The quasi-harmonic approximation (QHA) has been utilized in many forms, sometimes referred to as the Mie-Gruneisen Debye equation of state, it has been used to determine thermophysical properties of a wide range of metals [1], rare gas solids and diamonds [2]. However, few have addressed the QHA ability to predict solid-fluid equilibria, with the two notable exceptions being the models developed for CO_2 [3] and benzene [4]. The work on CO_2 and benzene was correlated to a vast amount of experimental data, however the equation of states ability to predict solid formation in mixtures was not used to assess the models. Given that solid formation risks are highly relevant in the development of new industrial processes, such as hydrogen liquefaction, presenting phase equilibria agreement for mixtures can be highly advantageous for those seeking to design mixtures for the purpose of cooling.

In this work we propose a QHA framework based on the work on CO_2 and Benzene, however we seek to highlight the models flexibility and propose some changes to better address the vast array of solids. We highlight the choice of the right cold curve model, which can highly affect agreement with experiments e.g. the use of the Vinet formulation would improve the representation of rare gas solids by several percentages. We also propose an alternative form of the Debye-Einstein approximation. Instead of fixing the contributions to 3/5 in the Debye formulations favor, we allow the weighting to run freely, while adhering to the Dulong-Petit limit. This yields an equation of state, which for the case of argon, gives melting lines with a below 1% average total deviation, and models which successfully predict the trend of the heat capacity, thermal expansivity and pressure. We also present a framework with the ability to predict solid-liquid-gas equilibria in argon-hydrogen and argon-Helium mixtures.

References:

[1] P. I. Dorogokupets and A. R. Oganov. Ruby, metals, and MgO as alternative

pressure scales: A semiempirical description of shock-wave, ultrasonic, x-

ray, and thermochemical data at high temperatures and pressures. Physical

Review B, 75(2):024115, 2007.

[2] A. Dewaele, F. Datchi, P. Loubeyre, and M. Mezouar. High pressure–high

temperature equations of state of and diamond. Physical Review B, 77(9):094106, 2008.

[3] J. Martin Trusler. Equation of state for solid phase i of carbon dioxide

valid for temperatures up to 800 k and pressures up to 12 gpa. Journal of

Physical and Chemical Reference Data, 40(4):043105, 2011.

[4] X. Xiao, J. Trusler, X. Yang, M. Thol, S. Z. Al Ghafri, D. Rowland, and E. F. May. Equation of state for solid benzene valid for temperatures up to 470 k and pressures up to 1800 mpa. Journal of Physical and Chemical Reference Data, 50(4), 2021.