$$S_{\mathrm{RPA}}(q) = \frac{S_0(q)}{1+\beta\rho S_0(q)\varphi_1(q)} \qquad (23)$$

$$S_{1\mathrm{RPA}} = \frac{1}{4\pi^2 T}\int_0^\infty \left\{\varphi_1(q)S_0(q) - \right.$$
$$\left. - \frac{1}{\rho\beta}\ln\left[1+\rho\beta S_0(q)\varphi_1(q)\right]\right\}q^2\mathrm{d}q \qquad (24)$$

In the mean density approximation (MDA) [25] the function $c(r)$ is defined in a more complex manner

$$c_{\mathrm{MDA}}(r) = c_0(r) - \frac{\beta}{2}\varphi_1(r)\left[\frac{\partial^2\left(\rho^2 g_0(r)\right)}{\partial\rho^2}\right] \qquad (25)$$

With the assumption that $g_0(r)$ is independent of ρ, an extended random phase approximation (ERPA) [26] follows from Eqn (25):

$$c_{\mathrm{ERPA}}(r) = c_0(r) - \beta\varphi_1(r)g_0(r) \qquad (26)$$

The Fourier transforms of the correlation functions (25) and (26) are respectively given by:

$$c_{\mathrm{MDA}}(q) = c_0(q) - \frac{2\pi\beta}{q}\int_0^\infty \varphi_1(r)\left[\frac{\partial^2\left(\rho^2 g_0(r)\right)}{\partial\rho^2}\right]\sin(qr)r\,\mathrm{d}r \qquad (27)$$

$$c_{\mathrm{ERPA}}(q) = c_0(q) - \frac{4\pi\beta}{q}\int_0^\infty \varphi_1(r)g_0(r)\sin(qr)r\,\mathrm{d}r \qquad (28)$$

The optimized random phase approximation (ORPA) [27] eliminates the drawback of the RPA, namely, non-physical behaviour of $g(r)$ at small r. Here, the pair potential $\varphi_1(r)$ is replaced at $r<\sigma$ [σ is the diameter of the hard core (HC)] by some optimized potential $\varphi_1^*(r)$ defined from the condition

$$\frac{\delta F_{\mathrm{RPA}}}{\delta\left(\beta\varphi_1^*(r)\right)} = 0,\ r<\sigma \qquad (29)$$

where $F_{\mathrm{RPA}} = F_{\mathrm{HTA}}^{(1)} - TS_{1\mathrm{RPA}}$ (30)

Expression (19) shows that the TPT–FT approach can be used to calculate the thermodynamic properties only in combination with the HTA. Each combination of a certain HTA method with a TPT–FT method will specify a particular form of expression (19). Structural parameters can be calculated using the TPT–FT approach only, but the HTA is often used to determine parameters of the reference system. For both procedures, key issues include the choice of the reference system, methods for its description and the choice of the model for effective pair interaction which describes the system to be studied within the framework of the TPT.

For simple metals, the pair potential is usually given by the nearly free electron (NFE) approximation which leads to effective pair interaction † (see, *e.g.*, Ref. 6)

$$\varphi_{\mathrm{NFE}}(r) = \frac{z^2}{r} + \frac{1}{8\pi^2\rho}\int_0^\infty F(q)\frac{\sin(qr)}{qr}q^2\mathrm{d}q \qquad (31)$$

where z is the valence of the metal and $F(q)$ is the energy wave number characteristic

$$F(q) = -\frac{q^2}{8\pi\rho}\omega^2(q)\frac{1}{\left(\varepsilon_{\mathrm{H}}(q)-1\right)^{-1}+1-f(q)} \qquad (32)$$

Here $\omega(q)$ is the form factor of the unscreened ion pseudopotential $\omega(r)$

$$\omega(q) = 4\pi\rho\int_0^\infty \omega(r)\frac{\sin(qr)}{qr}r^2\mathrm{d}r \qquad (33)$$

$\varepsilon_{\mathrm{H}}(q)$ is the Hartree dielectric function and $f(q)$ is the exchange-correlation function.

III. Model liquids used as reference systems

The HS model is most widely used as reference system. The pair potential of this model is defined as follows:

† From this point on, all quantities are given in atomic units (a.u.). In this case, the Planck constant ($\hbar$), electron charge and electron mass are equal to unity.

$$\varphi_{\mathrm{HS}}(r) = \begin{cases} \infty, & r < \sigma, \\ 0, & r \geqslant \sigma \end{cases} \tag{34}$$

The HS potential is the simplest partial case for the hard-core potential

$$\varphi_{\mathrm{HC}}(r) = \begin{cases} \infty, & r < \sigma, \\ \phi(r), & r \geqslant \sigma \end{cases} \tag{35}$$

Irrespective of the function $\phi(r)$, the following equality should always hold for a system with the potential (35):

$$g_{\mathrm{HC}}(r) = 0, r < \sigma \tag{36}$$

A feature of the HS model is that its potential energy is zero. In this case, the Helmholtz free energy is given by

$$F_{\mathrm{HS}} = \frac{3}{2} k_{\mathrm{B}} T - T S_{\mathrm{HS}} \tag{37}$$

where

$$S_{\mathrm{HS}} = S_{\mathrm{ig}} + \Delta S_{\mathrm{HS}} \tag{38}$$

Here ΔS_{HS} is the HS contribution and S_{ig} is the entropy of the ideal gas

$$S_{\mathrm{ig}} = k_{\mathrm{B}} \left\{ \frac{5}{2} + \ln \left[\frac{1}{\rho} \left(\frac{k_{\mathrm{B}} T m}{2\pi} \right)^{3/2} \right] \right\} \tag{39}$$

where m is the atomic mass.

The ΔS_{HS} contribution can be described in different approximations, *e.g.*, the Carnahan–Starling approximation.[28] The expression derived from the compressibility equation is also used:

$$\Delta S_{\mathrm{HS}} = k_{\mathrm{B}} \left\{ \ln(1-\eta) + \frac{3}{2} \left[1 - \frac{1}{(1-\eta)^2} \right] \right\} \tag{40}$$

where $\eta = (\pi \rho \sigma^3/6)$ is the packing function. Extension of Eqn (40) to binary mixtures was reported.[29]

Analytical expressions derived in the PY approximation describe structure functions of pure HS liquids,[3,4] binary additive HS mixtures [$c_{ij}^{\mathrm{HS}}(r)$,[30] $S_{ij}^{\mathrm{HS}}(q)$,[31,32] $g_{ij}^{\mathrm{HS}}(r)$,[33,34] where $c_{ij}(r)$ is the partial direct correlation function, $S_{ij}(q)$ is the partial structure factor and $g_{ij}(r)$ is the partial pair correlation function; $i, j = 1, 2$] and n-component additive HS mixtures [$c_{ij}^{\mathrm{HS}}(r)$,[35] $S_{ij}^{\mathrm{HS}}(q)$[36] ($i, j = 1, n$)]. In the last-mentioned case, the expressions for $g_{ij}^{\mathrm{HS}}(r)$, $S_{ij}^{\mathrm{HS}}(q)$ and $c_{ij}^{\mathrm{HS}}(r)$ were also obtained[37,38] by solving the PY equation within the framework of the 'rational function approximation' (RFA).[39]

In addition to the analytical expressions listed above, the Verlet–Weis (VW) correction[40] to $g_{\mathrm{HS}}^{\mathrm{PY}}(r)$ is widely used. It was determined by computer simulation in order to obtain consistency between $g_{\mathrm{HS}}^{\mathrm{PY}}(r)$ and the Carnahan–Starling equation of state.[28] Grundke and Henderson[41] reported the correlation function $c_{\mathrm{HS}}(r)$ that is consistent with $g_{\mathrm{HS}}^{\mathrm{VW}}(r)$. They also extended the Verlet–Weis approach to n-component additive HS mixtures. Some other expressions for $g_{\mathrm{HS}}(r)$ with different parameterizations were reported in the last 15 years.[42–50] A number of relationships for calculating the contact values of $g_{ij}^{\mathrm{HS}}(r)$ for binary and n-component additive mixtures and corresponding equations of state were proposed.[51,52] Computer code listings for some correlation functions mentioned above are available as supplementary materials to Ref. 53. Although simple, the HS model correctly describes the structure of metal melts.

Attempts to 'soften' the reference system in the TPT began in the late 1960s. In particular, the inverse power (IP) pair potential

$$\varphi_{\mathrm{IP}}(r) = \varepsilon \left(\frac{d}{r} \right)^{12} \tag{41}$$

is used as the reference system potential (here, ε and d are parameters having the dimension of energy and distance, respectively). For the IP potential, the expression for the Helmholtz free energy[54] (it was thoroughly fitted to the results of a Monte Carlo simulation) and the pair correlation functions[54] tabulated from the solution of the Rogers–Young integral equation[55] were obtained.

Yet another example of the soft reference system is provided by the one component plasma (OCP) model which includes a system of positively charged point ions that interact with one another in the Coulomb potential

$$\varphi_{\mathrm{OCP}}(r) = \frac{z^2}{r} \tag{42}$$

and a uniform electron background to ensure electroneutrality. The influence of the background is described by an additional contribution to the internal energy. This model is characterized by the parameter

$$\Gamma = \frac{z^2 \beta}{a}$$

where

$$a = \left(\frac{4\pi\rho}{3} \right)^{-1/3}$$

From expressions (31) and (42) is follows that $\varphi_{\mathrm{OCP}}(r)$ is a convenient reference potential in the NFE approximation because it is explicitly included in the pair potential $\varphi_{\mathrm{NFE}}(r)$.

A drawback of the reference system in question consists in the lack of corresponding analytical solution of the OZ equation in one or another approximation of the theory of liquids. Therefore, the OCP model is described by the expressions constructed using the results of computer simulations for the Helmholtz free energy[56,57] and structure functions[58–63] or by tabulated values based on the numerical solution[64] of the OZ equation in the modified hypernetted chain (MHNC) approximation.[65]

The one and only rigorous analytical solution for the OCP model can be obtained in a limiting case of the charged hard-sphere (CHS) model which occupies an intermediate position between the HS and OCP models and is described by the following pair potential:

$$\varphi_{\mathrm{CHS}}(r) = \begin{cases} \infty, & r < \sigma, \\ z^2/r, & r \geqslant \sigma \end{cases} \tag{43}$$

Namely, there exists an analytical solution[66,67] for the CHS model in the mean spherical approximation (MSA).[68] It poorly describes liquids at low packing fraction values, *i.e.*, when the CHS model should be replaced by the OCP model. Only derivation of an analytical solution[69] within the framework of the MHNC approximation (more accurate case for the CHS model) allowed both reference

systems, CHS and OCP, to be considered from a unified point of view.

The next example of a reference system is the three-parameter model with the hard-core Yukawa (HCY) potential

$$\varphi_{\mathrm{HCY}}(r) = \begin{cases} \infty, & r < \sigma, \\ \dfrac{\varepsilon_{\mathrm{Y}}\sigma \exp[-\kappa(r-\sigma)]}{r}, & r \geqslant \sigma \end{cases} \tag{44}$$

where ε_{Y} is the contact value of the potential

$$\varepsilon_{\mathrm{Y}} = \varphi_{\mathrm{HCY}}(r = \sigma)$$

and κ is the inverse screening length.

An analytical solution for this model was obtained within the framework of the mean spherical approximation.[70] At present, this solution is widely used in the simplest and convenient form reported by Ginoza.[71] It was used to derive [72] an analytical expression for $S_{\mathrm{HCY}}(q)$ which was then applied in calculations of the structure factors of liquid metals (Na, K, Rb, Al, Mg and Pb) with the repulsive and attractive HCY potentials (RHCY and AHCY, respectively). The RHCY model made it possible to achieve much better agreement with experimental data in a wide range of q values except the long-wavelength limit where excellent agreement with the experiment for most metals studied was attained using the AHCY model. Eventually, it was concluded [72] that the model with the HCY potential should be a good approximation to the reference system in the studies of liquid metals. Earlier, an analytical expression for $S_{\mathrm{HCY}}(0)$ was derived [73] within the framework of the MDA and used in the studies of liquid Na, K, Rb, Al, Mg and Pb. Thermodynamic properties can be calculated using semi-analytical expressions based on the MSA [74] as well as analytical expressions derived in the first-order mean spherical approximation (FMSA) [75, 76] and their simplified version.[77] Analytical expressions for the partial structure factors of a binary HCY mixture were derived within the framework of the MSA.[78]

The square well (SW) model with the following three-parameter pair potential:

$$\varphi_{\mathrm{SW}}(r) = \begin{cases} \infty, & r < \sigma, \\ \varepsilon_{\mathrm{SW}}, & \sigma \leqslant r < \lambda\sigma, \\ 0, & r \geqslant \lambda\sigma \end{cases} \tag{45}$$

where $\varepsilon_{\mathrm{SW}}$ and $\sigma(\lambda-1)$ are the depth and width of the potential well, respectively, can also be used as a reference system.[79–81] At $\varepsilon_{\mathrm{SW}} = 0$ or at $\lambda = 1$, the pair potential $\varphi_{\mathrm{SW}}(r)$ is transformed to $\varphi_{\mathrm{HS}}(r)$. The Fourier transform of the attractive part of $\varphi_{\mathrm{SW}}(r)$ is

$$\phi_{\mathrm{SW}}(q) = \frac{4\pi\varepsilon_{\mathrm{SW}}}{q^3}[\sin(q\lambda\sigma) - \sin(q\sigma) - q\lambda\sigma\cos(q\lambda\sigma) + q\sigma\cos(q\sigma)] \tag{46}$$

The SW model as reference system is illustrated by Fig. 1.

Application of the RPA to the SW model with the HS reference system gives the following analytical expression for the structure factor

$$S_{\mathrm{SW-RPA}}(q) = \frac{1}{1 - \rho c_{\mathrm{HS}}(q) + \beta\rho\phi_{\mathrm{SW}}(q)} \tag{47}$$

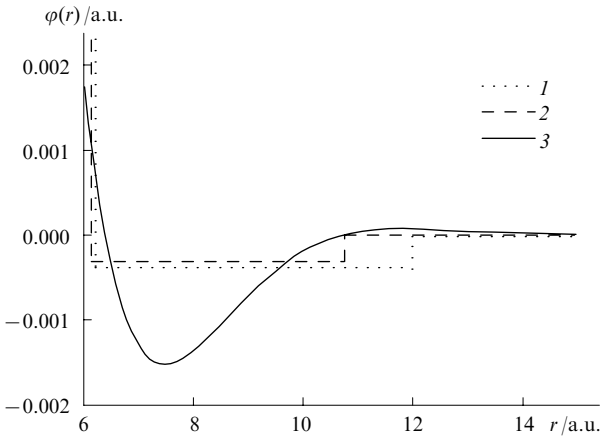


Figure 1. Pair potentials $\varphi_{0\,\mathrm{SW}}(r)$ obtained [81] for the local minima of the Helmholtz free energy of liquid sodium at 373 K using the SW–RPA (*1*) and SW–MSA (*2*) reference systems and the total effective potential $\varphi_{\mathrm{Na}}(r)$ (*3*).

However, since the condition (36) is not met in the RPA, expression (47) should not be considered reliable, especially, at large $\varepsilon\beta$ values.[82] Recently, we have proposed a new method of solution of the MSA and used it to derive a more accurate expression for $S_{\mathrm{SW}}(q)$, respectively.[82–84] The expressions for entropy in the SW–RPA [85] and SW–MSA [86] approaches are consistent with the expressions for $S_{\mathrm{SW-RPA}}(q)$ (47) and for $S_{\mathrm{SW-MSA}}(q)$, respectively.[82–84] The expression for the entropy of a binary SW mixture within the framework of the MSA was derived elsewhere.[87]

Analytical expressions derived within the framework of the RFA for structure functions and thermodynamic properties for the SW model in the PY approximation are available.[88–90] Also, an analytical solution in the PY approximation was obtained using the Wertheim approach [3] to the SW model.[91] Analytical expressions for $c_{\mathrm{SW}}(r)$ at $\lambda \leqslant 1$ (Ref. 92) and at $2 < \lambda \leqslant 3$ (Ref. 93) were obtained in the FMSA. In addition, expressions for F_{SW} (Refs 94 and 95) and $g_{\mathrm{SW}}(r)$ (Ref. 96) parameterized using the results of computer simulation are available.

All the reference systems mentioned above are explicitly independent of the model chosen to describe the system under study. There is also yet another type of reference systems. Here, $\varphi_0(r)$ is determined immediately from $\varphi(r)$ for the entire system and the difference between $\varphi_0(r)$ and $\varphi_{\mathrm{HS}}(r)$ is also treated as perturbation; correspondingly, the HS model is treated as an auxiliary system the quantities of which can be used to describe the reference system. The pair potential $\varphi_0(r)$ can be either effective or model depending on the total potential $\varphi(r)$. For this type of reference systems, the most widely used methods for separation of $\varphi(r)$ into $\varphi_0(r)$ and $\varphi_1(r)$ include the Barker–Henderson (BH) [97] and WCA [22] approaches.

In the BH method, the potentials $\varphi_0(r)$ and $\varphi_1(r)$ are defined as follows:

$$\varphi_{0\mathrm{BH}}(r) = \begin{cases} \varphi(r), & r < r_0, \\ 0, & r \geqslant r_0 \end{cases} \tag{48}$$

$$\varphi_{1\mathrm{BH}}(r) = \begin{cases} 0, & r < r_0, \\ \varphi(r), & r \geqslant r_0 \end{cases}$$

where r_0 is the coordinate of the first point of intersection of the function $\varphi(r)$ with the r axis.

Interrelation between the reference system and the HS system in the BH method is simple:

$$g_{0\mathrm{BH}}(r) = g_{\mathrm{HS}}(r) \tag{49}$$

and the hard-sphere diameter is defined as

$$\sigma_{\mathrm{BH}} = \int_0^{r_0} \left[1 - \exp(-\beta\varphi_0(r))\right] \mathrm{d}r \tag{50}$$

In the WCA method, $\varphi(r)$ is separated in a different manner:

$$\varphi_{0\mathrm{WCA}}(r) = \begin{cases} \varphi(r) - \varphi(r_{\min}), & r < r_{\min}, \\ 0, & r \geqslant r_{\min} \end{cases} \tag{51}$$

$$\varphi_{1\mathrm{WCA}}(r) = \begin{cases} \varphi(r_{\min}), & r < r_{\min}, \\ \varphi(r), & r \geqslant r_{\min} \end{cases}$$

where $r_{\min}$ is the coordinate of the first minimum of the function $\varphi(r)$. In this case, not only the functions $\varphi_0(r)$ and $\varphi_1(r)$, but also the first derivatives of these functions with respect to r are continuous; at $r < r_{\min}$, one has

$$\frac{\partial\varphi_0(r)}{\partial r} = \frac{\partial\varphi(r)}{\partial r}$$

An example of the WCA separation of the pair potential is presented in Fig. 2.

The approximation relating the WCA reference system to the HS system is as follows:

$$y_{0\mathrm{WCA}}(r) = y_{\mathrm{HS}}(r) \tag{52}$$

where

$$y(r) = g(r)\exp\left(\beta\varphi(r)\right) \tag{53}$$

Then, one gets

$$g_{0\mathrm{WCA}}(r) = g_{\mathrm{HS}}(r)\exp\left[\beta\left(\varphi_{\mathrm{HS}}(r) - \varphi_{0\mathrm{WCA}}(r)\right)\right] \tag{54}$$

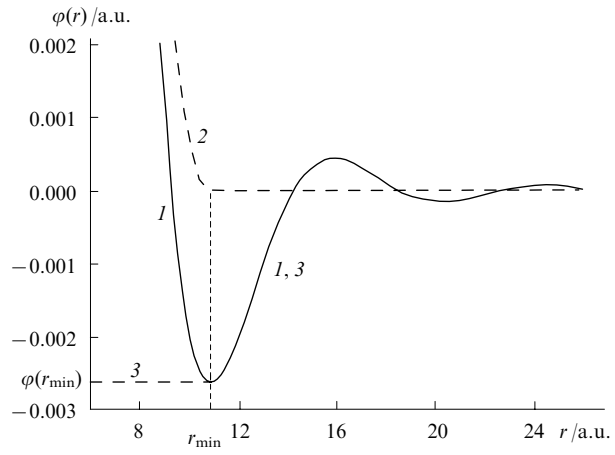


Figure 2. Effective pair potential of ion–ion interaction (*1*), pair potential of the reference system (*2*) and perturbation (*3*) obtained for liquid potassium at $1/\rho = 529$ a.u.[98]

$$S_{0\mathrm{WCA}}(q) = S_{\mathrm{HS}}(q) + \rho B(q) \tag{55}$$

where $B(q)$ is the Fourier transform of the blip function $B(r)$ which represents the deviation of $g_{0\mathrm{WCA}}(r)$ from $g_{\mathrm{HS}}(r)$

$$B(r) = g_{0\mathrm{WCA}}(r) - g_{\mathrm{HS}}(r) \tag{56}$$

Traditionally,[22] the σ_{WCA} value is determined from the condition

$$\int_0^{\infty} B(r) r^2 \mathrm{d}r = 0 \tag{57}$$

A correct illustration of meeting condition (57) is presented in Fig. 3.

Expression (57) can be written as follows:

$$\int_0^{\infty} y_{\mathrm{HS}}(r)\left[\exp\left(-\beta\varphi_{0\mathrm{WCA}}(r)\right) - \exp\left(-\beta\varphi_{\mathrm{HS}}(r)\right)\right] r^2 \mathrm{d}r = 0 \tag{58}$$

A correction to Eqn (58), *viz.*, replacement of the function $y_{\mathrm{HS}}(r)$ by its first derivative with respect to σ, was proposed [99]

$$\int_0^{\infty} \frac{\partial y_{\mathrm{HS}}(r)}{\partial\sigma}\left[\exp\left(-\beta\varphi_{0\mathrm{WCA}}(r)\right) - \exp\left(-\beta\varphi_{\mathrm{HS}}(r)\right)\right] r^2 \mathrm{d}r = 0 \tag{59}$$

Expression (59) represents a thermodynamically consistent condition for the determination of σ.

A modified WCA separation of $\varphi(r)$ was proposed:[100]

$$\varphi_{0\mathrm{WCA}^*}(r) = \begin{cases} \varphi(r) - V(r), & r < r^* \\ 0, & r \geqslant r^* \end{cases} \tag{60}$$

$$\varphi_{1\mathrm{WCA}^*}(r) = \begin{cases} V(r), & r < r^* \\ \varphi(r), & r \geqslant r^* \end{cases}$$

where $r^* = \mathrm{Min}(a, r_{\min})$, a is the mean distance between nearest neighbours,

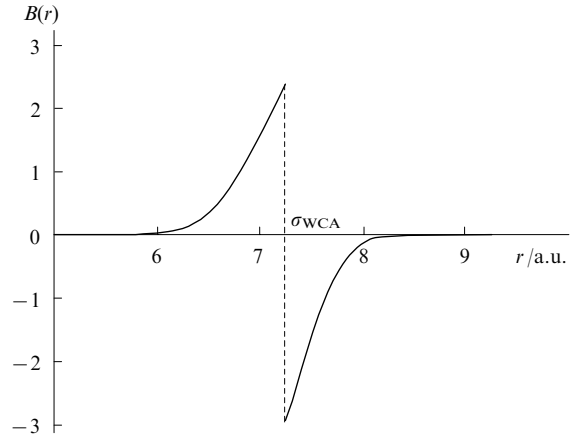


Figure 3. Blip function that meets condition (57).‡

‡ N E Dubinin, Candidate Thesis in Physical and Mathematical Sciences, Institute of Metallurgy, Ural Branch of the Russian Academy of Sciences, Ekaterinburg, 1995 (in Russian).

$$V(r) = \varphi(r^*) + (r - r^*)\left(\frac{\partial\varphi(r)}{\partial r}\right)_{r=r^*} \quad (61)$$

At $r^* = r_{\min}$, the derivative on the right-hand side of expression (61) becomes equal to zero and the separation (60) is reduced to separation (51). Note that the coordinate r^* is intermediate between r_0 and $r_{\min}$.

The thermodynamic properties of the WCA reference system can be determined using the expressions for its structure functions. The expression for $F_{0\mathrm{WCA}}$ was derived [22] by functional differentiation using the approximation (52)

$$F_{0\mathrm{WCA}} = F_{\mathrm{HS}} - 2\pi\rho k_{\mathrm{B}}T\int_0^\infty B(r)r^2\mathrm{d}r \quad (62)$$

The entropy of the reference system in the WCA method is given by [101, 102]

$$S_{0\mathrm{WCA}} = S_{\mathrm{HS}} + \frac{2\pi\rho}{T}\int_0^\infty \varphi_{0\mathrm{WCA}}(r)g_{0\mathrm{WCA}}(r)r^2\mathrm{d}r + \\ +2\pi\rho k_{\mathrm{B}}\int_0^\infty B(r)r^2\mathrm{d}r \quad (63)$$

If condition (57) is met, the rightmost terms on the right-hand side in expressions (62) and (63) vanish.

IV. The variational method

The variational method is based on the fact that the Helmholtz free energy of a system should not be higher than $F^{(1)}_{\mathrm{HTA}}$; *i.e.*, the Gibbs–Bogolyubov inequality is valid

$$F \leqslant F_0 + \langle U_1\rangle_0 \quad (64)$$

The right-hand side, F_{var}, is called the upper bound of the Helmholtz free energy of the system in question. The minimum value of F_{var} is achieved by varying parameters of the reference system.

This inequality was derived [103] as a continuation of Zwanzig's theory by proving the fact that the sum of all terms in expression (7) except the zero- and first-order ones will makes negative contributions.

For the liquid metals described within the framework of the NFE approximation, additional electronic contributions to the internal energy (U_{e}) and entropy (S_{e}) on the right-hand side of inequality (64) should be taken into account:

$$F \leqslant F_0 + U_{\mathrm{e}} + \langle U_1\rangle_0 - TS_{\mathrm{e}} \quad (65)$$

The general expression for calculating the electronic contribution to the entropy has the form

$$S_{\mathrm{e}} = (\pi k_{\mathrm{B}})^2\frac{Tn(\varepsilon_{\mathrm{F}})}{3} \quad (66)$$

where $n(\varepsilon)$ is the density of electronic states and ε_{F} is the Fermi energy. For free-electron gas (eg) one has

$$\varepsilon_{\mathrm{F}} = \frac{k_{\mathrm{F}}^2}{2}$$

where

$$k_{\mathrm{F}} = (3z\rho\pi^2)^{1/3}$$

is the Fermi wave vector.

As a result, one gets

$$S_{\mathrm{eg}} = zT\left(\frac{\pi k_{\mathrm{B}}}{k_{\mathrm{F}}}\right)^2 \quad (67)$$

This is a commonly accepted expression for the S_{e} contribution for simple metals.

Consideration of the potential energy in the inequality (65) in the reciprocal space gives the following contributions to the upper bound of the Helmholtz free energy of the metal:

$$F_{\mathrm{var-NFE}} = \frac{3}{2}k_{\mathrm{B}}T + E_{\mathrm{eg}} + E_{\mathrm{f}} + E_{\mathrm{bs}} + E_{\mathrm{M}} - T(S_0 + S_{\mathrm{e}}) \quad (68)$$

Here E_{eg} is the free-electron gas energy

$$E_{\mathrm{eg}} = \frac{3}{10}zk_{\mathrm{F}}^2 - \frac{z}{2}\left(\frac{\pi k_{\mathrm{B}}T}{k_{\mathrm{F}}}\right)^2 + E_{\mathrm{ec}} \quad (69)$$

(E_{ec} is the exchange-correlation energy), E_{f} is the contribution of the first-order perturbation theory with respect to the pseudopotential

$$E_{\mathrm{f}} = z\lim_{q\to 0}\left(\omega(q) + \frac{4\pi\rho z}{q^2}\right) \quad (70)$$

E_{bs} is the energy of the band structure (second-order contribution)

$$E_{\mathrm{bs}} = \frac{1}{2\pi^2\rho}\int_0^\infty S_0(q)F(q)q^2\mathrm{d}q \quad (71)$$

E_{M} is the Madelung energy (the contribution originating from ion–ion Coulomb interaction)

$$E_{\mathrm{M}} = \frac{z^2}{\pi}\int_0^\infty \big(S_0(q) - 1\big)\mathrm{d}q \quad (72)$$

Initially, studies of liquid metals were carried out using the simplest version of the variational method with the HS reference system. It was for the first time applied by Jones [104] to pure liquid metals and by Stroud [105] to binary alloys.

The Ross version [106] of the IP model was for the first time used within the framework of the variational method in a study [107] of liquid metals in which the thermodynamic properties of liquid lithium were calculated using the first-principle pseudopotential.

Now we will dwell on the application of the IP model in Ref. 106 in more detail. Starting with Eqn (8), expression (12) can be transformed to

$$F^{(1)}_{\mathrm{HTA}} = \frac{3}{2}k_{\mathrm{B}}T + \langle U\rangle_0 - TS_0 \quad (73)$$

where

$$\langle U\rangle_0 = 2\pi\rho\int_0^\infty \varphi(r)g_0(r)r^2\mathrm{d}r \quad (74)$$

Taking into account expression (73), the right-hand side of the inequality (64) for any reference system can be written as follows:

$$F_{\text{var}} = \frac{3}{2}k_{\text{B}}T - TS_0 + 2\pi\rho \int_0^\infty \varphi(r)g_0(r)r^2\mathrm{d}r \tag{75}$$

or

$$F_{\text{var}} = F_{\text{HS}} - T\Delta S_0 + 2\pi\rho \int_0^\infty \varphi(r)g_0(r)r^2\mathrm{d}r \tag{76}$$

where ΔS_0 is the difference between the entropy of the reference system and S_{HS}

$$S_0 = S_{\text{HS}} + \Delta S_0 \tag{77}$$

To determine ΔS_0, Ross [106] used the nesting of one variational procedure into another one, which involves simultaneous consideration of the IP model as reference system for the system under study and the HS model as reference system for the IP model. In this case, one can write

$$F \leqslant F_0 + 2\pi\rho \int_0^\infty \varphi_1(r)g_0(r)r^2\mathrm{d}r \tag{78}$$

$$F_0 \leqslant F_{\text{HS}} + 2\pi\rho \int_0^\infty \varphi_0(r)g_{\text{HS}}(r)r^2\mathrm{d}r \tag{79}$$

Here the quantities labelled with the subscript '0' refer to the IP model. Summing expressions (78) and (79), one gets the following expression for F_{var}

$$F_{\text{var}} = F_{\text{HS}} + 2\pi\rho \int_0^\infty \varphi_0(r)g_{\text{HS}}(r)r^2\mathrm{d}r + 2\pi\rho \int_0^\infty \varphi_1(r)g_0(r)r^2\mathrm{d}r \tag{80}$$

It follows that

$$F_{\text{var}} = F_{\text{HS}} + 2\pi\rho \int_0^\infty \varphi_0(r)\left[g_{\text{HS}}(r) - g_0(r)\right]r^2\mathrm{d}r + 2\pi\rho \int_0^\infty \varphi(r)g_0(r)r^2\mathrm{d}r \tag{81}$$

However, expression (81) was not then used in Ref. 106. Instead, the ΔS_0 value was determined by fitting to the results of computer simulation and it was accepted that

$$g_0(r) = g_{\text{HS}}(r)$$

Relation (76) thus transformed to

$$F_{\text{var}} = F_{\text{HS}} - T\Delta S_{\text{IP}} + 2\pi\rho \int_0^\infty \varphi(r)g_{\text{HS}}(r)r^2\mathrm{d}r \tag{82}$$

where

$$\Delta S_{\text{IP}} = k_{\text{B}}\left(\frac{\eta^4}{2} + \eta^2 + \frac{\eta}{2}\right) \tag{83}$$

It is noteworthy that, eventually, expression (82) is minimized only with respect to the HS diameter without using parameters of the IP model. It differs from the expression for F_{var} with the HS reference system only in the term $-T\Delta S_0$. In view of the approximations mentioned above the approach proposed by Ross cannot be treated as rigorous application of the IP model as reference system. Probably, that is why this approach was named in abstract manner 'variational method with soft-sphere (SS) reference system'. Since then, the approach has been used in combination with the NFE approximation in studies of the melting curve of aluminium,[108] melting of alkali metals at high pressures [109] and for systematic studies of the structure and thermodynamics of various liquid metals (Li, Na, K, Rb, Cs, Mg, Cd, Al, In, Tl, Pb).[110] For aluminium a comparative study of the accuracy of the SS, HS and OCP reference systems revealed [107] the advantage of the SS system. For lithium [108] and other alkali metals (Na, K, Rb, Cs),[109] the best results were obtained with the OCP reference system. Clearly, this can be explained by the fact that for aluminium the repulsive part of the pair potential is steeper than for the alkali metals and this respectively holds for the SS and OCP reference systems. It was also reported that for all metals under study the SS reference system gives better results than the CHS reference system.[110]

The Ross approach was used to derive analytical expressions for the equation of state and thermodynamic properties of a liquid with multi-Yukawa potential.[111]

Kitamura [112–114] used expression (82) with a Young–Rogers correction [54] instead of the ΔS_{IP} term [see Eqn (83)] to construct the effective pair interaction for the description of mercury by combining the 'spin–orbit corrected scalar relativistic coupled cluster' approach [115] and an empirically modified pseudopotential [116] rather than the NFE approximation inapplicable in this case.

Greeff [117, 118] used a rigorous approach to the description of the IP reference system in the variational method, where

$$F_0 = F_{\text{IP}} \text{ and } g_0(r) = g_{\text{IP}}(r)$$

(expressions for F_{IP} and $g_{\text{IP}}(r)$ were taken from Ref. 54). He calculated the Helmholtz free energy of liquid magnesium and copper up to the third-order of HTA in perturbation theory and showed that the second-order perturbation theory provides a sufficient accuracy. This agrees with expression (10). In these studies, the effective pair potential was described using the Voter–Chen version [119] of the embedded atom method (EAM).

In addition to the studies mentioned above the OCP reference system was used in some other variational calculations of liquid metals in the NFE approximation.[62, 120–126] This model gave a better description of the structure factor and Helmholtz free energy than the HS model for sodium and a poorer description for aluminium.[120] The reason is analogous to that discussed above in the context of the results obtained with the OCP and SS reference systems.[107–109]

The results of variational calculations with the CHS reference system in the NFE approximation were compared with those obtained using the HS and OCP reference systems.[127–132] In Ref. 127, minimization was performed only with respect to the parameter σ at fixed Γ value. The results of the Helmholtz free energy calculations for liquid alkali metals appeared to be poorer than the results obtained using the HS and OCP reference systems, but the calculated structure factors were in better agreement with experimental values. The first two-parameter minimization [128] gave better results for calculations of the thermodynamic and structural properties of both alkali and polyvalent metals compared to calculations using the HS reference system and calculations using the OCP reference

Table 1. Excess entropies of liquid simple metals near melting points.[128]

Metal	$-S_{ex}/k_B$			
	OCP	HS	CHS	experiment
Na	3.74	3.94	3.75	3.45
K	3.74	4.04	3.83	3.45
Rb	3.74	4.04	3.81	3.63
Cs	3.74	4.13	3.95	3.56
Mg	3.74	3.94	3.71	3.29
Al	3.74	4.33	3.71	3.49

system for polyvalent metals. The values of the excess entropy

$$S_{ex} = S - S_{ig}$$

are listed in Table 1. Although full-scale minimization in both parameters of the reference system was performed, calculations using the OCP and HS reference systems were carried out independently instead of considering them as limiting cases of the CHS reference system. The reason is inefficiency (see Section III) of the CHS–MSA approximation at $\eta = 0$, which corresponds to the OCP–MSA case. Therefore, the structure factor and entropy of each reference system to be compared were obtained in different manner, namely, in the PY approximation for the HS model and in the MSA approximation for the CHS model. Tabulated values were used for the OCP model. Eventually, the results obtained were affected by not only the reference system, but also the approximation used to describe it.

This uncertainty is characteristic of most comparative studies of different reference systems. A comparison from a unified point of view was reported only for (i) the HS and SS models (owing to specific features of the description of the latter, see above) and (ii) the HS, CHS and OCP models[132] owing the existence of analytical description of the CHS model[69] (it is transformed to the OCP model at $\eta = 0$ and to the HS model at $\Gamma = 0$). The rigorous approach[132] allowed one to minimize the Helmholtz free energy to η and Γ and to determine two minima of the Helmholtz free energy in the vicinity of the melting point for each metal studied. One minimum is near $\eta = 0$ (results corresponding to this minimum will be denoted 'CHS1' and those corresponding to the second minimum will be denoted 'CHS2').

Calculations[132] of thermodynamic properties revealed no advantages of the CHS reference system as compared to the HS and OCP ones. In particular, Table 2 shows that at $\Gamma = 0$ the best agreement with experimental data is observed for sodium and for the entropies of all alkali metals except lithium. For all polyvalent metals, the deeper minimum of $F(\eta, \Gamma)$ is at $\eta = 0$, *i.e.*, CHS1 corresponds to the OCP model. The results of calculations of F and E values for with respect to the points CHS1, CHS2 and $\Gamma = 0$ are much closer to one another than to experimental data. Contrary to this, the scatter of experimental data for entropy precludes unambiguous conclusions about preferableness of a particular result.

Comparative studies of simple metals using the HS and HCY reference systems were reported.[133, 134] Table 3 lists the Helmholtz free energy values. The results obtained in each of the two studies using different reference systems are much closer to each other rather than to experimental data. This also precludes the determination of the more preferable reference system. Entropy calculations (Table 4) with the HCY reference system gave better results for all metals except lead.[133] In the other study,[134] the HCY results are better only for polyvalent metals, whereas the HS reference system appears to be more appropriate in the case of alkali metals (for these systems, the results of Ref. 134 are closer to experimental data than the results obtained in Ref. 133).

Liquid transition metals were studied[135] using the HCY reference system in the Wills–Harrison (WH) approximation.[136] Namely, the $g(r)$, $S(q)$, F and S values for 3d metals were calculated. For all metals studied, calculations with the HCY reference system led to deeper minima of the Helmholtz free energy and to much better agreement of the position of the first peak of the function $g(r)$ with experimental data compared to calculations with the HS reference system. As to the entropy calculations, from the data in

Table 2. Thermodynamic properties of liquid alkali metals near melting points.[132]

Metal	PPP	$-F$/a.u.		$-E$/a.u.		$-S_{ex}/k_B$	
		I	II	I	II	I	II
Li	$\eta = 0$	0.2660	0.265	0.2584	0.254	3.98	3.7, 3.54
	CHS1	0.2660		0.2584		3.99	
	CHS2	0.2656		0.2586		4.41	
	$\Gamma = 0$	0.2647		0.2575		4.27	
Na	$\eta = 0$	0.2357	0.2352	0.2271	0.223	3.89	3.45
	CHS1	0.2358		0.2271		3.88	
	CHS2	0.2355		0.2273		4.29	
	$\Gamma = 0$	0.2349		0.2261		3.72	
K	$\eta = 0$	0.2011	0.201	0.1918	0.1956	3.80	3.45
	CHS1	0.2011		0.1918		3.80	
	CHS2	0.2008		0.1921		4.25	
	$\Gamma = 0$	0.2004		0.1910		3.72	
Rb	$\eta = 0$	0.1929	0.193	0.1829	0.1870	3.71	3.63
	CHS1	0.1929		0.1829		3.68	
	CHS2	0.1926		0.1831		4.18	
	$\Gamma = 0$	0.1922		0.1822		3.67	
Cs	$\eta = 0$	0.1810	0.182	0.1707	0.1757	3.79	3.56
	CHS1	0.1811		0.1707		3.79	
	CHS2	0.1808		0.1708		4.16	
	$\Gamma = 0$	0.1803		0.1700		3.78	

Note. Notations are as follows: PPP is point in the parameter plane, I is calculation and II is experiment.

Table 3. Helmholtz free energies of liquid simple metals near melting points.[133, 134]

Metal	$-F$/a.u.				
	HS [133]	HCY [133]	HS [134]	HCY [134]	experiment
Na	0.23526	0.23561	0.24216	0.24263	0.2352
K	0.20066	0.20102	0.20214	0.20233	0.201
Rb	–	–	0.19103	0.19122	0.193
Cs	0.18057	0.18098	–	–	0.182
Mg	0.89628	0.89676	0.90763	0.90809	0.905
Al	2.07756	2.07784	2.11546	2.11570	2.060
Pb	3.59027	3.59429	–	–	3.656

Table 4. Excess entropies of liquid simple metals near melting points.

Metal	$-S_{ex}/k_B$				
	HS [133]	HCY [133]	HS [134]	HCY [134]	experiment
Na	4.08	3.82	3.54	3.37	3.45 3.55
K	4.04	3.76	3.50	3.33	3.45 3.61
Rb	–	–	3.59	3.43	3.63
Cs	4.07	3.81	–	–	3.56
Mg	4.34	4.18	4.27	4.10	3.45
Ca	3.97	3.79	–	–	3.27
Al	4.33	4.19	4.29	4.18	3.60
Pb	4.16	4.37	–	–	4.10

Table 5. Entropies of liquid transition metals near melting points.[135]

Metal	S/k_B		
	HS	HCY	experiment
Ti	12.01	12.42	12.01
V	11.50	12.15	12.08
Cr	11.48	12.00	11.58
Mn	10.62	11.14	12.05
Fe	11.61	11.93	12.11
Co	12.22	12.44	12.08
Ni	12.49	12.76	11.69
Zr	11.69	12.54	13.24

Table 3 reported in Ref. 135 it remains unclear which reference system gives better agreement with the experiment; therefore, in this review we present the results [135] in the form that allows one to carry out such a comparison (Table 5). As can be seen, the HCY reference system is more appropriate only for half the number of the metals studied.

More recently, the WH approach was used in the variational calculations of the Helmholtz free energies of 3d, 4d and 5d metals with the HS reference system.[137] Also, transition metals were calculated using the CHS [138, 139] and the OCP [140] reference systems. The Bretonnet–Silbert model pseudopotential [141] proposed for the description of transition metals was also used.[138]

Recently, variational calculations have been carried out with the SW reference system which does not lead to a global minimum of the Helmholtz free energy as function of three SW parameters, but gives good results in finding local F minima when calculating the thermodynamic properties of alkali metals.[79–81] Tables in the studies cited include incorrect data; corrected results are collected in Table 6. However, it is still impossible to unambiguously conclude which reference system, SW or HS, is more preferable.

By and large, the authors of most studies cited above agree that in most cases, variational calculations of liquid metals using non-HS models as reference system improve the results obtained. However, we believe this is a minor improvement. Although the HS model is rough, the results obtained with the HS reference system are at least comparable in accuracy with the results obtained using other reference systems. In addition, it is commonly accepted that the deeper the minimum in F (*i.e.*, the lower F_{var}) achieved in the course of variational calculations the better the results obtained. However, if the F values calculated using both reference systems are lower than experimental value, it is unclear whether this interpretation is correct. Considering variational calculations with different reference systems, it seems appropriate to analyze the thermodynamic functions of mixing in binary melts, but to date, none of the reference systems, except HS, has been extended to binary mixtures.§

Table 6. Thermodynamic properties of liquid sodium and potassium at 373 K according to Refs 79–81.

Property	HS	SW		Experiment
		RPA	MSA	
For sodium				
$-F$/eV	6.397	6.464	6.426	6.399
$-E$/eV	6.156	6.232	6.190	6.149
S/k_B	7.49	7.22	7.38	7.79
For potassium				
$-F$/eV	5.413	5.451	–	5.475
$-E$/eV	5.119	5.169	–	5.170
S/k_B	9.15	8.77	–	9.45

Therefore, owing to simplicity in usage and to the possibility of being applied to binary systems, variational calculations using the HS reference system remain a reliable tool for investigation of liquid metals and liquid binary metal alloys under normal conditions as well in the supercooled or superheated state.[144–164] Interestingly, complication of the model pseudopotential is not necessarily followed by improvement of the results of calculations (Fig. 4).[164]

Extension of the variational method with the HS reference system to n-component mixtures using corresponding structure functions [35, 36] was done by Vatolin *et al.*,[165] who applied the technique to ternary alkali metal melts.[165–167]

Although the HS reference system makes it possible to obtain unexpectedly accurate results, it can be improved, namely, Mon proposed [168] that, since the hard spheres do not overlap, the configuration integral in the HS model should not be calculated over the entire volume of the system (V). As is known, the left-hand side of expression (1) looks as follows:

$$\exp(-\beta F_1) = \frac{1}{N}\frac{\int\limits_V \ldots \int\limits_V \exp(-\beta U)\mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_N}{\int\limits_V \ldots \int\limits_V \exp(-\beta U_0)\mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_N} = \tag{84}$$

$$= \frac{1}{N}\frac{\int\limits_\Omega \exp(-\beta U)}{\int\limits_\Omega \exp(-\beta U_0)}$$

the symbol $\int\limits_\Omega$ means the integral over the entire configuration phase space. If one deals with the HS reference system,

§ The only case where the variational method was applied to binary melts with non-HS reference system was reported by Hafner *et al.*,[142, 143] who used the HCY single-component reference system.

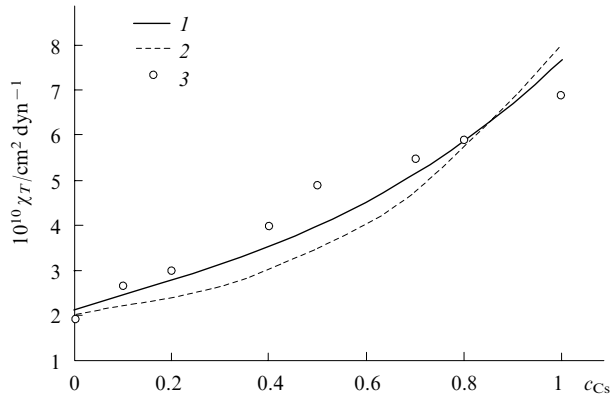


Figure 4. Isothermal compressibility (χ_T) of Na–Cs melt at 373 K obtained from the variational calculations using the HS reference system for the local pseudopotential (*1*) and nonlocal pseudopotential with inclusion of higher-order perturbation corrections (*2*); experimental data (*3*).[164]

Mon's idea [168] is realized by replacing the denominator in expression (84) by

$$\int_{\Omega_{HS}} \exp(-\beta U_{HS})$$

where Ω_{HS} is the configuration phase space containing no hard-sphere overlaps. This gives rise to an additional contribution

$$\frac{k_B T}{N} \ln \frac{\int_{\Omega_{HS}} \exp(-\beta U)}{\int_{\Omega} \exp(-\beta U)}$$

on the right-hand side of expression (7).

Mon numerically calculated his correction by the Monte Carlo method and included it in the variational calculations of model liquids with the IP pair potential [169, 170] and liquid metals [171] using the HS reference system. The new approach made it possible to improve [171] the results obtained earlier [120] for sodium and aluminium using the HS and OCP reference systems.

Ben-Amotz and Stell [172] derived an analytical expression for Mon's correction in the approximation (2)

$$-2\pi\rho k_B T \int_0^{\sigma} g(r) r^2 \mathrm{d}r$$

For a model liquid with the IP pair potential, this correction can be calculated using expression (54) and the Lado condition [99] (59). Theory thus proposed was then applied in studies of liquid gallium [173,174] using the potential $\varphi(r)$ based on a first-principle pseudopotential [175] that was thoroughly examined by Wu *et al.*[176, 177] and proved itself in a molecular dynamics simulation.[178] When the Lado condition was used in Refs. 173 and 174, the repulsive part $[\varphi_{0WCA}(r)]$ of the effective potential $\varphi(r)$ was taken. Combining the variational method and Lado condition makes the Ben-Amotz and Stell approach [172] internally inconsistent, which manifests itself in the appearance of two different values of the HS diameter in the course of one calculation.

V. The Weeks – Chandler – Andersen method

Like the variational method, the WCA method is a first-order method in the HTA and, therefore, the Helmholtz free energy is given by

$$F_{WCA} = F_{0WCA} + 2\pi\rho \int_0^{\infty} \varphi_{1WCA}(r) g_{0WCA}(r) r^2 \mathrm{d}r \qquad (85)$$

where $\varphi_{1WCA}(r)$ is defined by expression (51) and $g_{0WCA}(r)$ and $F_{0WCA}(r)$ are respectively defined by Eqs (54) and (62). Using these approximations, Eqn (85) can be transformed to

$$F_{WCA} = F_{var-HS} + 2\pi\rho \left\{ [\varphi(r_{min}) - k_B T] \int_0^{\infty} B(r) r^2 \mathrm{d}r - \int_{\sigma}^{r_{min}} \varphi_{0WCA}(r) g_{HS}(r) r^2 \mathrm{d}r \right\} \qquad (86)$$

where F_{var-HS} is F_{var} (see expression (75)) calculated using the HS reference system

$$F_{var-HS} = \frac{3}{2} k_B T - TS_{HS} + 2\pi\rho \int_0^{\infty} \varphi(r) g_{HS}(r) r^2 \mathrm{d}r \qquad (87)$$

If condition (57) is met, expression (86) is simplified and takes the form

$$F_{WCA} = F_{var-HS} - 2\pi\rho \int_{\sigma}^{r_{min}} \varphi_{0WCA}(r) g_{HS}(r) r^2 \mathrm{d}r \qquad (88)$$

Another method of determination of the HS diameter involves [179] minimization of the right-hand side of expression (86) with respect to this parameter. It was used in the calculations [98] of thermodynamic properties of simple metals using a first-principle pseudopotential.[180]

The BH method and variational calculations with the HS reference system are less accurate in the description of the structure and thermodynamic properties of liquid metals compared to the WCA method irrespective of the procedure for the determination of σ.[179] Earlier,[181] a comparison of the WCA method [using only one procedure for the determination of σ, namely, from condition (57)] and variational calculations with the HS reference system led to a similar conclusion.

In some cases, only the method for the determination of σ is taken from the WCA theory. For instance, the conditions (57) and (59) were used in calculations [182] of the diffusion coefficient of liquid sodium using the HS model.

The WCA method was extended to binary mixtures.[183] The complexity of transition to binary systems is due to the lack of trivial generalization of the condition (57) when using the additive HS model for which meeting the following condition is impossible

$$\int_0^{\infty} B_{11}(r) r^2 \mathrm{d}r = \int_0^{\infty} B_{22}(r) r^2 \mathrm{d}r = \int_0^{\infty} B_{12}(r) r^2 \mathrm{d}r = 0 \qquad (89)$$

where $B_{ij}(r)$ is the partial blip function.

This problem was solved in different manner. Sandler [184] proposed to minimize

$$\sum_{i,j=1}^{2} c_i c_j \left| \int_0^{\infty} B_{ij}(r) r^2 \mathrm{d}r \right|$$

(c_i is the concentration of the ith component) with respect to the partial HS diameters σ_{11} and σ_{22}. In another study,[185] the condition (89) was met by fitting the minimum of the partial pair potential $\varphi_{12}(r_{\min 12})$ in such a manner that the condition

$$\int_0^\infty B_{11}(r)r^2\mathrm{d}r = \int_0^\infty B_{22}(r)r^2\mathrm{d}r = 0 \qquad (90)$$

be valid.

The authors of other studies [186, 187] used the condition (90), and expression (86) included the additional contribution of $B_{12}(r)$. Kahl [188] proposed to use the model of non-additive hard spheres, which eliminates the problem of meeting condition (89) but makes calculations much more labour-consuming. Probably, the best solution to the problem in question is to determine the parameters of the HS model for binary systems using a method proposed [179] for pure metals.

As for pure liquid metals, WCA calculations of the structure [185, 188, 189] and thermodynamic properties [186, 187] of binary metal melts gave more accurate results than the variational method with the HS reference system. In particular, the values of the excess entropy of mixing of the Na–K melt obtained from WCA calculations [187] agree with experimental data much better than those obtained by the variational method with the same pseudopotential (Fig. 5).

The structure factors $S_{ij}(q)$ of K–Cs melts of different compositions were studied [185] by not only the conventional [22] WCA method, but also by its extension to binary mixtures, which was proposed by Jacobs and Andersen [190] (JA) for metals and includes a correction, $S_{0\mathrm{WCA}}(q)$:

$$S_{0\mathrm{WCA-JA}}(q) = \frac{S_{\mathrm{HS}}(q)}{1+\beta\rho S_{\mathrm{HS}}(q)B(q)} \qquad (91)$$

The JA method significantly improves the results of the WCA calculations for $S_{ij}(q)$ at small q values.

The WCA approach modified by Kang *et al.*[100] has been applied to liquid metals since the early 2000s.[191, 192] It was extended [192] to solid metals and thus gave an impetus to the development of a new research avenue [193–196] which combines the WCA method and the fundamental measure density functional theory (FMDFT) [197, 198] and involves the description of the pair interaction within the framework of the EAM.[199–203]

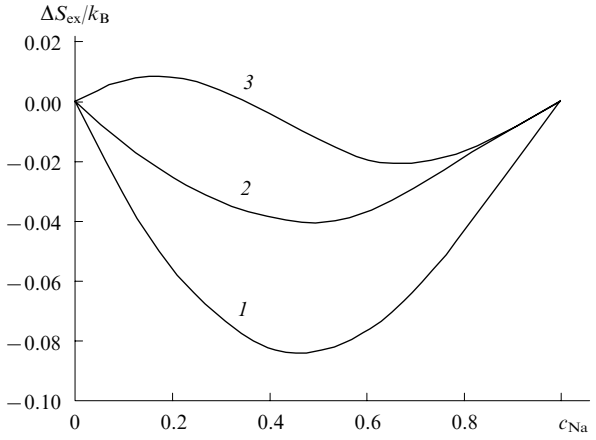


Figure 5. Excess entropy of mixing of a Na–K melt at 373 K. Obtained from variational calculations (*1*) and WCA calculations (*2*); experimental data (*3*).

Yet another modification of the WCA method,[204] namely, approximation of the blip function by tangent lines, is called linearized WCA (LWCA) and has been widely used recently for both pure liquid metals and binary metal melts.[205–215]

VI. TPT–FT calculations

Most TPT–FT studies of liquid metals and alloys are restricted to analysis of structure functions. The simplest version of this approach implies the use of model potentials $\varphi(r)$ with the HS reference system. In particular, the RPA was applied [76, 216] to the Cummings potential[217] and the MDA was used with the HCY potential. A combination of the RPA with the SW model is most widely used. The approach has been applied to liquid metals since 1974 when it was used [218] to calculate the structure functions of liquid mercury and aluminium. Silbert and Young [219] calculated the structure factors of the liquid metals having a shoulder near the first peak of the structure factor (the SW depth was assumed to be positive, *i.e.*, the 'well' was replaced by a 'step' or a 'barrier'). The SW–RPA was extended to binary metal melts [220] and is intensively used at present.[221–228]

Numerous RPA–NFE studies were carried out. Evans and Schirmacher, who reported the pioneering study,[26] used the HS model as reference system and the σ value determined from the condition (57). Evans and Sluckin [60] worked with the OCP instead of HS reference system and showed that the latter gives better results for alkali metals. When using the RPA with the HS reference system the HS diameter is sometimes determined [229–231] from the following relationship that appears in the LWCA approximation:

$$\varphi(\sigma) - \varphi(r_{\min}) \approx k_{\mathrm{B}}T \qquad (92)$$

The authors of Refs 230 and 231 reported the results obtained for the structure factors and calculated the thermodynamic properties, but the computational procedure was not described.

In some cases, the RPA was used [130, 232–236] with the OCP reference system the parameter of which was determined by fitting to experimental data. Parameters of the CHS as reference system used with the RPA were determined analogously.[67, 237]

Pastore and Tosi reported an ORPA study [238] with the OCP reference system. The necessary σ value was assumed to be equal to the maximum r value at which the $g(r)$ function found by computer simulation is zero.

Probably, the most promising direction of the development of the TPT for metals is to combine the HTA and TPT–FT methods. In this context, mention may be made of a pioneering study [239] where the WCA–JA approach was used in combination with the MDA. By and large, a combination of the WCA method with ORPA was most widely used. Technical aspects of practical implementation of this approach in the case of the NFE approximation were considered in detail by Hafner and Kahl.[240, 241] Such an approach was successfully used in studies of the structure of pure liquid metals and semimetals.[240–247] The WCA–ORPA combination better describes the structure of liquid metals than the WCA method. An interesting

feature of Ref. 247 consists in the use of the HS reference system obtained by numerical solution of the OZ equation and analysis of the influence of the choice of the integral-equation approximation of a given solution on the final results.

Next, the WCA–ORPA approach was utilized in studies of the structure of liquid transition metals.[248, 249] It was shown[249] that the results of calculations by the WCA–ORPA and WCA–JA–ORPA methods provide good illustrations of the influence of attractive and repulsive forces on the structure of liquids. The inclusion of attractive forces (ORPA) leads to an appreciable increase in the height of the first peak of the structure factor in the conventional WCA approximation. In the WCA–JA approximation, the heights of the first and second peaks of the structure factor are close to the observed values.

Extension of the NFE–WCA–ORPA approach to binary systems led to studies of the partial and total structure factors of K–Rb and K–Cs melts,[250] as well as Al–Ge melt.[251–253] As for pure metals, the WCA–ORPA approach better describes the structure of the liquid alloys studied compared to the WCA. Differences between the calculated[253] $S(q)$ values and the results of a molecular dynamics simulation appeared to be insignificant compared to the differences between the results of X-ray diffraction and neutron diffraction experments. A study[254] on the structure of a Li–Na melt was probably carried out by the NFE–WCA–RPA method (no methodological details concerning the WCA calculations were reported).

All publications metioned above were aimed to study the structure factors of metal melts. The only example of application of the WCA–ORPA approach to investigation of thermodynamic properties is provided by Ref. 255. The internal energy values of six equiatomic alkali metal melts at 373 K obtained in that study are listed in Table 7. As can be seen, the WCA–ORPA approach gives somewhat better agreement with experimental data than the WCA calculations.

Not only the WCA–ORPA–NFE, but also variational calculations with the ORPA were reported,[256, 257] with the HS[256] and OCP[257] reference system. The authors of Ref. 257 used a specific ORPA version[258] where the parameter σ is replaced by r_c, the parameter determined by minimizing F_{RPA}

$$\frac{\partial F_{RPA}}{\partial r_c} = 0 \qquad (93)$$

Formally, this approach can be treated as more versatile kind of the ORPA because it is applicable to all reference systems rather than hard-core or related (*e.g.*, WCA) ones. However, at present it is obviously needed only for two reference systems (OCP and IP in the Young–Rogers interpretation[54]) because no attempts to use other non-σ-based reference systems have been reported so far.

Table 7. Internal energies ($-\Delta E$/eV) of equiatomic alkali metal melts.[255]

Alloy	WCA	ORPA	Experiment
Na–K	0.0068	0.0071	0.0076
Na–Rb	0.015	0.014	0.013
Na–Cs	0.0292	0.0255	0.0095
K–Rb	0.0014	0.0013	0.0013
K–Cs	0.0053	0.0041	0.0012
Rb–Cs	0.0013	0.0005	−0.0014

VII. Conclusion

In this review we considered the most important aspects of application of the thermodynamic perturbation theory in studies of the structure and thermodynamic properties of metal melts. Various TPT methods and reference systems were analyzed. We demonstrated their efficiency in relation to a wide range of liquid metals and binary alloys. Interestingly, the efficiency of the TPT in studies of the metallic state is also indicated by the development of modern approaches to application of this theory to metals in the crystalline state[192, 194–196] and to metallic nanosystems.[259]

We believe that possible evolution paths of the TPT, aimed at improving calculations of the physicochemical properties of metal melts, may include:

— more intensive joint HTA–TPT–FT studies;

— extended application of the second-order HTA;

— the inclusion of Mon's correction[168] in calculations using the HC reference systems;

— extension of the variational method with non-HS reference systems to binary mixtures;

— elaboration of the variational method with new reference systems for which analytical expressions are available (*e.g.*, double-Yukawa,[260–262] multi-Yukawa[76, 111, 263] as well as the Lennard–Jones[264] models);

— application of new TPT methods (*e.g.*, those proposed in Refs 265–268);

— calculations using new or modified pair potentials for elements[269, 270] including transition metals.[271, 272]

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