# Journal Name

# ARTICLE TYPE

Cite this: DOI: 00.0000/xxxxxxxxx

Accurate Elemental Boiling Points from First Principles: Supporting Information

Jan-Michael Mewes\**a*,*b* and Odile R. Smits<sup>*b*</sup>

# 1 Supporting Information

In addition to the information presented on the following pages, the spreadsheets (in open-document format) used to conduct all calculations starting from the raw data (simulation averages) to the final boiling points are available upon request from the corresponding author.

Table 1 Settings used for the DFT-MD calculations in the thermodynamic integration and perturbation theory in the form (TDI $\rightarrow$ TPT). The reduced timestep used in the simulations near the non-interaction limit is given in parenthesis.

element	cut-off	<i>k</i> -grid	timestep [fs]	
Xe (165 K, 200 K)	$200 \to 400$	$\Gamma \rightarrow 2^3$	8 (4)	
K (923, 1023, 1123 K)	$200 \to 400$	$\Gamma  ightarrow 3^3$	8 (1)	
K (1000 K)	$250 \rightarrow 500$	$\Gamma \rightarrow 2^3$	4 (1)	
Na (1000 K)	$250 \rightarrow 500$	$\Gamma  ightarrow 2^3$	4 (1)	
B (4000 K)	$350 \to 600$	$2^3  ightarrow 3^3$	1 (0.25)	
Al (2800 K)	$400 \rightarrow 600$	$\Gamma \rightarrow 2^3$	2 (1)	
Ca (1800 K, 2100 K)	$200 \to 400$	$\Gamma \rightarrow 2^3$	4 (1)	
Sr (1800 K)	$200 \to 400$	$\Gamma \rightarrow 2^3$	4 (1, 0.5)	
Ba (2000 K)	$200 \to 400$	$\Gamma \rightarrow 2^3$	5 (0.5)	
Cu (2700 K, 3000 K)	$350 \rightarrow 600$	$\Gamma  ightarrow 2^3$	2(1)	
Mn (2400 K)	$300 \to 600$	$\Gamma  ightarrow 2^3$	2(1)	
Mn (3200 K)	$300 \to 600$	$\Gamma \rightarrow 2^3$	1.5 (0.3)	
sr/so Hg (700 K)	$250 \rightarrow 500$	$2^3  ightarrow 3^3$	12 (3)	

## 1.1 Calculation of the Gibbs Energy of the Liquid

The Gibbs energy of the liquid is calculated through TDI from a non-interacting reference (ideal gas). For this purpose the difference of the internal energies is integrated along the coupling parameter  $\lambda$ 

$$\Delta G_{0-1} = \int_0^1 d\lambda \langle U_1(\mathbf{R}) - U_0(\mathbf{R}) \rangle_{\lambda} \quad , \tag{1}$$

which relates the liquid with  $U_1$  to the ideal gas with  $U_0$  at the same *T* and *V* by scaling the forces, and added to the Gibbs energy of the ideal gas at the liquid equibrium volume (eqs. 5

and 6). Since the kinetic energy part of  $U_1$  and  $U_0$  is identical it cancels, and the potential part vanishes at zero interaction stength  $(u_0)$ , the value of the integrand is the average internal potential energy calculated at full interaction strength  $\langle U_1^{\text{pot}}(\mathbf{R}) \rangle$ for configurations **R** generated with reduced interaction strength (at the respective  $\lambda$ ). This integral is evaluated using numerical quadrature in the form of a *n*-point Gauss-Lobatto rule, in principle requiring one NVT simulation for each  $\lambda$ . Although most of these simulations are straightforward, the ones very close to the ideal-gas limit ( $\lambda \ll 0.01$  or < 1% of the DFT forces) are tedious, whereas the simulation for the end point  $\lambda = 0$  is not possible with a PAW+DFT methodology. This is because close-encounters between the (almost) non-interacting atoms lead to singularity in the energy resulting in numerical instabilities in errors in the simulations, partly resulting from overlapping core-electrons. An approach to circumvent these issues was devised and implemented by Kresse and coworkers and will be used here with slight modifications.<sup>1</sup>

The approach is based on substituting  $\lambda$  in eq. (1) with  $\lambda(x) = (\frac{x+1}{2})^{1/(1-\kappa)}$ , which yields

$$\Delta G = \frac{1}{2(1-\kappa)} \int_{-1}^{1} f(\lambda(x))\lambda(x)^{\kappa} dx \,. \tag{2}$$

This introduces an explicit dependency on  $\lambda$  in the integrand, which not only dampens the impact of the technically challenging calculations near the non-interacting limit (*cf.* effective weights in Fig. 1), but also completely eliminates the point for  $\lambda = 0$ . This is because the substitution introduces a parameter  $\kappa$ , which fulfils another role: It guides the mapping of the quadrature points between the domains. While a value close to 0 retains the original (equidistant) spacing of the Gauss-Lobatto quadrature, choosing  $\kappa$  close to 1 increases the density of quadrature points in the  $\lambda$  domain in the region close to  $\lambda = 0$ , where the slope of  $f(\lambda)$  is the largest (*cf.* Fig. 1). While Kresse and coworkers suggest  $\kappa > 0.8$ , we demonstrate here that at least for the calculation of NBPs, much smaller values suffice. This dramatically reduces the computational effort as it allows to avoid the technically challenging simulations near the non-interacting limit almost entirely.

Since it is nevertheless prohibitively expensive to carry out the TDI at a converged level of theory, it is instead combined with

<sup>&</sup>lt;sup>a</sup> Mulliken Center for Theoretical Chemistry, University of Bonn, Beringstr. 4, 53115 Bonn, Germany, janmewes@janmewes.de

<sup>&</sup>lt;sup>b</sup> Centre for Theoretical Chemistry and Physics, The New Zealand Institute for Advanced Study, Massey University Auckland, 0632 Auckland, New Zealand



Fig. 1 Effective weight plotted against the  $\lambda$ s (logarithmic scale) at which simulations have to be conducted for a 6-point Gauss-Lobatto rule for several different choices of  $\kappa$ . The interaction-strength for the most "non-interacting" simulation (min) is given in the legend in %. For reference, the evolution of the value of the integrand taken from B at 4000 K with PBE-D3 is shown in blue on the secondary axis. The effective weight is  $(w_i\lambda^{\kappa})/(2(1-\kappa))$  where  $w_i$  is the weight from the respective Gauss-Lobatto rule.

thermodynamic perturbation theory (TPT)

$$\Delta G_{1-2} = -\frac{1}{\beta} \ln \langle e^{-\beta [U_2(\mathbf{R}) - U_1(\mathbf{R})]} \rangle_1 \quad , \tag{3}$$

where the index after the angle bracket indicates that the difference  $\Delta U_{1-2}$  is evaluated for configurations generated by  $H_1$ . Thus, by exploiting the linear shift of a refined Hamiltonian (*e.g.* increased cut-off, *k*-points or even another functional), TPT can often provide a very good estimate for the respective Gibbs-energy difference from as few as 5-20 single-point calculations. Instead of the exact equation, we use the second-order cumulant expansion

$$\Delta G_{1-2} \approx \langle \Delta U \rangle_1 - \frac{\beta}{2} \langle (\Delta U - \langle \Delta U \rangle)^2 \rangle_1 \quad , \tag{4}$$

which is sufficiently accurate since already the second-order term is  $\ll 1$  meV/atom in all cases, and can thus be neglected. Using TPT, all final results are converged to within  $\approx 2$  meV/atom, which translates into a error in the NBP of about 2 K.

#### 1.2 Calculation of the Gibbs Energy of the Gas Phase

The Gibbs energy of the gas phase is calculated for the noninteracting (ideal) gas at its equilibrium volume and ambient pressure. For a given atomic degeneracy  $\Theta$ , volume *V*, temperature *T*, particle number *N* and mass *m* this is

$$G^{\rm id} = F^{\rm id} + pV = -k_B T \ln \left( Z(\Theta, T, V, N) \right) + pV, \text{ with }$$
(5)

$$Z(T,V,N) = \frac{(\Theta V)^N}{\Lambda^{3N} N!} \text{ and } \Lambda = h \sqrt{\frac{\beta}{2\pi m}} \quad . \tag{6}$$

For the gas phase, this equation is solved using the Stirling approximation, which is sufficiently accurate since we are consider-

ing an arbitrary number of particles. The same equation is also used to calculate the Gibbs energy of the non-interacting reference for the liquid (at the equilibrium volume of the liquid). Here, however, the Stirling approximation is no longer suitable since the number of particles is finite (61 or 64), and the pV term is negligible. Moreover, since – in contrast to the real atoms in the gas phase – the non-interacting reference for the liquid consists of hypothetical point-masses, they are not degenerate.

To validate the accuracy of the non-interacting model, we evaluate the first virial (two-body) correction for each of the examples assuming a Lennard-Jones (12,6) potential with the parameters derived from first-principles calculations for the respective dimers. This leads to the following integral

$$G_{\rm LJ}^g = G_{\rm id}^g - \frac{2\pi N^2}{V\beta} \int \left[ r^2 e^{-4\varepsilon\beta \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]} - 1 \right] dr \tag{7}$$

which can be evaluated as described in ref. 2. This provides generally very small corrections ( $\leq 1.0$  meV/atom), which in turn have a negligible impact on the calculated boiling points ( $\leq 1$  K).

# 2 Determination of Equilibrium Volumes

To calculate the equilibrium volume, the 61 or 64-atom supercells are simulated with the default settings (cf. Tab. 1) at several slightly different volumes until the statistical average of the pressure is converged to within 0.3 kBar. For about 5-20 equidistant snapshots from the trajectory, single-point calculations are conducted with the converged settings to obtain a correction for the influence of Pulay stress, a finer k-point grid, and increased numerical precision (as well as spin-orbit coupling in case of Ba and Hg). The corrected pressures at each point are fitted with a second-order polynomial and interpolated to the x-intersection (p = 0, note that using p = 0.001 kBar consistent with ambient)pressure would provide virtually identical volumes). Final volumes are confirmed during the TDI, where the simulation with  $\lambda = 1$  and subsequent TPT provides the residual pressures given in Tab. 2, along with the calculated atomic volumes and corresponding densities.

#### 2.1 Derivation of the Scaling-Relation of the Gibbs Energy

The following derivations built on those presented to ref. 3, which demonstrates that for any atomic system in the classical Born-Oppenheimer picture, a scaling of the interatomic potential  $\phi$  with a factor  $\lambda$ , phase-transition temperatures scale with the same factor. Although ref. 3 explicitly includes the boiling points, we will show in the following that the simple transition-temperature scaling is incorrect for the BP. Instead, the corrected BP, or in other words the BP for a scaled interaction potential  $\lambda \phi$ , has to be determined from the intersect of corrected (scaled) Gibbs energy for the liquid with the (unaffected) Gibbs energy of the gas. For this purpose, we go beyond the derivations presented in ref. 3 and provide an analytical expression for the absolute Gibbs energies of the solid and liquid phase as a function of a linear scaling of the potential.

Let us begin with the description of the Gibbs energy for the

Table 2 Calculated equilibrium volumes (in Å<sup>3</sup>/atom), corresponding densities  $\rho$  (in g/cm<sup>3</sup>), and residual pressures (in kBar) for all studied elements. Volumes of Al, Cu, B, and Cn are calculated with  $2^{3}k$ -point grid in the simulations, all others employ the  $\Gamma$ -point approximation and include the effect of more *k*-points perturbatively.

element/DFA/T <sub>sim</sub>	V/atom	ρ	residual p	
Xe/PBE-D3/165 K	79.8	2.73	0.1	
Xe/PBE-D3/200 K	85.8	2.54	0.1	
Xe/revPBE-D3/165 K	79.8	2.73	-0.1	
K/PBE-D3/1000 K	90.42	0.718	0.0	
K/PBEsol/1000 K	93.22	0.696	0.3	
K/PBE/1000 K	101.9	0.637	0.1	
B/PBE-D3/4000 K	8.820	2.04	-0.2	
Al/PBE/2800 K	23.62	1.90	0.1	
Na/PBEsol/1000 K	46.24	0.825	0.2	
Ca/PBE/1800 K	52.51	1.27	-0.5	
Ca/PBED3/1800 K	47.63	1.40	0.2	
Ca/PBEsol/1800 K	49.22	1.35	-0.2	
Sr/PBE/1570 K	66.92	2.17	0.0	
Sr/PBED3/1800 K	64.00	2.27	-0.2	
Sr/PBEsol/1800 K	65.55	2.22	-0.7	
Ba/PBE/2000 K	81.25	2.81	0.0	
Ba/PBED3/2000 K	73.40	3.11	0.1	
Mn/PBE/3200 K	12.75	7.16	0.5	
Mn/RPBE/2400 K	12.49	7.30	-0.4	
Mn/SCAN/2400 K	11.58	7.89	-1.2	
Cu/PBE/2400 K	12.49	7.30	-0.4	
Hg/soPBEsol/700 K	25.86	12.9	-0.1	

solid and liquid phase. In ref. 3 it is shown that

$$U(\lambda T, \lambda \phi) = \lambda U(T, \phi) . \tag{8}$$

However, no such relation was derived for the absolute entropy, but only for the relative melting entropy  $\Delta S^{s-l}$ . While this is sufficient to derive the transition-temperature scaling for the MP, it was insufficient to calculate the change in the absolute Gibbs energy upon scaling the potential.

To derive an analytical relation also for *S*, let us consider a simple solid and liquid. At sufficient high temperatures, such that classical mechanics is applicable, it follows from the equipartition theorem that the total mean energy, the sum of kinetic and potential energy, is proportional to the temperature.<sup>4</sup> Hence, the term  $p^2$  in the kinetic part to the general expression for the entropy scales linearly with *T*,

$$S(T,\phi) = \frac{U}{T} + k_B \ln Z \tag{9}$$

$$= \frac{U}{T} + k_B \ln\left(\int e^{-\phi(r)/k_B T} dr + \int e^{-p^2/2mk_B T} dp\right) \quad (10)$$

$$S(\lambda T, \lambda \phi) = \frac{\lambda U}{\lambda T} + k_B \ln \left( \int e^{-\lambda \phi(r)/k_B \lambda T} dr + \int e^{-\lambda p^2/2mk_B \lambda T} dp \right)$$
(11)

such that as evident from the last line, the  $\lambda$ s cancel out. This is because the accessible configuration space remains exactly the same when potential depth  $\phi$  and available kinetic energy *T* are multiplied by the same factor  $\lambda$ . This concludes that for both

the solid and the liquid phases the entropy is unaffected by the scaling and thus

$$S(\lambda T, \lambda \phi) = S(T, \phi) . \tag{12}$$

Accordingly, the respective Gibbs energy (assuming pV = 0) becomes

$$G(\lambda T, \lambda \phi) = U(\lambda T, \lambda \phi) - \lambda T S(\lambda T, \lambda \phi)$$
(13)

$$= \lambda U(T,\phi) - \lambda TS(T,\phi)$$
(14)

$$=\lambda G(T,\phi), \qquad (15)$$

showing that the Gibbs energy of the condensed phases is linear with respect to a simultaneous scaling of T and  $\phi$ . This proves eq. (3-5) in the manuscript, and provides the means to correct the Gibbs energy. It should be pointed out that this holds for any temperature sufficiently high to consider the system in the classical picture, which thus certainly including the boiling and melting points of most elements.

Let us now move to the ideal gas and rationalize why it behaves different, or, in other words, why it does not scale like the solid and liquid. Using Stirling's approximation,  $\ln N! = N \ln N - N$ , the Helmholtz energy of the ideal gas takes the form

$$F^{id} = -k_B T \ln Z \tag{16}$$

$$= -Nk_BT \ln\left[\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}\frac{V}{N}\right] - kT_BN$$
(17)

The partial derivatives

$$S = \left. \frac{\partial F}{\partial T} \right|_{V,N} = -k_B T \left. \frac{\ln Z}{\partial T} \right|_{V,N}$$
(18)

$$p = \left. \frac{\partial F}{\partial V} \right|_{T,N} \tag{19}$$

are used to obtain expressions for the entropy and pressure

$$S = Nk_B \left(\frac{5}{2} + \ln\left[\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} \frac{V}{N}\right]\right)$$
(20)

$$pV = Nk_BT \tag{21}$$

since U = F + TS, we have

$$U = k_B T^2 \left. \frac{\ln Z}{\partial T} \right|_{V,N} \tag{22}$$

$$=\frac{3}{2}Nk_BT.$$
 (23)

and because G = F + pV

$$G = -Nk_BT \ln\left[\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}\frac{V}{N}\right].$$
 (24)

Upon scaling of the temperature (and potential) with  $\lambda$ , a new

term shows up in the Gibbs energy of the ideal gas

$$G(\lambda T) = -Nk_B \lambda T \ln\left[ (\lambda T)^{5/2} \left( \frac{mk_B}{2\pi\hbar^2} \right)^{3/2} \frac{k_B}{P} \right]$$
(25)

$$= Nk_B \lambda T \ln \left[ T^{5/2} \left( \frac{mk_B}{2\pi\hbar^2} \right)^{3/2} \frac{k_B}{P} \right] + Nk\lambda T \ln[\lambda^{5/2}] \quad (26)$$

$$= \lambda F(T) + Nk_B \lambda T \ln[\lambda^{5/2}].$$
(27)

Since the ideal gas is – in constrast to the condensed phases – independent on the interaction potential, the above derived relation merely show the temperature-dependence of the Gibbs energy of the gas. Unsurprisingly,  $G^g(T)$  is not linear in T, and as a consequence, the simple scaling of the BP is not possible. However, as evident from eqs. (21-23), the entire Gibbs energy curve for the liquid phase can be corrected for linear changes in the potential, and the corrected BP extracted as the intersect between the corrected Gibbs energy of the liquid  $G^l(T, \lambda \phi)$  and the unaltered Gibbs energy of the gas phase  $G^g(T)$ .

### Notes and references

- 1 F. Dorner, Z. Sukurma, C. Dellago and G. Kresse, *Phys. Rev. Lett.*, 2018, **121**, 195701.
- 2 B. Cowan, *Topics in Statistical Mechanics*, Imperial College Press, 2005, vol. 3.
- 3 J.-M. Mewes, O. R. Smits, G. Kresse and P. Schwerdtfeger, *Angewandte Chemie International Edition*, 2019, **58**, 17964–17968.
- 4 M. Reif, *Fundamentals of Statistical and Thermal Physics*, Waveland Press, New York, 2009.

Table 3 Calculated Gibbs energies, internal energies (in eV/atom), as well as classical and electronic entropies (in meV/[atom\*K]) for the liquid phase of all studied elements.

DFA, $T_{\rm sim}$ , $T_{\rm eff}$	G	U	S	$S_{\rm el}$
Xenon				
PBE-D3, 165, 165	-0.2368	-0.1406	0.5831	0.0
Sodium				
PBEsol, 1000, 959	-1.8091	-0.8605	0.9486	0.0112
Potassium				
PBE, 1000, 1073	-1.6822	-0.5685	1.1137	0.0200
PBE-D3, 1000, 945	-1.7617	-0.6803	1.0822	0.0182
PBEsol, 1000, 1002	-1.7311	-0.6371	1.0940	0.0188
Boron				
PBE-D3, 4000, 3664	-8.5304	-4.8373	0.9233	0.0248
Aluminum				
PBE, 2800, 2782	-5.5099	-2.5913	1.0488	0.0327
Calcium				
PBE, 1800, 1729	-3.2486	-1.3322	1.0644	0.0658
PBE-D3, 1800, 1540	-3.4238	-1.5414	1.0327	0.0657
PBEsol, 1800, 1568	-3.4256	-1.5298	1.0458	0.0656
PBEsol, 2100, 1829	-3.7680	-1.4770	1.0909	0.0755
Strontium				
PBE, 1570, 1680	-2.9156	-1.1088	1.1509	0.0621
PBE-D3, 1800, 1712	-3.3560	-1.2506	1.1697	0.0707
PBEsol, 1800, 1714	-3.3618	-1.2305	1.1841	0.0708
Barium				
PBE, 2000, 2026	-3.9186	-1.2899	1.3144	0.1088
PBE-D3, 2000, 1830	-4.0781	-1.4942	1.2920	0.1020
Manganese				
PBE, 3200, 2402	-6.3447	-2.9140	1.0721	0.1307
RPBE, 2400, 2198	-4.7648	-2.3975	0.9852	0.0987
SCAN, 2400, 2342	-4.4795	-2.1522	0.9697	0.0833
Copper				
PBE, 2700, 2705	-5.5273	-2.5896	1.0881	0.0175
PBE, 3000, 3006	-5.8769	-2.5039	1.1243	0.0220
Mercury				
soPBEsol, 700, 753	-1.0814	-0.3609	1.0279	0.0045