Thermal convection in Liquid Metal Batteries

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Liquid metal batteries (LMBs)

- 3 superimposed fluid layers in a stable stratification.
- The top electrode usually made of alkaline metals.
- The bottom electrode composed of a dense alloy.
- The electrolyte layer consist of molten salts.
Applications

Charging

Discharging

Distribution
Instabilities in LMBs


Research interest
Flow configuration under study

- The non-dimensional thickness of the electrolyte is defined to be,
  \[ H_E = 1 \]
- The thickness ratio \( d_A \) of electrode A is defined as
  \[ d_A = \frac{H_A}{H_E} \]
- The thickness ratio of the electrode C \( d_C \) is defined as,
  \[ d_C = \frac{H_C}{H_E} \]
Flow equations and scaling quantities

\[ \vec{v}_i = 0 \]
\[ \frac{\partial \vec{v}_i}{\partial t} + \vec{v}_i \cdot \nabla \vec{v}_i = -\nabla p_i + \nu_i \Delta \vec{v}_i + \alpha_i \theta_i g e_z \]

Buoyancy force

\[ \rho_i C_{pi} \left( \frac{\partial \theta_i}{\partial t} + (\vec{v}_i \cdot \nabla) \theta_i \right) = \nabla \cdot (\lambda_i \nabla \theta_i) + Q \]

Internal heating: Joule’s volumetric heating

The scaling quantities are all derived from the properties of the electrolyte layer,
Length: \( d_E \)
Temperature: \( \Delta T = \frac{Q_0 d_E^2}{\lambda_E} = \frac{L^2 d_E^2}{\sigma_E \lambda_E} \)

The velocity scale comes from the Archimedean buoyancy,

\[
\begin{align*}
U_{ThE} &= \frac{d_E}{\tau_A} \\
\tau_A &= \sqrt{\frac{d_E}{\alpha_E \Delta T g}} \\
U_E &= \sqrt{\alpha_E g \Delta T d_E}
\end{align*}
\]

Velocity: \( U_E = \sqrt{\alpha_E g \Delta T d_E} \)
Time: \( d_E U_E^{-1} \)
Pressure: \( \rho E U_E^2 \)

Subscripts (i):
A: Electrode A
E: Electrolyte
C: Electrode C

\( \sigma \): Electrical conductivity \( S/m \)
\( \lambda \): Thermal conductivity \( W/(mK) \)
Flow equations in non-dimensional form

\[
\begin{align*}
\nabla^* \cdot \vec{v}_i^* &= 0 \\
\frac{\partial \vec{v}_i^*}{\partial t^*} + \vec{v}_i^* \cdot \nabla^* \vec{v}_i^* &= -\frac{1}{\rho_{iE}} \nabla^* \pi_i^* + \frac{\nu_{iE}}{\sqrt{\frac{Ra}{Pr}}} \Delta^* \vec{v}_i^* + \alpha_i E \theta_i^* \vec{e}_z \\
\frac{\partial \theta_i^*}{\partial t^*} + (\vec{v}_i^* \cdot \nabla^*) \theta_i^* &= \frac{\kappa_{iE}}{\sqrt{Ra \cdot Pr}} \Delta^* \theta_i^*
\end{align*}
\]

Non-dimensional numbers

\[
Pr = \frac{\nu_E}{\kappa_E}
\]

\[
Ra = \alpha_E \Delta T g \frac{d_E^3}{\nu_E \kappa_E} = \frac{\alpha_E g J_0^2 d_E^5}{\sigma_E \lambda_E \nu_E \kappa_E}
\]

\[
\chi_i E = \frac{\chi_i}{\chi_E} \quad \text{where } i = A/C
\]

All the non-dimensional numbers are defined with respect to the properties of the electrolyte.
Conduction state

In the base state, \( \vec{V} = 0 \).
Assumption: \( L_X, L_Y \gg H_E \), hence only vertical dependence of the temperature
The non-dimensional temperature profile given by,

\[
\Theta(z) = -\frac{1}{\sigma_{iE} \lambda_{iE}} \frac{1}{2} \frac{z^2}{2} + \Gamma_1^i z + \Gamma_2^i
\]
Linearized equations

To linearize the equations infinitesimal perturbations are added to the base state \((\Psi + \psi')\)

\[
\begin{aligned}
\nabla \cdot \mathbf{v}'_i &= 0 \\
\frac{\partial \mathbf{v}'_i}{\partial t} &= -\frac{1}{\rho_i E} \nabla \pi'_i + \frac{\nu_i E}{\sqrt{Gr}} \Delta \mathbf{v}'_i + \boxed{\alpha_i E \theta'_i \mathbf{e}_z} \\
\frac{\partial \theta'_i}{\partial t'} + w'_i \frac{\partial \Theta_i}{\partial z} &= \frac{\kappa_i E}{\sqrt{Gr \cdot Pr}} [\Delta \theta'_i]
\end{aligned}
\]

Buoyancy force

The boundary conditions in our system are defined as,

\[
\mathbf{v}'_A = 0, \quad \theta'_A = 0, \quad \text{at} \quad z = 0.5 + A.d_E \\
\mathbf{v}'_C = 0, \quad \theta'_C = 0, \quad \text{at} \quad z = -(0.5 + C.d_E)
\]
Conditions at the Liquid interfaces

The conditions at the interfaces, Anode-Electrolyte at $z = +0.5$

\[
\begin{align*}
&\frac{u_A'}{u_E'} - 0 \\
&\frac{v_A'}{v_E'} = 0 \\
&w_A' = 0 \\
&\frac{\theta_A'}{\theta_E'} = 0 \\
&\mu_{AE} \left( \frac{\partial u_A'}{\partial z} - \frac{\partial u_E'}{\partial z} \right) - \frac{\mu_{AE}}{\sqrt{Ra.Pr}} \frac{\partial u'}{\partial x} = 0 \\
&\mu_{AE} \left( \frac{\partial v_A'}{\partial z} - \frac{\partial v_E'}{\partial z} \right) - \frac{\mu_{AE}}{\sqrt{Ra.Pr}} \frac{\partial v'}{\partial y} = 0 \\
&w_E' = 0 \\
&\lambda_{AE} \frac{\partial \theta_A'}{\partial z} - \frac{\partial \theta_E'}{\partial z} = 0 \\
\end{align*}
\]

Viscous stress

Interface stress

Electrolyte cathode at $z = -0.5$

\[
\begin{align*}
&\frac{u_E'}{u_C'} = 0 \\
&\frac{v_E'}{v_C'} = 0 \\
&w_E' = 0 \\
&\frac{\theta_E'}{\theta_C'} = 0 \\
&\left( \frac{\partial u_E'}{\partial z} \right) - \mu_{CE} \left( \frac{\partial u_C'}{\partial z} \right) - \frac{\mu_{CE}}{\sqrt{Ra.Pr}} \frac{\partial u'}{\partial x} = 0 \\
&\left( \frac{\partial v_E'}{\partial z} \right) - \mu_{CE} \left( \frac{\partial v_C'}{\partial z} \right) - \frac{\mu_{CE}}{\sqrt{Ra.Pr}} \frac{\partial v'}{\partial y} = 0 \\
&w_C' = 0 \\
&\frac{\partial \theta_E'}{\partial z} - \lambda_{CE} \frac{\partial \theta_C'}{\partial z} = 0 \\
\end{align*}
\]

The Marangoni number $Ma$ is defined with respect to the upper interface $A/E$.

\[
Ma = -\frac{1}{\mu_E} \frac{d\gamma}{d\theta} \frac{\Delta T dE}{\kappa_E} = -\frac{1}{\mu_E} \frac{d\gamma}{d\theta} \frac{J_0^2 dE^3}{\sigma_E \lambda_E \kappa_E}
\]

The ratio of interfacial changes.

\[
\Xi = \frac{\partial \gamma}{\partial \theta} \bigg|_{Upper} - \frac{\partial \gamma}{\partial \theta} \bigg|_{Lower}
\]

$\Xi = 1$ for symmetric battery
**Eigenvalue problem**

- Normal mode expansion of the perturbations: \( X \sim e^{(st+i(k_x+k_y))} \)
- \( s = \sigma + i\omega \): complex growth rate of the perturbations (\( \omega \): frequency)
- Boundary conditions defined on the previous slide

\[
\vec{A} \vec{\psi} = s \vec{B} \vec{\psi}
\]

\[
s = \sigma + i\omega
\]

Investigations are made for marginal state \( \sigma = 0 \)

where
\[
\omega = 0 \quad \text{Stationary modes}
\]
\[
\omega \neq 0 \quad \text{Oscillatory modes}
\]
Results
Battery of Y. Shen et al.

- This battery is an hypothetical battery.
- The fluid layers have the same density and viscosity but differ in the electrical and thermal conductivities.
- This situation is considered to just focus on the electrolyte.


### Ratio of the interfacial tension between the upper interface and lower interface

\[
\Xi = \frac{\frac{\partial \gamma}{\partial \Theta} \mid_{Upper}}{\frac{\partial \gamma}{\partial \Theta} \mid_{Lower}} = 1
\]

<table>
<thead>
<tr>
<th></th>
<th>Electrode – A (A)</th>
<th>Electrolyte (LiCl – KCl)</th>
<th>Electrode – C (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\rho \ (Kg/m^3))</td>
<td>(1.63 \times 10^3)</td>
<td>(1.63 \times 10^3)</td>
<td>(1.63 \times 10^3)</td>
</tr>
<tr>
<td>(\nu \ (m^2/s))</td>
<td>(0.71 \times 10^{-6})</td>
<td>(0.71 \times 10^{-6})</td>
<td>(0.71 \times 10^{-6})</td>
</tr>
<tr>
<td>(\lambda \ (W/mK))</td>
<td>(21)</td>
<td>(0.42)</td>
<td>(21)</td>
</tr>
<tr>
<td>(C_p \ (J/kgK))</td>
<td>(1.21 \times 10^3)</td>
<td>(1.21 \times 10^3)</td>
<td>(1.21 \times 10^3)</td>
</tr>
<tr>
<td>(\sigma \ (S/m))</td>
<td>(1.7 \times 10^6)</td>
<td>(170)</td>
<td>(1.7 \times 10^6)</td>
</tr>
<tr>
<td>(\alpha \ (1/K))</td>
<td>(2.93 \times 10^{-4})</td>
<td>(2.93 \times 10^{-4})</td>
<td>(2.93 \times 10^{-4})</td>
</tr>
<tr>
<td>(\kappa \ (m^2/s))</td>
<td>(1.0647 \times 10^{-5})</td>
<td>(2.1294 \times 10^{-7})</td>
<td>(1.0647 \times 10^{-5})</td>
</tr>
<tr>
<td>(Pr)</td>
<td>0.0666</td>
<td>3.3342</td>
<td>0.0666</td>
</tr>
</tbody>
</table>
Temperature profile of the Base state

Marginal stability curve

- $Ma = 0$
- $Pr = 3.33$
- $k_c = 3.32$
- $Ra_c = 2.38 \times 10^4$
Battery of T. Köllner et al.


Change in the interfacial tension as a function of temperature

\[
\frac{\partial \gamma}{\partial \Theta}|_{Upper} = 7.98 \times 10^{-5}
\]

\[
\frac{\partial \gamma}{\partial \Theta}|_{Lower} = 3.1 \times 10^{-5}
\]

Ratio of the interfacial tension between the upper interface and lower interface

\[
\Xi = \frac{\frac{\partial \gamma}{\partial \Theta}|_{Upper}}{\frac{\partial \gamma}{\partial \Theta}|_{Lower}} = 2.57
\]

<table>
<thead>
<tr>
<th></th>
<th>Electrode – A</th>
<th>Electrolyte</th>
<th>Electrode – C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho ) (Kg/m(^3))</td>
<td>484.7</td>
<td>1597.9</td>
<td>1.0065 \times 10^4</td>
</tr>
<tr>
<td>( \nu ) (m(^2)/s)</td>
<td>6.64 \times 10^{-7}</td>
<td>1.38 \times 10^{-6}</td>
<td>1.29 \times 10^{-7}</td>
</tr>
<tr>
<td>( \lambda ) (W/mK)</td>
<td>50.12</td>
<td>0.365</td>
<td>14.41</td>
</tr>
<tr>
<td>( C_p ) (J/kgK)</td>
<td>4169</td>
<td>1201.6</td>
<td>141.05</td>
</tr>
<tr>
<td>( \sigma ) (S/m)</td>
<td>3 \times 10^6</td>
<td>187.1</td>
<td>7.81 \times 10^5</td>
</tr>
<tr>
<td>( \alpha ) (1/K)</td>
<td>2.08 \times 10^{-4}</td>
<td>3.32 \times 10^{-4}</td>
<td>1.28 \times 10^{-4}</td>
</tr>
<tr>
<td>( \kappa ) (m(^2)/s)</td>
<td>2.48 \times 10^{-5}</td>
<td>1.90 \times 10^{-7}</td>
<td>1.015 \times 10^{-5}</td>
</tr>
<tr>
<td>( \gamma ) (N/m)</td>
<td>0.349</td>
<td>0.132</td>
<td>0.387</td>
</tr>
<tr>
<td>( Pr )</td>
<td>0.0267</td>
<td><strong>7.263</strong></td>
<td>0.0127</td>
</tr>
</tbody>
</table>
Temperature profile of the Base state

Marginal stability curve

- \( Ma = 0 \)
- \( Pr = 7.26 \)
- \( k_c = 2.99 \)
- \( Ra_c = 1.65 \times 10^4 \)
Battery of D. J. Bradwell et al.

- Magnesium-Antimony battery.

Change in the interfacial tension as a function of temperature

\[
\left. \frac{\partial \gamma}{\partial \Theta} \right|_{Upper} = 8.50 \times 10^{-5}
\]

\[
\left. \frac{\partial \gamma}{\partial \Theta} \right|_{Lower} = 2.83 \times 10^{-5}
\]

Ratio of the interfacial tension between the upper interface and lower interface

\[
\Xi = \frac{\left. \frac{\partial \gamma}{\partial \Theta} \right|_{Upper}}{\left. \frac{\partial \gamma}{\partial \Theta} \right|_{Lower}} = 3.0
\]
For a laboratory LMB; \( d = 3 \text{cm} \),

\[
\Delta T = \frac{J_0^2 d^2}{\sigma \lambda} = R_{ac} \frac{\nu \kappa}{\alpha g d^3} \approx 0.04 \text{K},
\]

\( J_{0c} = 36.86 \text{ A/m}^2 \)

- \( Ma = 0 \)
- \( Pr = 3.09 \)
- \( k_c = 3.27 \)
- \( Ra_c = 2.24 \times 10^4 \)
Eigenfunctions and stream functions at the critical limit

- $Ma = 0$
- $Pr = 7.26$
- $k_c = 2.99$
- $Ra_c = 1.65 \times 10^4$

The threshold \((k_c, Ra_c)\) of stationary modes do not depend on \(Ma \in [0, 100]\).
Influence of the fluid property ratios on the stability

The linearized system of equations contains two parameters $G_{AE}$ and $G_{CE}$ characterizing the ratio of the electrodes and electrolyte properties

\[
G_{AE} = \frac{\alpha_A \nu_E \kappa_E}{\alpha_E \nu_A \kappa_A} \quad G_{CE} = \frac{\alpha_C \nu_E \kappa_E}{\alpha_E \nu_C \kappa_C}
\]

- $G_{AE}$ defines the ratio between the anode and electrolyte
- $G_{CE}$ between the cathode and electrolyte
- The viscosities of the electrodes have been varied between $[1 \times 10^{-7}, 5 \times 10^{-6}]$
- The other fluid properties are kept constant with values of T.Köllner.
Conclusion and perspectives

Conclusion

• The LSA code for 3 layer system has been developed and validated.
• 3 different types of batteries have been studied to understand the differences in the threshold of convection and which parameters could influence the stability.
• The threshold variation with respect to the Marangoni number has been studied till the limit of $Ma = 100$, a negligible influence on the stability has been noted.

Perspectives

• Energy analysis will be performed to analyse the destabilization mechanisms of the LMB.
• Include the magnetic effects to study the influence on the stability of the battery.
• LSA in cylindrical configuration of LMB
Acknowledgements

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Thank you for your attention
Annex

Influence of the fluid property ratios on the stability

- Two constants have been defined
  - $G_{AE}$ defines the ratio between the anode and electrolyte
  - $G_{CE}$ between the cathode and electrolyte
- The viscosities of the electrodes have been varied between $[1 \times 10^{-7}, 5 \times 10^{-6}]$
- The other fluid properties are kept constant with values of T. Köllner.

\[ G_{AE} = \frac{\alpha_A \nu_E \kappa_E}{\alpha_E \nu_A \kappa_A} \]
\[ G_{CE} = \frac{\alpha_C \nu_E \kappa_E}{\alpha_E \nu_C \kappa_C} \]


Battery geometry

Ref:
Shen and Zikanov,

Ref:
T. Köllner et al.,
Internal heating in the electrolyte (Free-Slip)

- $Ra_c = 1.70 \times 10^4$
- $k_c = 3.03$


Eigenfunctions
(Laboratory size)

\[ Pr = 3.33 \quad d = 3\text{cm} \]

\[ Ra_c = \alpha \Delta T_c g \frac{d^3}{\nu \kappa} \]

\[ \Delta T_c = Ra_c \frac{\nu \kappa}{\alpha gd^3} \]

\[ \Delta T = \frac{J_0^2d^2}{\sigma \lambda} \]

\[ \Delta T_c = 3.31 \times 10^{-2} \text{K} \]

\[ J_{0c} = 51.26 \text{A/m}^2 \]

(Industrial size)

\[ Pr = 3.33 \quad d = 30\text{cm} \]

\[ Ra_c = \alpha \Delta T_c g \frac{d^3}{\nu \kappa} \]

\[ \Delta T_c = Ra_c \frac{\nu \kappa}{\alpha gd^3} \]

\[ \Delta T = \frac{J_0^2d^2}{\sigma \lambda} \]

\[ \Delta T_c = 3.31 \times 10^{-5} \text{K} \]

\[ J_{0c} = 0.16 \text{A/m}^2 \]

Ref:

Internal heating in the electrolyte (No-Slip)

Marginal stability curve
- $Ra_c = 3.73 \times 10^4$
- $k_c = 3.99$

Good agreement with the values from D. Goluskin “Internally heated convection and Rayleigh-Bénard convection”, Springer (2016).

Eigenfunctions
\[ \Delta T_c = Ra_c \frac{\nu \kappa}{\alpha gd^3} \]

\( \Delta T_c = 7.27 \times 10^{-2} \text{ K} \)

\[ J_{0c} = 75.96 \text{ A/m}^2 \]

\[ Ra_c = 3.73 \times 10^4 \]

Ref:

\( Pr = 3.33 \quad d = 3 \text{cm} \)

\[ Ra_c = \alpha \Delta T_c g \frac{d^3}{\nu \kappa} \]

\( \Delta T_c = Ra_c \frac{\nu \kappa}{\alpha gd^3} \)

\[ \Delta T_c = 7.27 \times 10^{-2} \text{ K} \]

\[ J_{0c} = 75.96 \text{ A/m}^2 \]

\( Ra_c = 3.73 \times 10^4 \)

\( Pr = 3.33 \quad d = 30 \text{cm} \)

\[ Ra_c = \alpha \Delta T_c g \frac{d^3}{\nu \kappa} \]

\[ \Delta T_c = Ra_c \frac{\nu \kappa}{\alpha gd^3} \]

\[ \Delta T_c = 7.27 \times 10^{-5} \text{ K} \]

\[ J_{0c} = 0.24 \text{ A/m}^2 \]

(Laboratory size) (Industrial size)