# The Quasi-Harmonic Approximation: Solid Equation of State for the Prediction of Thermodynamic Properties and Solid Formation in Fluid Mixtures

Tage W. Maltby[1, S, C], Morten Hammer[2], Ailo Aasen[3] and Øivind Wilhelmsen[2]

[1] *Institute of chemistry, NTNU, Trondheim, Norway*
[2] *NTNU, Sintef Energy, Trondheim, Norway*
[3] *Sintef Energy, Trondheim, Norway*
*tage.maltby@ntnu.no*

The quasi-harmonic approximation (QHA) has been utilized in many forms and is often referred to as the Mie-Gruneisen Debye equation of state. It has been used to determine the thermophysical properties of a wide range of metals [1], rare gas solids and diamonds [2]. However, few works have addressed the QHA's ability to predict solid-fluid equilibria, with two notable exceptions being the models developed for $CO_2$ [3] and benzene [4]. The equations of state for solid-phase $CO_2$ and benzene were correlated to a vast amount of experimental data. However, the equation of states ability to predict solid formation in mixtures was not assessed thoroughly. It is of key importance to determine the risk of solid formation in the development of new industrial processes and in the design of novel mixed refrigerants.

In this work, we present a QHA framework. We highlight the importance of the cold curve model, which can significantly influence the model's ability to reproduce experimental results. We also propose an alternative form of the Debye-Einstein approximation. Instead of fixing the contributions to 3/5 in the Debye formulation, we allow the weighting to change while adhering to the Dulong-Petit limit. This yields an equation of state, which for the case of neon and argon gives melting lines that deviate from experimental results by less than 1%. The model also successfully reproduces the heat capacity, thermal expansivity and pressures from experiments. We also discuss the ability of the framework to represent solid-liquid-gas equilibria in 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 neon 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.