

Thermodynamic Properties of Sea Air

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Final Response (Author Comment)

The authors thank the reviewers for their hints and comments. They will be considered in the revised paper.

Referee #1:

Thank you for your comments and suggestions. It appears that we must further clarify that this paper does not aim at the construction of thermodynamic potentials. The potential functions we refer to were published by IAPWS or in scientific journals such as the Journal of Physical and Chemical Reference Data. We repeat these functions in the Appendices for the readers' convenience, with some explanations and comments relevant for the topic of the paper. We do not generally discuss the correctness of these functions; this is done in the related publications. There are only minor exceptions in this paper where we compare with experimental data; e.g. to check the maximum density limit of the somewhat novel cross-virial expansion of humid air that we propose, or to extend the IAPWS-95 vapour formulation below 130 K.

In brief, the paper aims to consider how the previously published potential functions can be mathematically exploited to calculate properties of interest in oceanography and meteorology. Most of the equations we derive and discuss are thermodynamically exact relations. Thus, we do not feel that it would be particularly useful or desirable to discuss in this paper the correctness of any particular selection of the various published empirical geophysical correlation equations. In most cases, the validity of those empirical equations has been demonstrated in many practical applications as discussed in the literature. For similar reasons, we do not discuss the mutual consistency of the pair-wise and higher-order combinations in order to, say, demonstrate the higher accuracy of the potential functions we employ. Rather, it is a fundamental feature of our systematic building-block approach that the quantitative accuracy of the thermodynamic potentials used as "inputs" is not relevant to the mathematical correctness of the fundamental thermodynamic relations which are the primary subject of this paper. These relations constitute the mathematical "processing pipeline" applied to extract from the given "input" the various special properties of interest. If improved formulations for any of the chosen potential functions become available in the future, they may be substituted for our current choices without the need for any fundamental changes of the relations collected and published in this paper.

In our paper we suggest a conceptually different approach to the usual collection of separate empirical equations for some properties of interest. Starting from very few internationally recognised formulations, ALL thermodynamic properties can be computed (within the range of validity and the related uncertainty) in a consistent and highly accurate way. Based on this approach, studies of different authors will be much better comparable. We also note that although limitations of space and time have not permitted it, virtually unlimited sets of tailored correlation equations can be derived from the exact thermodynamic relations and the chosen potential functions, even for properties for which direct measurements are unavailable or show significant uncertainties (e.g., sublimation pressures at low temperatures or freezing points at high pressures).

In slightly different words, the basic idea behind this paper is the proposal to formally, mathematically and numerically separate the empirical and theoretical correlations (in our case, the currently available thermodynamic potentials, given as an “input”) from the thermodynamic relations (in our case, the equations derived in this paper, as a “transfer function” that transforms the “input” into the property requested). The two parts are linked by a standard interface (in our suggestion, the potentials together with their first and second partial derivatives to serve as the “exchange protocol”). This splitting permits update, substitution, extension or correction of either part independent of the other (Feistel et al., 2009, Wright et al., 2009).

Although we have attempted to make these points clear in the original presentation, we are considering the possibility of adding a " Discussion" section to re-emphasize these basic points at the end of the paper.

The presentation of the radiosonde profiles from section 11 should also be placed there. At this point, I would like the authors to specify the assumptions on the salinity profile of these air parcels.

The properties of sea air are computed from the sea-surface salinity and temperature. No assumption is made regarding the salinity profile at greater depth.

- salinity-dependent bulk formulae for latent and sensible heat: How big is the expected error if clear water formulae are used instead of sea water?

As shown in Fig. 5, the latent heat of seawater depends very weakly on salinity and is almost the same as for pure water. Thus, our approach does not falsify the common approach of ignoring salinity in this case; rather, it quantifies the error with high reliability. Moreover, our systematic derivation permits, via the Gibbs function of sea air, to calculate the enthalpy of evaporation under any process conditions rather than just isobaric ones.

There is no thermodynamic equation for sensible heat.

- salinity effects in coastal fog or sea smoke: How changes sea salt the dew point, for example?

The dewpoint is, by definition, the temperature at which atmospheric vapour starts to condense as liquid water (or ice), by homogeneous or heterogeneous nucleation. If sea smoke is present, then the atmospheric vapour will condense when in contact with saline droplets (or at the sea surface) at temperatures still above the dewpoint; this occurs due to the lowered vapour pressure of seawater compared to pure liquid water. The formation of pure-water droplets is impossible since they will be metastable and evaporate. If we ignore here for simplicity the Laplace pressure which depends on the surface curvature of the droplets, then at equilibrium all droplets have the same brine salinity, independent of their size (i.e. salt content). Under non-equilibrium conditions, droplets with higher salinity (and hence lower vapour pressure) will grow and dilute, those with lower salinity will shrink and concentrate, and those without salt will shrink to zero, i.e., disappear.

This process is controlled by the so-called Köhler equation (Köhler, 1936; Seinfeld and Pandis, 1998; Jacobson, 2005; http://en.wikipedia.org/wiki/K%C3%B6hler_theory). It is related to the Ostwald ripening of nuclei that emerge along with phase transitions of first kind (Ostwald, 1896; Schmelzer and Schweitzer, 1987).

At temperatures below the freezing point of seawater at the given droplet salinity, the aerosol particles consist of ice and brine. At equilibrium, the brine salinities of all droplets are the same, but the ice/brine mass ratio is not constrained by the equilibrium conditions. Thus, pure-ice fog can coexist with sea smoke at temperatures lower than the freezing point of the aerosol.

Referee #2:

We are particularly grateful to reviewer #2 for his careful and very detailed review and the independent verification of various equations derived in the paper.

Remark #1: *P. 2197, line 4: The authors distinguished between fluid water and seawater. According to p. 2205, lines 13-14, fluid water is used as a generic term for liquid and gaseous water (water vapour). Thus, seawater is also fluid water. Please check notions.*

Seawater and fluid water have liquid pure water as their intersection set. Seawater does not include vapour, nor does fluid water include sea salt. We will check whether a clarification is required in the revised version.

Remark #6: *P. 2203, line 4: Millero [...] provides an equilibrium vapour pressure formula for seawater.*

The term “vapour pressure of seawater” is common and refers to the equilibrium value (e.g., Robinson, 1954).

Remark #7: *P. 2204, line 9: Be more specific, which “properties of marine aerosol” are meant in the present context. Write “by O’Dowd et al. ...”.*

Although related to this paper, marine aerosol is an extended field of research on its own that is not particularly addressed here (see also our response to reviewer #1 regarding the Köhler equation). We prefer to refrain from any details of marine aerosol properties and leave the reference as general as it is.

Question #8: *P. 2205, line 6: Do you mean “high-speed applications” in the sense of “real-time applications” such as in numerical weather predictions models etc.?*

Yes. To our knowledge, the fastest numerical representation of any function is a look-up table with a resolution that requires linear interpolation at most. The time it takes to compute and store the tabulated values is irrelevant for its later usage as a look-up table. The sea-air functions (SIA library) permit the computation of look-up tables for practically any desired combination of input and output properties, since the thermodynamic potentials provide a *complete* description. Real-time models require the highest computation speeds; so, we believe that our equations may well feed such models with the most accurate properties available. However, we recognize that for particular applications such as in oceanographic or climate models computation (or look-up) speed may be critical, too.

Question #11: *P. 2206, line 15: Just to know: Is the enthalpy of a sample seawater, H_w^{SW} , a measurable field quantity?*

The Gibbs function of seawater depends on four adjustable constants A, B, C, D , the absolute energies (or enthalpies) and entropies of water and salt, in the form

$$g^{\text{SW}}(S, T, P) = A + BT + CS + DST + \dots$$

The enthalpy,

$$h^{\text{SW}}(S, T, P) = g^{\text{SW}} - Tg_T^{\text{SW}} = A + CS + \dots$$

depends on only two of them, the absolute energies of water and salt. The partial specific enthalpy of water in seawater

$$H_w^{\text{SW}}(S, T, P) = h^{\text{SW}} - Sh_s^{\text{SW}} = A + \dots$$

still depends on one unknown constant, the absolute energy of water.

Thus, only differences between partial specific enthalpies can be measured rather than their absolute values.

Remark #12. *P. 2208-2209, Eqs. (9), (10): Considering Appendix D it is more plausible to start with Eq. (10) with reference to Eq. (D14) and to arrive at Eq. (9).*

This may be a matter of taste. For a mixture of two substances that have the same temperature T and occupy the same volume V it seems evident that their individual Helmholtz energies $F(T, V)$ are additive, plus an interaction term that follows from the canonical partition function which evaluates to an extensive property, too. The corresponding relation for the specific Helmholtz energies follows then easily by division by the total mass. To us, the addition rules for specific Helmholtz energies appear less obvious as a starting point.

Question #14: *P. 2209, line 15: Considering that the water vapour with the mass fraction q is the minor fraction in humid air, the employment of the mass fraction of dry air A instead of $q = 1 - A$ needs getting used to (at least with respect to atmospheric applications.) I mean, the property q corresponds better to salinity S . Is the use of A motivated by technical applications, as mentioned in line 24?*

Admittedly, the use of A as the composition variable is not common. This decision was made independently of the usual ambient mass ratios. The formalisms used here are very similar for the ocean and the atmosphere. Water in its three phases forms the reference system; in particular its two fluid phases are described by one and the same Helmholtz potential (IAPWS-95) for rigorous consistency between ocean and atmosphere. As in nature, also in our theoretical model the water is exactly “the same” on both sides of the sea surface. These fluid phases are “polluted” with natural mixtures of almost constant composition, salt in the liquid and air in the gas phase. For these additives, their pure properties are described plus a density expansion with respect to their interaction with water. As a result, the equations for humid air look very similar to those of seawater if just S is exchanged with A .

Remark #19. *P. 2216, Eq. (39), line 19 (first appearance): Just a comment: The use of subscript v to denote the gas constant of water vapour would better fit into the system of annotations.*

As with the molar mass, the value of the specific gas constant of water is independent of the actual phase the water takes. Here we use the sub/superscripts V for water vapour and W for liquid water as well as for water in general as a substance, similar to common speech.

Remark #20. *P. 2217, Eq. (40): This equation has already been introduced by Eq. (1). Instead of Eq. (40), for a later use the authors could have introduced here a representation of the Gibbs free energy of seawater via the Gibbs-Duhem and Duhem-Margules relations in terms of the chemical potentials of the solute and solvent, similar to Eqs. (21)-(23) for humid air.*

Eq. (40) is just a simple reminder to ease the reading at this point, without introducing additional details or variables. We prefer it this way.

Question #21: *P. 2219, line 1: The definition of a phase-transition latency operator $\Lambda_{AS}[z]$ is a powerful concept, allowing for a very compact codification of the thermodynamic information. As employed in the calculus, one could add $\Lambda_{AS}[-z] = -\Lambda_{AS}[z]$. I am curious about the root of the notion “latency” operator.*

The operator was originally introduced for sea ice in a slightly modified version and regarded as the “melting operator”. On writing of this paper it turned out that a similar expression is a very useful tool for humid air, too. “Latency” appeared as a natural generalization of “melting”. We will clarify this point in our revisions.

Question #22: *P. 2219, 2220, Eqs. (47), (48): Are the chemical coefficients D_A and D_S observable properties or do some empirical proxies exist?*

The chemical coefficients are measurable, at least in principle. Negative coefficients correspond to a chemical instability of the homogeneous mixture, leading to its decomposition. We are not aware of any experiments to determine these coefficients. A good theoretical estimate is given by eq. (H15).

Question #29: *P. 2224, line 20-23: The authors defined “wet air” (cloudy air) as saturated humid air combined with liquid water. Thus, I guess the generic notion “saturated humid air” is sufficient in the caption.*

Wet air contains a liquid fraction; its gaseous part is saturated humid air. Thus, the distinction must be made from our point of view in order to emphasize the presence of a liquid condensate.

Remark #33. *P. 2227, Eqs. (74), (75): I arrived at this equation by means of Eqs. (42), (44), (51), (54), and (55). Maybe, add reference to these equations.*

All we need here is eqs. (73) and (47), as referred to in the text, as well as the definitions of s and v . The equations mentioned in the reviewer’s remark refer to seawater.

Remark #38. *P. 2244, lines 13-14: [...] that humid air in equilibrium with seawater above its freezing temperature is always subsaturated with respect to pure bulk water (or freshwater).*

We think just “subsaturated” is correct and even includes the case of ice (between the freezing temperatures of water and of seawater). Saturation is when vapour starts to condense; this

condensate is evidently pure water/ice as long as we neglect the dissolution of air in the condensate.

Remark #39: P. 2245, line 10 - p. 2246, line 3: Just a comment: Considering a layer of the atmosphere between two constant-pressure surfaces (planes) with constant total mass, assuming that layer being in hydrostatic equilibrium, and supposing, that the layer is isolated from its surrounding, neither heated nor cooled by radiation nor by interaction with adjacent air (or ground), Bohren and Albrecht (1998, cf. pp. 164-169 therein) showed, that of all linear potential temperature profiles, a constant potential temperature maximises the entropy of that isolated atmospheric layer. The entropy maximisation requires the equilibrium temperature of the isolated layer to decrease with height at the dry adiabatic lapse rate, $\Gamma_{dry} = -(dT/dz)_{adiab} = g/c_p$, i.e., the equilibrium temperature profile is non-isothermal... etc.

The usual symmetry between the equilibrium state and the well-stirred state of a fluid is broken in the presence of a gravity field (Feistel and Feistel, 2006). Without gravity, temperature and its thermodynamic conjugate, entropy, exhibit constant values all over the volume when at equilibrium as well as when turbulently mixed (neglecting friction). Under external (non-relativistic) gravity, without turbulent mixing, equilibrium implies constant in-situ temperature but a gradient of entropy or potential temperature (Landau and Lifschitz, 1987). Turbulent mixing, on the other hand, causes constant entropy and potential temperature but a gradient of in-situ temperature proportional to the adiabatic lapse rate, and thus permanent heat conduction (flux proportional to the Onsager force, i.e. the temperature gradient) and entropy production (flux times force, proportional to the square of the gradient).

When a layer of air is sufficiently thin and does not include a phase boundary, any of its profiles are to any desired degree of approximation linear functions of the pressure/altitude. When a layer possessing internal in-situ temperature gradients is thermally isolated (i.e., no entropy flow through its boundary), then its internal entropy will always increase rather than decrease, due to the Second Law (Glansdorff and Prigogine, 1971).

Thus, the isothermal equilibrium state must have a higher entropy than its related isentropic non-equilibrium state.

Question #40: P. 2247, line 12: I recommend to include the reference to Fig. 19 right here, when the authors describe RS 37 (cf. also lines 19-21). Just a comment: The entropy computed from Eq. (24) in conjunction with the related sea-air entropy, computed from ocean surface properties by means of the equilibrium Eq. (43), seems to be a good synoptic air mass indicator. As seen from the top panel in Fig. 19, the deviation between both measures reflect a disturbance of the seawater-humid-air equilibrium, caused by nonseasalt debris, here Saharan dust. This opens the way to quantify the deviation from the equilibrium in terms of aerosol load and of different proxies, such as aerosol optical depth derived from spaceborne platforms or ground-based remote sensing (Lidar) etc. It would be interesting to see, how the deviation from the equilibrium is correlated with several proxies of contamination. I consider such an approach as an interesting supplementary method for the desert dust community.

This is an interesting idea. The profiles shown in Fig. 20 are from cruises that examined the impact of Sahara dust on the Atlantic. Those colleagues did not respond to the theory of this paper in a similarly enthusiastic way as the reviewer, at least so far.

Question #41. P. 2248, line 12: Can the increasing upper-ocean salinity overcompensate

the desalination, resulting from the increasing freshwater flux from melting ice? Are the net changes relevant for a displacement of the seawater-humid air equilibrium (via the Raoult effect, cf. Fig. 10) on a global scale or over geological time scales (impact on cloud formation)?

The authors are not experts on global water flux estimates. Our simplified summary from the cited articles is the impression that the spatial and temporal distribution of relative humidity over the global ocean is relatively invariant under the conditions of global warming. This implies an increased absolute water content of the atmosphere, maintained by an accelerated water cycle in the atmosphere, accompanied by intensified precipitation and evaporation, such that the salty ocean patches get saltier and the fresher ones get even fresher. Of course there are various other processes involved on different space and time scales. For example, there is a displacement of the intertropical convergence zone that changes the westerly wind belt at Cape Agulhas and intensifies the leakage of Indian Ocean water into the South Atlantic (Bjastoch et al., 2009). Processes such as this will also locally influence the salinity of the Atlantic, in addition to evaporation etc.

Certainly, these global feedback loops will also modify the climatological cloud patterns, but an answer to this question is far beyond the expertise of the authors.

Figures, Remark #2: *3. The sizes of the “twin” figures 1, 3, 4, 6, 9-12, 19, 20 are too small and should be enlarged to the format size of, e.g., Fig. 2.*

This was specified by the typesetting of Ocean Science.

Figures, Remark #6: *Can the difference between the IML and IFL denoted as thermal hysteresis? Please remove once “near very” in the legend.*

Hysteresis implies overturning and/or ambiguous (history-dependent) curves for the order parameter. None of this applies here. Below the IFL are water clouds, above the IML are ice clouds, and in between are mixed-phase clouds

References:

Bjastoch, A., Böning, C.W., Schwarzkopf, F.U. and Lutjeharms, J. R. E.: Increase in Agulhas leakage due to poleward shift of Southern Hemisphere westerlies, *Nature* 462, 495-498, 2009.

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