

Thermodynamic response functions in a cell fluid model

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August 21, 2024

Abstract

Thermodynamic response functions, namely the isothermal compressibility, the thermal pressure coefficient, and the thermal expansion coefficient, are calculated for a many-particle system interacting through a modified Morse potential. These calculations are based on an equation of state previously derived for a cell fluid model in the grand canonical ensemble. The calculated quantities are presented graphically as functions of density and chemical potential.

Keywords: Simple fluids, Morse potential, Thermodynamic response functions.

1 Introduction

In this work we continue our study of the thermodynamic behavior of a cell fluid model, which was defined in [1,2]. In works [3–6] this model was used with a modified Morse potential describing the particle interaction. In particular, the equation of state was obtained in [3] in the zero-mode approximation. This equation of state is used in the current work to calculate thermodynamic response functions, namely the isothermal compressibility, the thermal pressure coefficient, and the thermal expansion coefficient.

2 The interaction potential

The potential of interaction between particles is taken in a form of a modified Morse potential

$$U(r) = \varepsilon C_H \left[A e^{-n_0(r-R_0)/\alpha} + e^{-\gamma(r-R_0)/\alpha} - 2e^{-(r-R_0)/\alpha} \right], \quad (1)$$

where R_0 is the coordinate of the potential minimum, α is an effective range of interaction, γ and n_0 are parameters of the model. Other two constants C_H and A are expressed via γ and n_0 as

$$C_H = \frac{n_0}{n_0 + \gamma - 2}, \quad A = \frac{2 - \gamma}{n_0}, \quad (2)$$

where ε is the depth of the potential well at $r = R_0$. This potential is reduced to the ordinary Morse potential [7] at $\gamma = 2$. For a more detailed discussion of such modified Morse potential, see Sections 1 and 2 in [3].

Modifications of the Morse potential were used in other works as well. For example, in [8] a repulsive term in a form of a power of r^{-1} was added to the ordinary Morse potential, and the influence of the softness of such a term was investigated on the coordinates of the critical point. The generalized form of the Morse potential was suggested in [9]

$$U(r) = A_1 e^{-\lambda_1 r} + A_2 e^{-\lambda_2 r} \quad (3)$$

with application to silicon structural energies, and was also considered in [10] as the potential for Be-S and H-Na compounds.

Our modification contains an additional repulsive term, similar to [8], as well as introduces parameter γ , which can vary as opposed to being strictly equal to 2 in the Morse potential. Including the repulsive term enables us to single out a reference system and apply the method of collective variables to calculating the grand partition function [REFERENCE NEEDED].

3 The equation of state

3.1 Pressure as a function of temperature and chemical potential

The equation of state obtained in [3, see Eq.(42)] reads

$$Pv\beta = E_\mu(M, T) + M\bar{\rho}_0 + \frac{1}{2}\tilde{D}(0)\bar{\rho}_0^2 - \frac{a_4}{24}\bar{\rho}_0^4. \quad (4)$$

The quantities in the left-hand side of the equation are P , the pressure; $\beta = (k_B T)^{-1}$, the inverse temperature; k_B , the Boltzmann constant; T , the temperature; v , cell volume. The quantities in the right-hand side are, in general, functions of the temperature T and the chemical potential μ . Let us present their expressions explicitly.

First, the quantity M depends linearly on the chemical potential

$$M = \frac{\tilde{\mu}}{W(0)} + g_1 - \frac{g_3}{g_4}\tilde{D}(0) - \frac{1}{6}\frac{g_3^3}{g_4^2}, \quad (5)$$

$$\tilde{\mu} = \mu - \mu^*(1 + \tau), \quad (6)$$

where μ^* is some positive constant, τ is the relative temperature $\tau = (T - T_c)/T_c$, T_c is the critical temperature. We will call M the effective chemical potential.

The quantity $W(0)$ is expressed via parameters of the potential (1) as follows

$$W(0) = \Phi^{(r)}(0) [B - 1 + \chi_0 + \tau(\chi_0 + A_\gamma)], \quad (7)$$

where

$$B = 2\gamma^3 e^{(1-\gamma)R_0/\alpha},$$

$$A_\gamma = A e^{(n_0-\gamma)R_0/\alpha} (\gamma/n_0)^3,$$

and $\Phi^{(r)}(0)$ is the Fourier transform of the repulsive part of the potential at $|\mathbf{k}| = 0$

$$\Phi^{(r)}(0) = \varepsilon C_H 8\pi e^{\gamma R_0/\alpha} \left(\frac{\alpha}{\gamma R_0} \right)^3.$$

The parameter χ_0 is used in [3] to single out a contribution in the Fourier transform of the potential that is treated as a reference system defined in the reciprocal space, and is selected as $\chi_0 = 0.07$ [3, see Eq.(24)].

The coefficients g_n are given by the formulas:

$$\begin{aligned} g_0 &= \ln T_0, & g_1 &= T_1/T_0, & g_2 &= T_2/T_0 - g_1^2, \\ g_3 &= T_3/T_0 - g_1^3 - 3g_1g_2, & g_4 &= T_4/T_0 - g_1^4 - 6g_1^2g_2 - 4g_1g_3 - 3g_2^2, \\ a_4 &= -g_4, \end{aligned} \tag{8}$$

where $T_n(p, \alpha^*)$ are the following special functions

$$T_n(p, \alpha^*) = \sum_{m=0}^{\infty} \frac{(\alpha^*)^m}{m!} m^n e^{-pm^2}. \tag{9}$$

Here $\alpha^* = ve^{\beta_c \mu^*}$, and the parameter p has the form

$$p = \frac{\beta_c}{2} \Phi^{(r)}(0) [\chi_0 + A_\gamma]. \tag{10}$$

NOTE 1: Quantities α^* has the dimension of volume.

The quantity β_c denotes the critical value of the inverse temperature. In [3, see Eq.(31)] it was found that

$$\varepsilon \beta_c = 0.200, \quad \frac{k_B T_c}{\varepsilon} = 4.995.$$

Since p is independent of temperature, the coefficients g_n are also independent of temperature. The numerical values for other coefficients used in this paper are the same as those in [3, see Eqs.(5), (23), and (24)]:

$$\chi_0 = 0.07, \quad \gamma = 1.65, \tag{11}$$

$$n_0 = 1.521, \quad R_0/\alpha = 2.9544, \tag{12}$$

$$\alpha^* = 5.0 \quad p = 1.0. \tag{13}$$

The quantity $\tilde{D}(0)$ entering equations (4) and (5) is a function of temperature

$$\tilde{D}(0) = g_2 - \frac{1}{2} \frac{g_3^2}{g_4} - \frac{1}{\beta W(0)}. \tag{14}$$

The condition $\tilde{D}(0) = 0$ defines the critical temperature [3, see Eq.(31)]

$$k_B T_c = \left(g_2 - \frac{1}{2} \frac{g_3^2}{g_4} \right) (B - 1 + \chi_0) \Phi^{(r)}(0). \tag{15}$$

The function $E_\mu(M, T)$ from the equation (4) is provided by

$$E_\mu(M, T) = -\frac{\ln(2\pi\beta W(0))}{2N_v} + g_0 - \frac{\beta W(0)}{2} \left(\frac{\tilde{\mu}}{W(0)} \right)^2 - \frac{g_3}{g_4} M - \frac{g_3^2}{2g_4^2} \tilde{D}(0) - \frac{1}{24} \frac{g_3^4}{g_4^3}. \tag{16}$$

Here the quantity N_v defines the number of cubic cells in volume V for the initial model. In the thermodynamic limit, $N_v \rightarrow \infty$.

The quantity $\bar{\rho}_0$ is a solution to the following cubic equation

$$M + \tilde{D}(0)\bar{\rho}_0 - \frac{a_4}{6}\bar{\rho}_0^3 = 0. \quad (17)$$

For any $\tau > 0$, the latter equation has one real root

$$\bar{\rho}_0 = \left(-\frac{3M}{g_4} + \sqrt{Q_t} \right)^{1/3} - \left(\frac{3M}{g_4} + \sqrt{Q_t} \right)^{1/3}, \quad (18)$$

where

$$Q_t = \left(\frac{2\tilde{D}(0)}{g_4} \right)^3 + \left(-\frac{3M}{g_4} \right)^2, \quad g_4 < 0. \quad (19)$$

Thus, $\bar{\rho}_0$ is a function of the temperature and the chemical potential.

3.2 Pressure as a function of temperature and density

In this work, by density we mean the particle number density $\rho = \langle N \rangle / V$. In the framework of the grand canonical ensemble the average number of particles $\langle N \rangle$ is a partial derivative of natural logarithm of the grand partition function Ξ with respect to the product $\beta\mu$.

$$\begin{aligned} \langle N \rangle &= \left(\frac{\partial \ln \Xi}{\partial \beta\mu} \right)_{T,V} \\ &= \left(\frac{\partial(PV)}{\partial \mu} \right)_{T,V} \\ &= V \left(\frac{\partial P}{\partial \mu} \right)_{T,V}. \end{aligned}$$

From this equation it follows

$$\frac{\langle N \rangle}{V} = \frac{\langle N \rangle}{vN_v} = \left(\frac{\partial P}{\partial \mu} \right)_{T,V}$$

and thus

$$\bar{n} \equiv \frac{\langle N \rangle}{V} v = \frac{\langle N \rangle}{N_v} = v \left(\frac{\partial P}{\partial \mu} \right)_{T,V} = \left(\frac{\partial(Pv\beta)}{\partial(\beta\mu)} \right)_{T,V}. \quad (20)$$

The quantity \bar{n} , on the one hand, has the meaning of the reduced particle number density. On the other hand, it is the average number of particles per cell. Taking explicit derivatives, we arrive at

$$\bar{n} = n_g - M + \frac{\bar{\rho}_0}{\beta W(0)}. \quad (21)$$

The quantity n_g in the equation (21) is the critical density

$$\begin{aligned} n_g &= g_1 - \frac{g_3}{g_4} \left(g_2 - \frac{1}{2} \frac{g_3^2}{g_4} \right) - \frac{1}{6} \frac{g_3^3}{g_4^2} \\ &= g_1 - \frac{g_2 g_3}{g_4} + \frac{g_3^3}{3g_4^2} \end{aligned} \quad (22)$$

Its numerical value for parameters (11) is

$$n_g = 0.978.$$

Combination of the equations (21) and (17) reveals the explicit expression for the effective chemical potential M as a function of the density and the temperature

$$\bar{M} = \frac{\rho_n}{\beta W(0)} - (\bar{n} - n_g), \quad (23)$$

where

$$\begin{aligned} \rho_n &= -2 \left(\frac{g_3^2 - 2g_2g_4}{g_4^2} \right)^{\frac{1}{2}} \cos \left(\frac{\alpha_n}{3} + \frac{\pi}{3} \right), \\ \alpha_n &= \arccos \left(\frac{3}{2} \left(-\frac{g_4^4}{(2g_2g_4 - g_3^2)^3} \right)^{\frac{1}{2}} (n_g - \bar{n}) \right). \end{aligned} \quad (24)$$

At $T > T_c$ the equation of state of a cell fluid model in terms of the density and the temperature has the following form

$$Pv\beta = E_\eta(\bar{n}, T) + \bar{M}\rho_n + \frac{\tilde{D}(0)}{2}\rho_n^2 - \frac{a_4}{24}\rho_n^4, \quad (25)$$

The function $E_\nu(\bar{n}, T)$ in (24) is the function $E_\mu(M, T)$ (16) rewritten in terms of density and temperature taking into account the expression (23).

Figure 1 shows the isotherms for the pressure P following from the equation of state (4) in terms of (chemical potential, temperature) and (25) in terms of (density, temperature).

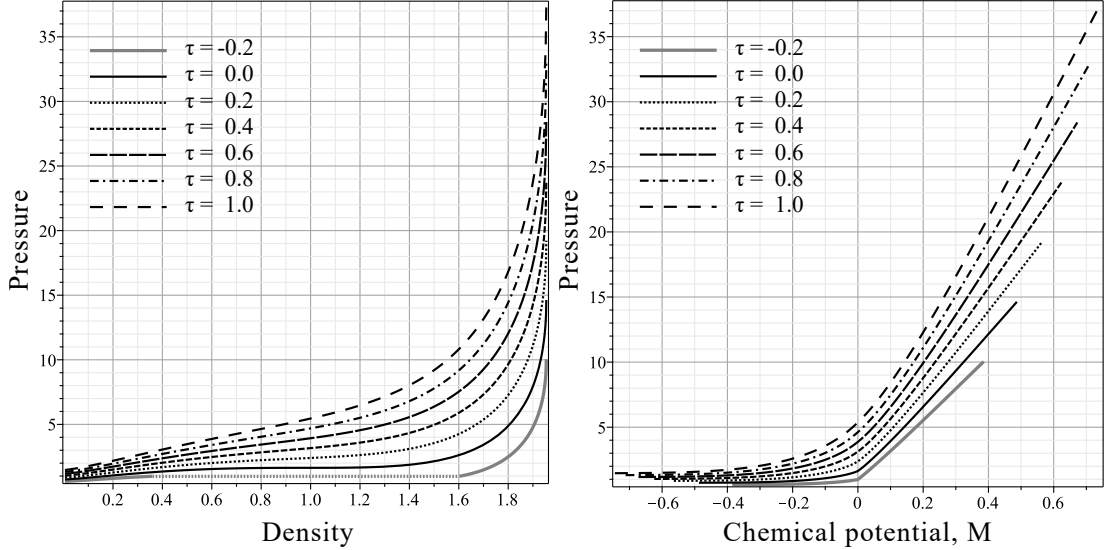


Figure 1: Plots of isotherms of the pressure P as a function of the density \bar{n} (on the lefthand side) and a function of the effective chemical potential M (on the righthand side) at $T \geq T_c$ represented by black lines. Thick grey lines on both figures correspond to isotherms of pressure at $T < T_c$ based on the results taken from [3].

4 Thermodynamic response functions (coefficients)

4.1 Isothermal compressibility

The isothermal compressibility is defined by

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T, \langle N \rangle} \quad (26)$$

Let us perform some transformations to rewrite the definition for K_T into a form that is more suitable for the equation of state (4).

$$\begin{aligned} K_T &= -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T, \langle N \rangle} \\ &= -\rho \left(\frac{\partial \left(\frac{1}{\rho} \right)}{\partial P} \right)_{T, \langle N \rangle} \\ &= \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_{T, \langle N \rangle} \\ &= \frac{1}{\rho} \frac{(\partial \rho / \partial \mu)_{T, \langle N \rangle}}{(\partial P / \partial \mu)_{T, \langle N \rangle}}, \end{aligned}$$

where $\rho = \langle N \rangle / V$ is the particle number density. Applying the Gibbs–Duhem equation

$$N d\mu = -S dT + V dP, \quad (27)$$

at $T = \text{const}$ one has

$$dP = \rho d\mu,$$

or

$$\rho = \left(\frac{\partial P}{\partial \mu} \right)_T. \quad (28)$$

Substituting this into the last expression for K_T , one gets

$$K_T = \frac{1}{\rho^2} \left(\frac{\partial \rho}{\partial \mu} \right)_{T, \langle N \rangle} \quad (29)$$

Finally, from (28) it follows that

$$\left(\frac{\partial \rho}{\partial \mu} \right)_T = \left(\frac{\partial^2 P}{\partial \mu^2} \right)_T \quad (30)$$

and ultimately we arrive at the very useful expression for the isothermal compressibility

$$K_T = \frac{1}{\rho^2} \left(\frac{\partial^2 P}{\partial \mu^2} \right)_{T, \langle N \rangle} \quad (31)$$

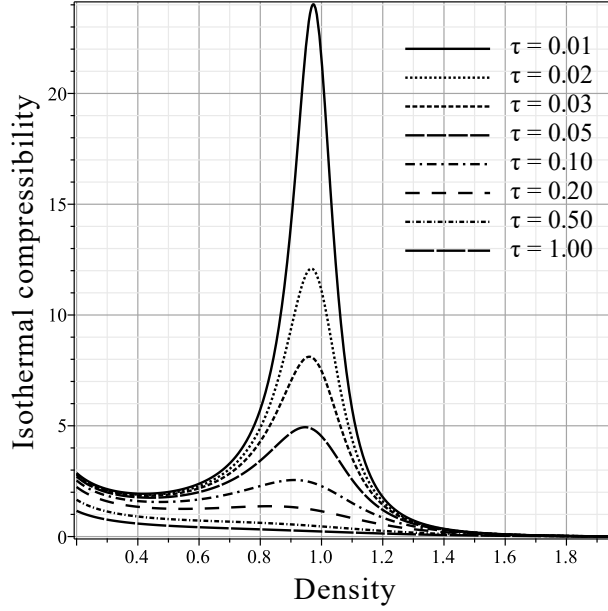


Figure 2: The isothermal compressibility K_T as a function of the density \bar{n} at different values of reduced temperature $\tau > 0$ ($T > T_c$).

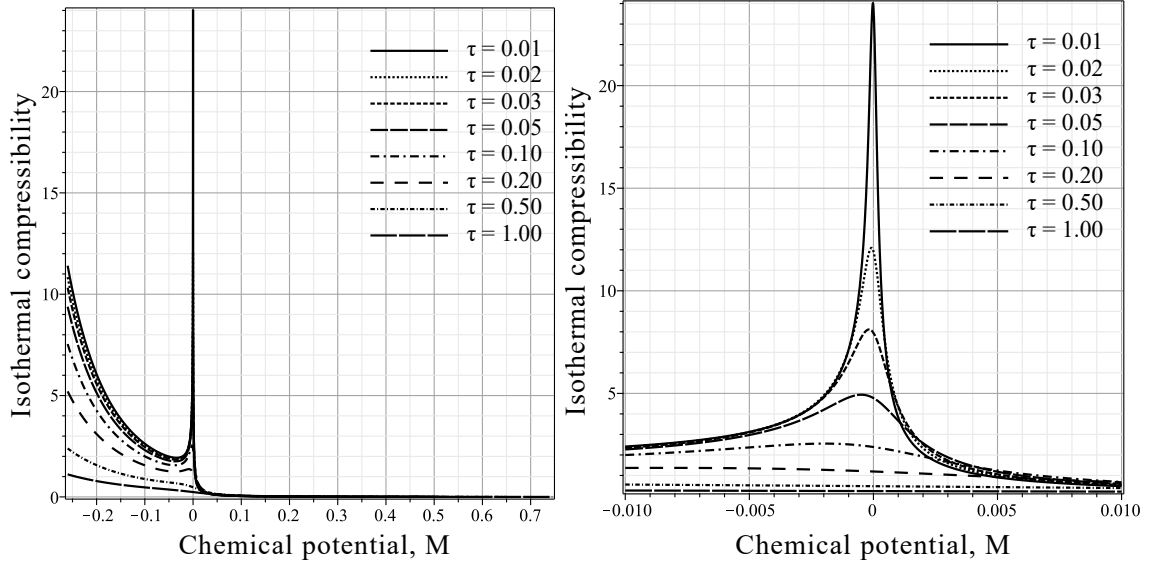


Figure 3: The isothermal compressibility K_T as a function of the effective chemical potential M for different temperatures $\tau = (T - T_c)/T_c$ at $T > T_c$. The two figures differ in the scale of M . The left-hand-side figure covers a wider range of M , while the right-hand-side one focuses on a range of M around its critical value 0.

4.2 Thermal pressure coefficient

The thermal pressure coefficient is defined by

$$\beta_V = \left(\frac{\partial P}{\partial T} \right)_{V, \langle N \rangle} \quad (32)$$

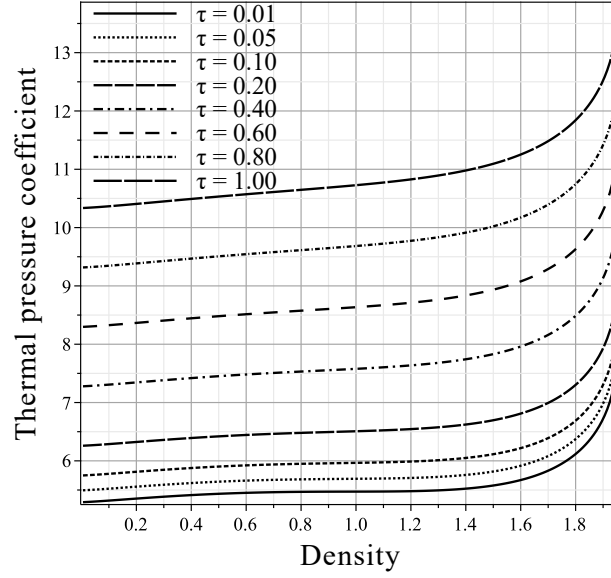


Figure 4: The thermal pressure coefficient β_V as a function of the density \bar{n} at different values of relative temperature $\tau > 0$ ($T > T_c$).

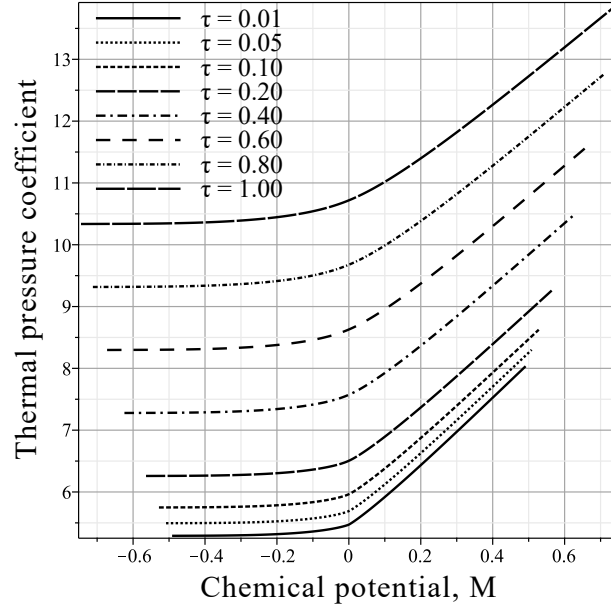


Figure 5: The thermal pressure coefficient β_V as a function of the effective chemical potential M at different values of relative temperature $\tau > 0$ ($T > T_c$).

4.3 Thermal expansion coefficient

The thermal expansion coefficient is defined by

$$\alpha_P = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P, \langle N \rangle} \quad (33)$$

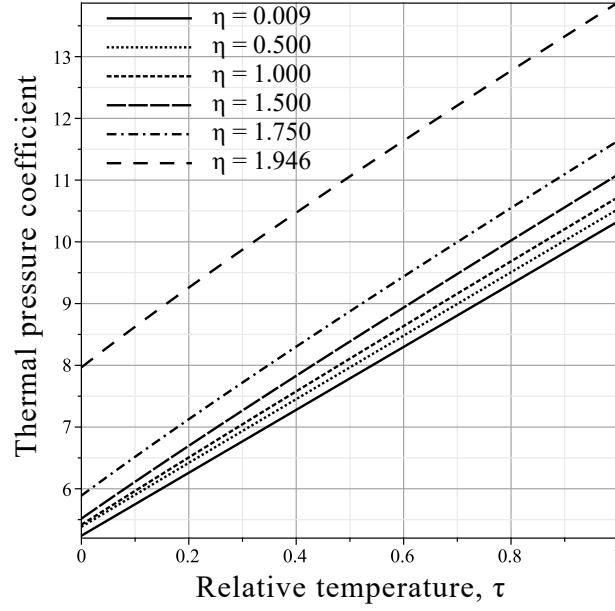


Figure 6: The thermal pressure coefficient β_V as a function of the relative temperature τ at different values of the density η .

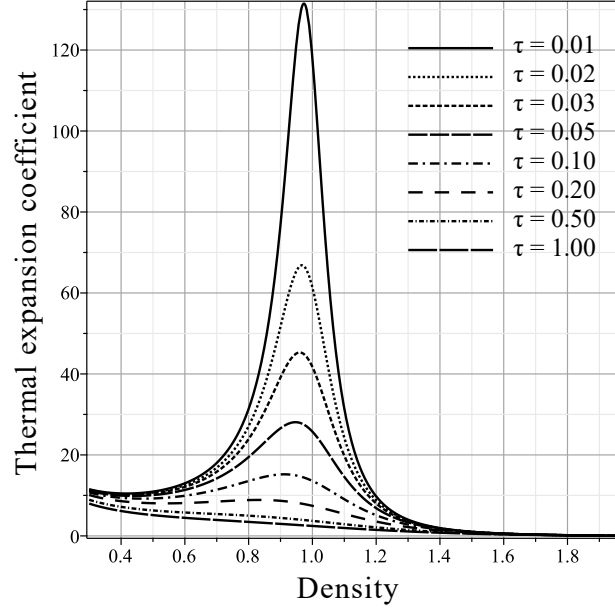


Figure 7: The thermal expansion coefficient α_P as a function of the density \bar{n} at different values of relative temperature $\tau > 0$ ($T > T_c$).

5 Conclusions

Thermodynamic response functions, namely the isothermal compressibility, the thermal pressure coefficient, and the thermal expansion coefficient, are calculated for a many-particle system interacting through a modified Morse potential.

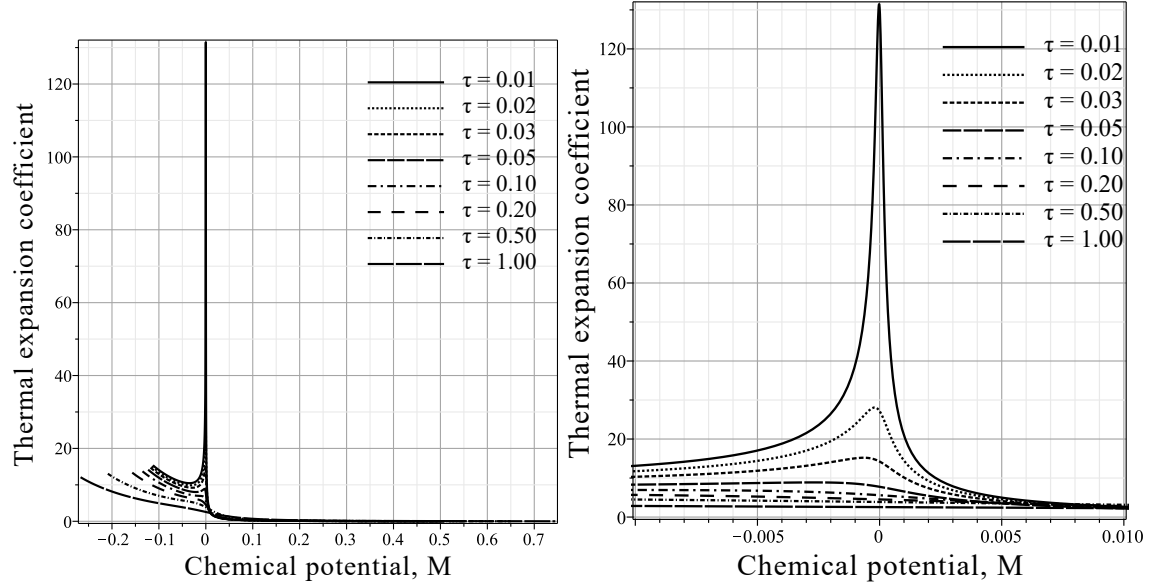


Figure 8: The thermal expansion coefficient α_P as a function of the effective chemical potential M for different temperatures $\tau = (T - T_c)/T_c$ at $T > T_c$. The two figures differ in the scale of M . The left-hand-side figure covers a wider range of M , while the right-hand-side one focuses on a range of M around its critical value 0.

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