Lecture 3. Properties of Sea Water

In this section we will discuss the properties of sea water. The properties of sea water include the pressure $p$, temperature $T$, salinity $S$, density $\rho$, sound velocity, heat capacity, optical characteristics, and compressibility. All are important to various aspects of physical oceanographers. This part of oceanography is very strictly defined. Probably more so than any part of the field you will encounter. Many properties are strictly defined by an international body called International Association for the Physical Sciences of the Ocean (IAPSO).

Typical ranges of $T$, $S$, $\rho$ and sound velocity in the ocean will be discussed later. Many of the physical chemical studies that have lead to the standard equations were limited to the typical ranges found in the open ocean. One should always check when working in unusual environments that the tables are appropriate.

**TEMPERATURE**

A typical temperature profile in the ocean shows maximum values at the surface that decrease with depth (Fig. 1). In high latitudes, like in the Arctic and around Antarctica, the temperature changes little with depth. The maximum vertical variations are usually seen in the tropics, where strong thermoclines can be identified. The thermocline is a region (not only one given depth, but a range of depths) where temperature changes most rapidly.

How do we measure temperature? Methods range from the mercury thermometer to platinum resistance thermometers and thermistors. Most conductivity-temperature-depth (CTD) systems (Fig. 2) have a highly accurate platinum resistant sometimes matched with a fast response thermistor sensor. Reversing mercury thermometers and digital thermometers are used for ultimate calibration that connects the field instrument to the national/international standards.

The Celsius temperature ($T$) is the difference between the thermodynamic temperature $T_d$ and the temperature $T_0 = 273.15$ K. Temperature is measured using the International Temperature Scale established in 1990 (ITS-90). Previous to 1990 temperature measurements were made using the IPTS-68 scale. With this change the Joint Panel on Oceanographic Tables and Standards recommended that the following conversion be used for oceanographic measurements.

$$T_{68} = 1.00024 \ T_{90}$$ (1)

This is an important conversion because the computation of practical salinity (PSS-78) and density (EOS-80) requires use of the IPTS-68 scale but temperature measurements are made with the ITS-90 scale. The temperature differences between the two scales ranges from 0.002 at -10°C to -0.010 at 40°C. As was noted in a 1991 Unesco report, the main effect will be on salinity calculations, with a lesser effect on density calculations and essentially no effect on other properties.
A typical cross-section along the ocean (from north to south) reveals the warmest waters located near the equator at a relatively thin layer (Fig. 3). Most of the ocean features cold water < 4°C. Again, a strong thermocline is usually found in tropical latitudes. These thermoclines exhibit strong seasonal variability in temperate latitudes (Fig. 4). Summer months feature the shallowest thermocline, which deepens from autumn cooling and wind forcing increase. Late in winter, the thermocline is practically non-existent and begins to develop again in the spring, when heating increases and wind forcing tends to decrease. These mid-latitudes also show great seasonal variability in surface temperature (animation of Fig. 5). This is most evident over the western part of the oceans as the surface current systems throughout the ocean move warm, tropical waters to the north. This process continues in winter, but the cold air masses that move from land to the ocean cool down the ocean very rapidly.

PRESSURE

The great depths of the ocean impart considerable pressure on the water and the instruments we lower into it. Pressure is defined as the force per unit area resulting from the water overlying a specific point. The units are N/m² = 1 Pascal = 10⁻⁵ bar = 10 dyne cm⁻². Pressure is usually measured with a strain gauge transducer. When working in shallow waters the ‘wire out’ can be used to approximate depth but care must be taken to know the angle of the wire in the water. Quite often we measure pressure but report it as depth assuming that 1 m depth equals about 1 decibar or 10⁴ Pa.

The total hydrostatic pressure at any location is

\[ p_z = \int_0^z \rho g \, dz \tag{2} \]

Figure 6 illustrates hydrostatic pressure for different water column. Given a water density of 1020 kg m⁻², a depth increment of 1 m and letting \( g = 9.8 \text{ m s}^{-2} \) yields a pressure of 1.02 x 10⁴ Pa.

Pressure sensors are calibrated by checking the wire out depth to pressure reported on deck and by sending to calibration service who will calibrate it using a dead weight tester.

An error of 2.5 dbar causes a 0.001 error in the salinity calculation. Consider what the errors are in the depth measurement caused by ship roll and other motion of a sensor suspended by a wire sometimes miles long.

DEPTH

Depth is the linear distance in the vertical to a point below the surface. Units = m. We often assume 1 m = 1 decibar = 10⁴ Pascal.
SALINITY - A DETERMINED QUANTITY. 

Salinity was originally defined as "the salinity of a sample of sea water represents the total mass of solid material dissolved in a sample of sea water divided by the mass of this sample, when all the carbonate has been converted into oxide, the bromine and iodine replaced by chlorine and all organic matter completely oxidized." (Sorensen and Knudsen, date). With the development of conductivity sensors and the need for more accurate and comparable salinity measurements two new definitions were developed. They are the absolute and practical salinity. The absolute salinity is defined as follows:

"Absolute Salinity is defined as the ratio of the mass of dissolved material in sea water to the mass of sea water. In practice, this quantity cannot be measured directly and a Practical Salinity is defined for reporting oceanographic observations. (Reference)

Practical salinity is defined as:

“The Practical Salinity, symbol S, of a sample of sea water, is defined in terms of the ratio K_{15} electrical conductivity of the sea water sample at the temperature of 15C and the pressure of one standard atmosphere, to that of a potassium chloride (KCL) solution, in which the mass fraction of KCl is 32.4356 \times 10^{-3}, at the same temperature and pressure. The K_{15} value exactly equal to 1 corresponds, by definition, to a Practical Salinity exactly equal to 35. The practical salinity is defined in terms of the ratio of K_{15} by the following equation:

\[
S = a_0 + a_1 K_{15}^{1/2} + a_2 K_{15} + a_3 K_{15}^{3/2} + a_4 K_{15}^{-1} + a_5 K_{15}^{5/2}
\]

where

\[
\begin{align*}
  a_0 &= 0.0080 \\
  a_1 &= -0.1692 \\
  a_2 &= 25.3851 \\
  a_3 &= 14.0941 \\
  a_4 &= -7.0261 \\
  a_5 &= 2.7080 \\
  \Sigma a_i &= 35.000
\end{align*}
\]

This equation is good for 2 < S < 42.

“\nThis quantity has only one symbol, S, and for considerable time it should be called “practical salinity” in full, and not “salinity”. However, once all possibility of confusion has disappeared, after a sufficient lapse of time, or when it becomes quite clear from the text that practical salinity is concerned, it will be quite acceptable to speak simply of “salinity”.

3
Salinity has become a very simple quantity to determine however the measuring devices (CTDs) must be frequently checked and calibrated. Simple calibrations to check for drift and other offsets should be done daily while calibrations done by professional groups should be done yearly.

Typical profiles of salinity in the open ocean at different latitudes are shown in Figure 7a. In high latitudes, the freshwater from rivers or ice thawing produces a profile with minimum salinity at the surface and increasing values with depth. In temperate latitudes, water vapor loss produces highest salinity at the surface that decreases with depth down to ~1000 m and then changes little according to different major water masses. The highest surface salinity in the open ocean is observed at the subtropical latitudes where intense solar radiation and steady winds produce large evaporation rates that concentrate salinity. Similarly to temperate latitudes, the salinity profile at subtropical latitudes shows decreasing salinity down to ~1,000 m and little change below that depth. A cross-section from north to south in the ocean (Fig. 7b) shows the different water masses with different salinities that are reflect the typical profiles.

A global distribution of surface salinity (Fig. 8) offers a good idea on where evaporation processes dominate over precipitation, namely in the tropics, and where precipitation overwhelms evaporation, i.e., tropics and high latitudes. This is also reflected by the latitudinal distribution of surface salinity along a meridian (or line of longitude) and the difference between evaporation and precipitation (Fig. 9).

### Density and Specific Volume

A typical profile of seawater density shows increasing values regardless of where you are in the ocean (Fig. 10). This makes sense because you cannot have a situation of heavy water over light water as it represents an unstable situation that quickly reverses to stable. In the open ocean, the density profile closely resembles that of temperature, but in coastal waters influenced by freshwater, the density profile will be more similar to that of salinity.

Seawater density is determined using the Equation of State (EOS80). This equation was developed after the redefinition of salinity. EOS80 is a lengthy polynomial expression. The code is available in the reference reports listed or from most oceanographic institutions computer centers. Specific volume is defined as

\[ v(S, T, p) = v(S, T, 0)[1-p/K(S, T, p)] \]

Density is defined as

\[ \rho(S, T, 0) = 1/v(S, T, 0) = A + BS + CS^{\frac{1}{2}} + DS^2 \]
where

\[ K(S, T, p) = E + FS + GS^2 + (H + IS + JS^2)p + (M + NS)p^2 \]

The coefficients \( A \) through \( N \) are temperature-related coefficients. Salinity is in PSS-78 scale. Temperature is in °C. **Pressure is in bars**, Density, \( \rho \) is in \( \text{kg m}^{-3} \). Specific volume, \( \nu \), is in \( \text{m}^3 \text{kg}^{-1} \).

**Density and Specific Volume (Steric) Anomalies**

Since density in the ocean varies little is convenient to define density and specific volume anomalies. The density anomaly is defined as:

\[ \gamma(S, T, p) = \rho(S, T, p) - 1000 \ \text{kg/m}^3 \]

and specific volume or steric anomaly is defined as

\[ \delta(S, T, p) = \nu(S, T, p) - \nu(35, 0, p) \ \text{m}^3/\text{kg} \]

Note that while gamma is simply scaled against 1000 \( \text{kg m}^{-3} \) the specific volume anomaly is scaled against a standard sea water of observed salinity and pressure but zero temperature.

Until recently the term a specific gravity anomaly ("sigma-t") was used as a similar anomaly. Because it was based on the older methods of determining density its relation to the new density measurements are

\[ \sigma_t = 10^3 (\rho/\rho_m - 1) \]

where \( \rho_m \) is the maximum density of pure water that was at the time accepted to be 1 g/cm³. Since the new density is expressed as shown in the previous equations the relation between the old and new density anomalies are

\[ \gamma = 10^3 \rho_m \sigma_t + (\rho_m - 1000) \]

Using the new standards for maximum density of ocean water the relation is
\[ \gamma = 0.999975 \sigma_i - 0.025 \]

Thus \( \gamma \) is consistently 0.025 kg m\(^{-3}\) lighter than \( \sigma_i \). They cannot be used interchangeably and the difference must be accounted for. The difference between steric anomalies calculated using the old and new density formula are insignificant and geostrophic calculation, as will be carried out later in the course, are not affected by the differences.

**Freezing point of seawater**

The freezing point of seawater is defined as (UNESCO Report No. 28, 1978):

\[ T_f = a_0 S + a_1 S^{3/2} + a_2 S^2 + b p \]

where \( a_0 = -0.0575 \), \( a_1 = 1.710523 \times 10^{-3} \), \( a_2 = -2.154996 \times 10^{-4} \), and \( b = -7.53 \times 10^{-4} \). \( S \) is the salinity and \( p \) is the pressure in decibars. At \( S = 40 \) and \( p = 500 \), \( T_f = -2.588567°C \).

Figure 12 shows the freezing point of seawater and the temperature of maximum density on a T/S plot. Note that at low salinities, the water acquires its maximum density before it freezes. Therefore, the water column is turned over before freezing. In contrast, at high salinities (< 24.7) water freezes before it acquires its maximum density and therefore the water column tends to remain stratified as it freezes.

**TS Plots**

TS plots were developed by Helland-Hansen (1918) as a way to meaningfully plot oceanographic data. This came about when observations made clear that ocean waters had distinctive temperature and salinity characteristics that were not dependent on depth. They were finding that characteristic water masses were formed in various parts of the ocean and flowing to other parts along density surfaces in the ocean. The T/S plot (Fig. 13) was well suited to demonstrate the types of water masses at any location. The T/S plot is an excellent way to conceptually visualize the structure of ocean waters and the manner in which they mix.

The T/S plot is a useful way to examine the vertical T and S properties of a location in the ocean. The plot in which we look at the ocean in T/S space also shows the relationship of T and S to density or steric values.
TEMPERATURE, SALINITY AND PRESSURE EFFECTS ON DENSITY

The vertical stability of the ocean depends on the vertical gradient of temperature, salinity and pressure. The effect of temperature, pressure and salinity on density are called the volumetric coefficients. They are as follows:

Coefficient of Thermal Expansion:

\[ \alpha = -\frac{1}{\rho} \left[ \frac{\partial \rho}{\partial T} \right] \]

Coefficient of Saline Contraction:

\[ \beta = \frac{1}{\rho} \left[ \frac{\partial \rho}{\partial S} \right] \]

Adiabatic Lapse Rate:

\[ \Gamma = \frac{\rho g}{C_p} = \frac{\partial T}{\partial p} \]

where \( T \) is the absolute temperature and \( C_p \) is the specific heat of seawater.

Figure 14 shows the variation of the thermal and haline contraction coefficients over ranges of temperature and salinity. Density increases about .80 sigma-t units for each 1 unit of salinity increase. Density decreases by about .2 sigma-t units for each one degree increase in temperature. Note that at low temperatures and low salinities, temperature has little effect on density while salinity changes stay approximately the same throughout the normal salinity and temperature ranges.

POTENTIAL TEMPERATURE and ADIABATIC ADJUSTMENT

While potential temperature is defined classically as the temperature a parcel of seawater would have if it was raised to the surface with no change in salinity. A more strict definition would be "... the potential temperature can be defined as the temperature resulting from an adiabatic displacement to a reference pressure \( p_r \) that may be greater or less than the initial pressure \( p \)." (UNESCO Report 44). The potential temperature can be computed from the adiabatic lapse rate using the following equation
\[\Theta(S,T,p') = T + \int_p \Gamma(S,T,p') dp'\]

where \(\frac{\partial T}{\partial p'} = \Gamma\): an adiabat. The complete equation numerical code is given in UNESCO Report 44.

If you are looking at water that is moving over considerable depths ranges you may want to eliminate the effect of adiabatic heating and cooling. Then we use \(\gamma_\theta = \rho(S,\Theta,0) - 1000\).

Figure 15 shows an example of a station in an oceanic trench.

**DENSITY RATIO**

The coefficients we just discussed are important especially in coastal environments or when considering the causes of stratification or destratification or in the interleaving of different water masses. By examining the vertical temperature and salinity gradients we can determine whether the temperature or salinity gradient is most important in stratification. The density ratio, \(R_p\), expresses the relative importance of thermal expansion and haline contraction and is defined as the following:

\[R_p = \frac{\alpha(dT/dp)}{\beta(dS/dp)}\]

Exercise: An example of the use of \(R_p\) is shown in the following table.

<table>
<thead>
<tr>
<th>Depth</th>
<th>Temp</th>
<th>Salinity</th>
<th>Depth</th>
<th>Temp</th>
<th>Salinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20</td>
<td>25</td>
<td>0</td>
<td>20</td>
<td>35</td>
</tr>
<tr>
<td>5</td>
<td>19</td>
<td>28</td>
<td>5</td>
<td>17</td>
<td>34.9</td>
</tr>
<tr>
<td>10</td>
<td>18</td>
<td>31</td>
<td>10</td>
<td>14</td>
<td>34.8</td>
</tr>
<tr>
<td>15</td>
<td>17</td>
<td>34</td>
<td>15</td>
<td>11</td>
<td>34.7</td>
</tr>
</tbody>
</table>

The data set on the left is from an inshore area where salinity is decreased because of river flow while offshore the river flow is unimportant but the water column is vertically stratified. Determine the vertical temperature and salinity gradients, obtain approximate values for \(\alpha\) and \(\beta\) and determine \(R_p\) for each station.
Vertical Stability and the Buoyancy (Brunt-Väisälä) Frequency

The vertical stability of the water column is an important parameter relevant to many aspects of oceanography. Stability was originally defined by Hesselberg and Sverdrup as

$$gE = \rho g^2 \left[ -\alpha \frac{dT}{dp} - \Gamma - \rho \frac{d\zeta}{dp} \right] = N^2$$

where \( g \) is the acceleration of gravity and \( E = (1/\rho) \frac{dp}{dz} \). \( E \) is the stability parameter simply expressing the vertical salinity gradient. \( N \) is called the Buoyancy or Brunt-Väisälä Frequency and vertical stability is proportional to the square of it. The Buoyancy or Brunt-Väisälä Frequency is the natural frequency of oscillation a water parcel would have if raised or lowered from its rest position to denser or lighter waters below or above.

A simplified expression for \( N \) is

$$N = \sqrt{g \left[ -\frac{1}{\rho} \frac{\partial \zeta}{\partial z} \right]}$$

Frequency = \( N/2\pi \) and period = \( 2\pi/N \).

Specific Heat

The specific heat of seawater, \( C_p \), is the amount of heat required to increase the temperature of one kilogram of seawater one degree C at constant pressure. \( C_p \) is a function of \( S, T \) and \( p \) and the units are J (kg C)^{-1}. In normal oceanic conditions \( C_p \) increases with \( T \) and decreases with \( S \) and \( P \).

The equation for \( C_p \) is

$$C_p(S,T,0) = C_{p0}(T,0) + AS + BS^{3/2}$$

where

$$C_{p0}(T,0) = C_0 = C_1 T + C_2 T^2 + C_3 T^3 + C_4 T^4$$
The coefficients are given in the UNESCO report 44.

The pressure dependence of $C_p$ is computed from the expression

$$\frac{\partial C_p}{\partial p} = -T \frac{\partial^2 V}{\partial T^2}$$

where $V$ is the specific volume, $T$ the absolute temperature and $p$ the pressure. The solution of this and the equation for the fully $T$, $S$ and $p$ depended $C_p$ is given in the UNESCO Report 44.

**Sound**

Sound energy, unlike light energy, is transmitted quite efficiently through seawater. Because of this, sound is used both actively and passively in oceanography. The thermodynamic form of the sound speed equation is as follows:

$$\frac{1}{c^2} = \left(\frac{\partial \rho}{\partial p}\right)_\eta$$

where $c$ is the sound speed, $\rho$ is the density of sea water, $p$ is pressure and $\eta$ is the entropy. A simpler engineering formula is as follows:

$$c = c_0 + \alpha_0(T-10) + \beta_0(T-10)^2 + \gamma_0(T-18)^2 + \delta_0(S-35) + \epsilon_0(T-18)(S-35) + \zeta_0|z|$$

Where $c_0 = 1493, \alpha_0 = 3.0, \beta_0 = -.006, \gamma_0 = -.04, \delta_0 = 1.2, \epsilon_0 = -0.01, \zeta_0 = 0.0164$.

Or an even more simple equation is:

$$c = 1449 + 4.6T - 0.55T^2 + 1.4(S-35) + 0.017D \text{ m/s}$$

Sound velocity varies about 4 m/s for each degree change in temperature, about 1.4 m/s for each unit change in salinity, and about 17 m/s for each 1000 m of depth.
Typical sound profiles are shown in Figure 16.

**Misc.**

2D, and 3D measurements.

**Time Dependence**

X, Y and Z constant and time varies: tide gauge, anchor station, beach station

X and Y constant, Z varies and time varies: anchor station or mooring with more than one sensor at different depths

Multiple X, Y and Z and time varying: many mooring or array ships, or satellite

**Data Definition**

All data must be located in space and time. Space is latitude, longitude and depth. Routinely we use GPS and echo sounders for these measurements.

Time is UCT (Universal Coordinated Time) but we use GMT in practice. Always note the time zone and whether you are using local and or daylight time or not. It is best to note the time difference from UCT for clarity.

For plotting data it is usually easiest to go to a numerical time system. That is usually referred to as Julian date. However there are the following differences: Julian date = number of days since a specific fixed time; military Julian = days since 1900; Year day is the simple day of the year from 1 to 365.

**Scales of Temporal Variability**

Diurnal - 24h - daily heating and cooling cycle, sea breeze

Storm cycle - 3 - 14 days - winter storms, jet stream variability

Spring/neap tidal cycle - 14 days

Seasons - several months - movement of ITCZ

Monsoon - annual cycle

Annual cycle

ENSO - 7 - 10 years
Solar - 21 year and TIDAL

**Temporal Variability and the Thermoclines**

Most of the global ocean remains stratified to some degree throughout the year because mixing forces do not overcome buoyancy forces. In coastal waters and higher latitudes this may not be the case because of additional mixing forces. **Figure xx** Shows a schematic of the seasonal progression of the thermocline. Note that surface heating causes the surface layer to become lighter, gain buoyancy, and thus restricts the downward penetration of heat. With the coming of fall wind mixing and cooling cause the warmer surface waters to mix downward. The result is a deepening thermocline in the fall and a maximum heat flux in the fall at depth rather than in the summer.

A look at the whole ocean shows the seasonal thermocline and the main thermocline. The main thermocline represents the boundary between the surface waters formed in the subtropics and tropics and the deeper waters formed in high latitudes such as NADW.

**Measurements and Errors**

Since observations are so very important to our science and whether we are making them ourselves or use exiting data we must understand the principles of measurement and errors associated with measurement. Some definitions:

- Determination - a direct measurement such as length, weight, temperature.

- Estimation - calculated from knowledge of determined variables. Ie. Salinity = f(t,c,p).

Now to talk a bit about statistics of measurements. As the VG shows there is accuracy and precision.

- Accuracy - Difference between the determination or estimation and the TRUE VALUE. This is why we calibrate. The accuracy will be as good as the calibration.

- Precision - the reproducibility of the measurement. The difference between one result and others. The random error. By taking additional samples we can improve the precision. This has nothing to do with accuracy.

- Systematic error - effects results because of basic fault with method causing values to consistently differ from true value. Calibration can determine the systematic error.

The basic properties of seawater are one of the few things in the ocean that can be measured easily and with great accuracy. There are international standards and agreed upon procedures. These data are routinely exchanged thus there is a great need to assure the data are of the highest quality. Also, since many of the parameters are watched over long times to note global change
effects, the measurement must be reliably made.

**Reference Documents**


"Algorithms for computation of fundamental properties of seawater". UNESCO Technical Papers in Marine Science No.44.

"The International System of Units (SI) in Oceanography". UNESCO Technical Papers in Marine Science No. 45.

"The acquisition, calibration, and analysis of CTD data". Unesco technical papers in marine science No. 54.

You can order these from

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